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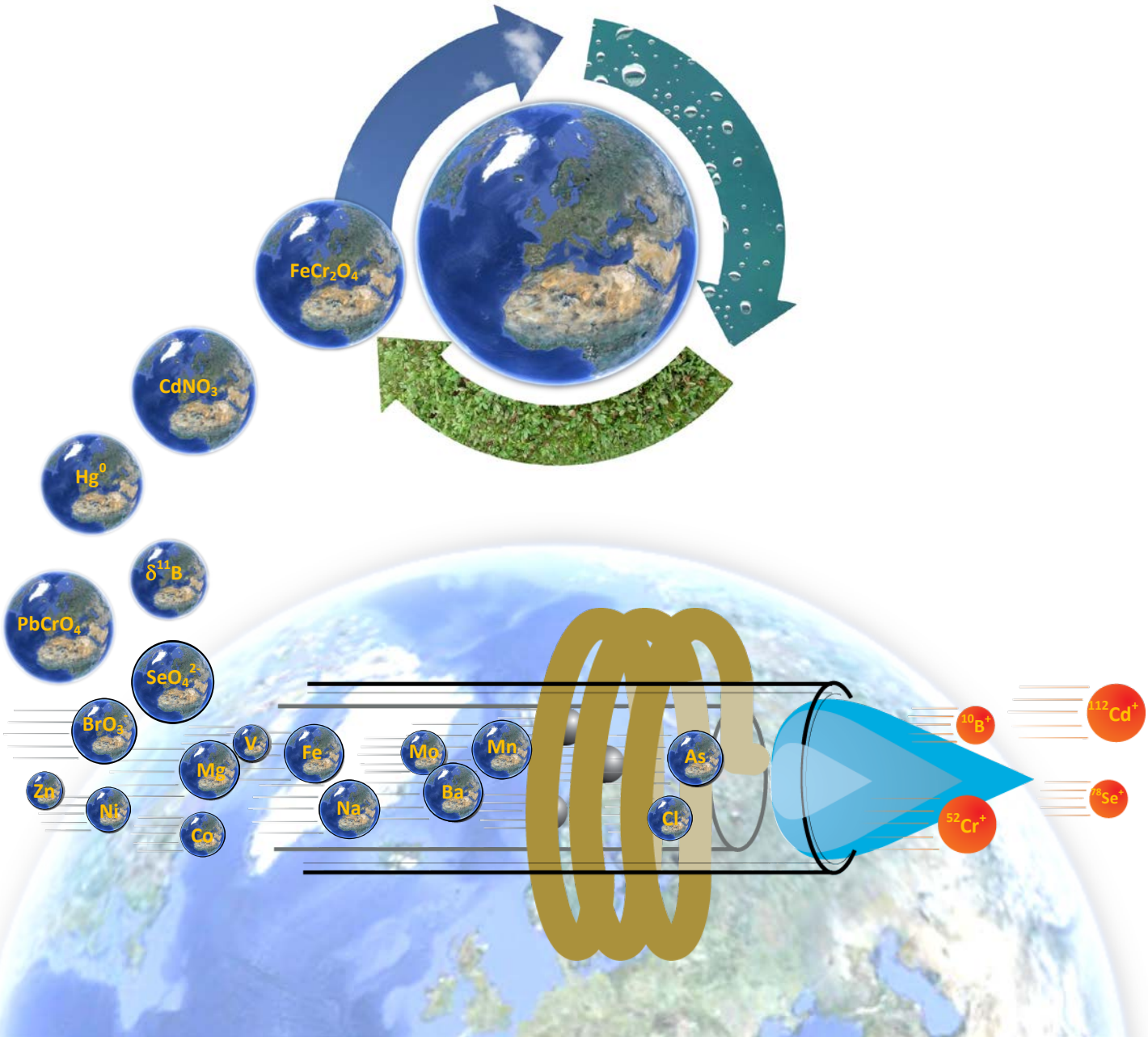
# Development of methods based on ICP-mass spectrometry for the determination, speciation and isotopic analysis of metals and oxy-anions in an environmental context

Kristof Tirez



# Development of methods based on ICP-mass spectrometry for the determination, speciation and isotopic analysis of metals and oxy-anions in an environmental context

**Ghent University, Faculty of Sciences, Department of Analytical Chemistry, Atomic and Mass Spectrometry**

**Flemish Institute for Technological Research (VITO)**

**Doctoral dissertation to meet the requirements to take the doctoral exam**
**Doctor of Science: Chemistry**
**by**

**Kristof Tirez**

**Promoter: Prof. Dr. Frank Vanhaecke**
**Co-promoter: Dr. Nicole De Brucker**

**Ghent, 2013**

## Acknowledgements

This research would not have been possible without the support of a lot of people. I wish to thank several people who accompanied and guided me along the route.

After a few years, it soon became clear to my parents that no talented sportsman or writer was created, but rather a playful scientist with a strong tendency to tease his brothers and sister. I started my master in chemistry almost by accident, but by the time I graduated as environmental chemist, I had found my interest. My parents supported me all along this learning process, while brothers and sister underwent my practical jokes. Many thanks!

Herman De Schepper (†) (Flemish Environmental Agency) and Prof. Richard Dams (Institute for Nuclear Sciences, UGhent) introduced me into environmental chemistry. Under their supervision, I performed my master of science in environmental sanitation thesis in the laboratory of the Flemish Environmental Agency, headed by Dirk Quaghebeur (†). During this thesis, Rudy Cautaerts and Ingrid Temmerman taught me the importance of quality control analysis in a laboratory environment and the practical skills were instructed to me by Gerda Degent. I remember the good atmosphere and collegiality in the laboratory and I am grateful I could be part of it. Many thanks!

The first steps in my professional research career were performed in 1996 in the laboratory of Prof. L. Hosten (†) (Laboratory for Chemical Technology, UGhent) and under the auspices of the same persons from the Flemish Environmental Agency mentioned before. After the sudden demise of Herman De Schepper, Rudy Cautaerts became mentor of the project and he introduced me further in the professional aspects of environmental related issues. I was given the opportunity to learn and work together with passionate colleagues of the Flemish Environmental Agency dealing with the implementation of environmental regulations. Many thanks!

In 1997, a call for a PhD dissertation dealing with the use of ICP-MS in environmental related issues was announced at VITO. A PhD proposal was written in co-operation with Nicole De Brucker (VITO), Prof. Frank Vanhaecke and Prof. Luc Moens (Department of Analytical Chemistry, UGhent). Unfortunately, the project was not awarded. However, I did get a position of researcher at the analytical laboratory of VITO. Nicole De Brucker, Pierre Geuzens and Theo Rymen encouraged me to develop methods based on ICP-MS for the determination of elements in an environmental context at VITO and I want to thank them for giving me this opportunity.

In 2000, I became responsible for the inorganic analytical team and I'm (still) very grateful to work together with these experienced laboratory technicians and devoted researchers: Filip Beutels, Wilfried Brusten, Jos Broeckx, Suzy Bleyen, Annick Cluyts, Valère Corthouts, Nicole De Brucker, Jef De Wit, Karlien Duyssens, Ludwig Goetelen, Bart Noten, Ellen Poelmans, Peter Van Bree, Chris Van Hoof, Mai Wevers and Wendy Wouters. Many thanks!

Since then, I have been involved in numerous environmental related studies giving me the opportunity to work together with a lot of VITO colleagues and external researchers. The list is long, and will probably be incomplete if I had to sum up all the professional contacts I have to acknowledge. Therefore, I will acknowledge the co-authors of the papers as representation for all the scientific collaborations: Ludo Diels, Sandra Van Roy, Johan Patyn, Holger Scharf, Domenico Calzolari, Rob Cleven, Monika Kisser, Detlef Lück, Geert Silversmit, Nico Bleux, Elke Adriaenssens, Edward Roekens, Kelly Servaes, Laszlo Vincze, Patrick Berghmans, Petru Jitaru, Piet Seuntjens, Michael Berglund, Philip Taylor, David Widory, Emmanuelle Petelet, Agnès Bregnot, Dongmei Xue, Pascal Boeckx, Jan Bronders, Nele Desmet and Guy Vanermen. Many thanks!

I have always considered team work as a stimulating habitat and I am very grateful to the VITO management and directors that I got the opportunity to do my professional work with a large input of my own personality, knowledge and creativity.

Thanks to the European Winter Conferences on Plasma Spectrochemistry and the hospitality of Frank Vanhaecke, I became integrated in the ICP-MS community. I felt at ease in the relativising scientific community and remember with great pleasure also the company of Stefaan Van Winckel, Lieve Balcaen, Prof. Martin Resano and Prof. Jorge Ruiz Encinar at these occasions.

The sporadic encounters with Frank Vanhaecke have finally led to the idea of writing a PhD dissertation on the research I have been involved so far. I am very grateful to Frank and Nicole, my promoters, for giving me the time and support needed to accomplish it.

For providing me analytical data of regulatory monitoring studies of trace elements in the Flemish environment, I would like to thank the following persons from the Flemish Environmental Agency: Martin Verdievel, Henk Maeckelberghe, Johan Annys, Ilse Theuns, Ward De Cooman, Koen Toté, Elke Adriaenssens, Bo Van den Bril, Jordy Vercauteren, Ywan De Jonghe and Ralf Eppinger.

The reported analytical work in my PhD dissertation has been performed by the “heavy metal” team at VITO, which consists (besides me) of Wilfried Brusten, Filip Beutels, Karlien Duyssens and Chris Vanhoof. The team works on the basis of an intensive theory-practice interaction, *i.e.*, theory is when you (think to) know everything but nothing works, practice is when everything works but nobody knows why. Many thanks!

I wish to thank the Public Waste Agency of Flanders (OVAM), in particular Luc Debaene and Dominique Suys, the Flemish Environmental Agency (VMM), in particular Ward Roekens and Elke Adriaenssens, the Belgian Federal Public Service (FOD) of Health, Food chain safety and Environment, in particular Robert Martens, the Environment, Nature and Energy Department (LNE) and the Institute for Reference Materials and Measurements (IRMM), in particular Thomas Linsinger, for funding some of the research projects mentioned in this PhD dissertation.

At this point, I also would like to thank my wife, Katrien, for loving and supporting me, for sharing the good and the lesser moments in my life, for help guiding our children, Nathan, Arne and Charlotte to their own future and to make us all feel at home. A woman seems always to have one more child extra in the family to educate, since a man does what he can, but a woman does what a man cannot (Isabel Allende) ... I cannot thank her enough.

I thank my kids for distracting me from the moment I open my eyes (even sometimes before) and to incite me to go through the full spectrum of possible emotions on a daily basis.

Finally, I wish to thank the reader, for your interest in my work.

Kristof, december 2013

## Scope and contents of the PhD dissertation

*"Where is the wisdom we have lost in knowledge?*
*Where is the knowledge we have lost in information?"*
*T. S. Eliot* (*Nobel Prize in Literature, 1948)*

In this PhD dissertation, the development of methods based on inductively coupled plasma-mass spectrometry (ICP-MS) for the determination, speciation and isotopic analysis of metals and oxy-anions in an environmental context is discussed.

What about *heavy metals*? Although the use of the term "*heavy metals*" has been criticized as ambiguous and pointless, this has not banned the term itself in scientific literature and legislation. The oldest recorded scientific use dates back to 1936 (related to elemental density), but today, this term represents an ill-defined umbrella term for various elements (primarily transition metals, but also some non-metals). In the dissertation, a pragmatic approach is followed on how to deal with the term "*heavy metals*", *i.e.* the term is frequently used in legislation without a widely accepted scientific rationale and is simply defined as a set of elements. However, preference will be given to the use of the terms elements (trace and major), metals and oxy-anions.

The success story of ICP-MS in regulatory environmental monitoring of elements was written in the stars with the adage: *to measure is to know*. With its multi-element capability (determination of 80 elements in 3 minutes), excellent sensitivity (µg/L, ng/L), combined with linearity over several orders of magnitude, ICP-MS was embraced by the environmental analytical community in the 1990s and this only 10 years after the first description of the ICP-MS technique [1,2].

Around the turn of the millennium, ICP-MS instruments began their march in the Flemish commercial environmental laboratories and were mainly deployed for the analysis of water and thereafter, for the analysis of solid matrices. At this moment and with the current (European) regulatory environmental limits in force, ICP-MS is increasingly being considered as the method of choice. This market demand resulted in its turn in the development of ICP-MS units as reliable (limited downtime), robust (no/limited interference from matrix) and high-throughput instrumentation, ideally suited for research purposes and routine analysis. As an example of the latter, the cost price on the international market for the determination of 51 elements with ICP-MS in geological survey after *aqua regia* digestion amounts to 16,4 € only [3].

With high-throughput analysis and an almost exponentially growing amount of measurement data, the adage of the regulatory environmental community slightly started to change to: *to measure is to know … but do we understand?* Traditionally, inorganic chemical analysis has been used to investigate the presence (qualitative) and concentration (quantitative) of (trace) elements in environmental matrices. However, total elemental determination does not provide information on the physicochemical characteristics, biological activity, toxicity, mobility and bioavailability of elements in these samples, because such information can only be derived through the determination of chemical species. This triggered the development of the so-called *hyphenated ICP-MS techniques*. Separation techniques such as liquid or gas chromatography were hyphened (or interfaced) with ICP-MS instruments, making it possible to quantify one or more individual chemical species. This market demand resulted in the development of commercial interfaces to easily hyphen different separation techniques (primarily GC, LC) to ICP-MS over the last 10 years.

In summary, since its introduction 30 years ago, ICP-MS conquered a large part of the market of environmental monitoring of metals and oxy-anions. Riding on the waves of this analytical success story and starting 15 years ago, the research described in this dissertation is in essence related to the

environmental monitoring adage *to measure is to know … but do we understand?* This understanding is both related to the analytical measurement itself, as to the environmental processes studied and at a given point, this also led sometimes to the insight that "*all I know is that I know nothing*" (or at most a subtle part of it).

The year 1980 is not only considered as the starting point of the history of ICP-MS, but it is also the year in which the environmental policy in Belgium was transferred from the federal level to the regions (Flemish, Walloon and Brussels Capital Region). Since then, different Flemish environmental agencies were founded, rolling out the implementation and enforcement of the environmental legislation related to *heavy metals* in Flanders. Also in 1980, Lars Ulrich posted an advertisement to start up the metal band *Metallica,* a landmark in heavy metal music.

As an introduction to the actual experimental work carried out and described in this PhD dissertation, the synchronicity in the emergence of environmental legislation on the one hand and that of ICP-MS in environmental analysis since 1980 on the other will be discussed.

Thereafter, and as part of the *to measure is to know* adage, examples will be given of regulatory monitoring in the field of water, air and soil, where the superior sensitivity combined with multi-element capabilities of ICP-MS have played - and still play - an important role. This is especially the case for the derivation of ambient background concentrations of elements present in the different environmental compartments. As metals and oxy-anions are naturally present in our environment, knowledge of ambient background concentrations is needed to provide baseline data for pollution and risk assessment studies. The range of background concentration of elements, derived and compiled in this PhD dissertation, will illustrate *a match made in heaven* with the sensitivity of ICP-MS instruments.

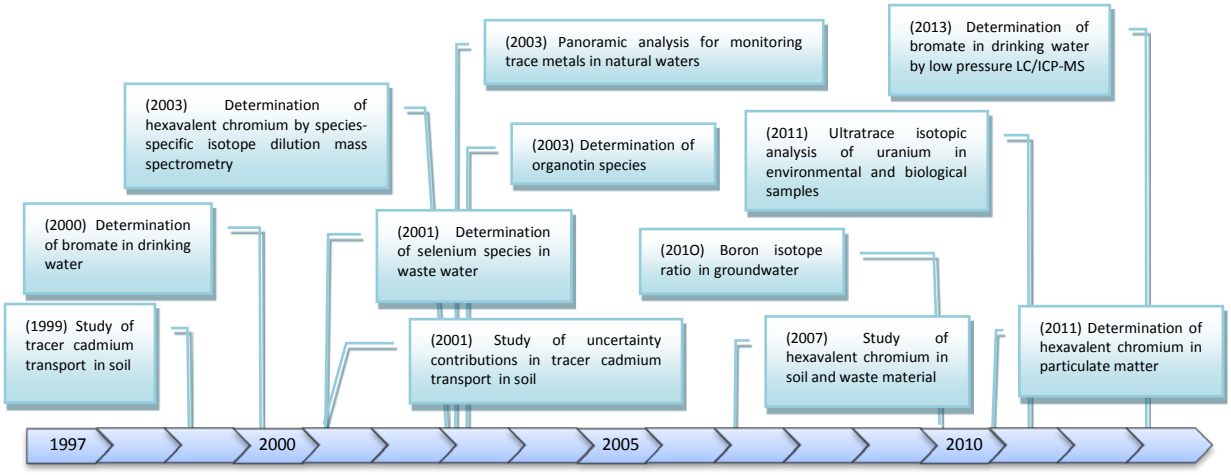
The focus of the first part of the dissertation is on the analysis (of acid digests) of environmental samples by ICP-MS to achieve a multi-elemental determination of elements. Special attention is given to the impact of European harmonisation efforts in order to prevent environmental pollution "to stop" at national (or regional) borders.

Subsequently, the scientific papers covering the development of methods based on ICP-MS for the determination, speciation and isotopic analysis of metals and oxy-anions in an environmental context are presented with emphasis on the connecting thread of the PhD dissertation, *i.e.,* the relation between the ICP-MS measurement, the environmental issue and the regulatory context.

The scientific papers have been arranged chronologically in the following chapters (see also timeline):

- Speciation-Determination of oxy-anions in water and solid samples
    - Characterization of inorganic selenium species by ion chromatography with ICP-MS detection in microbial-treated industrial waste water
    - Determination of hexavalent chromium by species-specific isotope dilution mass spectrometry and ion chromatography-1,5-diphenylcarbazide spectrophotometry
    - Validation of a European Standard for the determination of hexavalent chromium in solid waste material
    - Determination of hexavalent chromium in ambient air: a story of method-induced Cr(III) oxidation?
    - Determination of bromate in drinking waters using low pressure liquid chromatography / ICP-MS

- Tracer experiments with stable isotopes in environmental studies and use of natural isotopic variation as a proxy
    - Full uncertainty calculation on quantitative determination of tracer and natural cadmium in soil column effluents with ICP-MS
    - Boron isotope ratio measurements in WFD monitoring programs: comparison between double-focusing sector-field ICP (ICP-SFMS) and thermal ionization mass spectrometry (TIMS)




Timeline (1997 – 2013) showing the chronological order of the development of methods based on inductively coupled plasma-mass spectrometry (ICP-MS) for the determination, speciation and isotopic analysis of metals and oxy-anions in an environmental context.

**References :**
A numerical style of references (*i.e.*, [14]) is used throughout the dissertation, the reference list starts at p. 226. Except for the scientific papers, for which the reference lists are separately provided at the end of each paper.

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# CHAPTER 1 SYNCHRONICITY IN THE EMERGENCE OF THE FLEMISH ENVIRONMENTAL LEGISLATION AND ICP-MS IN ENVIRONMENTAL ANALYSIS SINCE 1980

In the following section, the synchronicity in the emergence of the Flemish and European environmental legislation dedicated to *heavy metals* and the emergence of ICP-MS in environmental analysis since 1980 is described. In addition to a timeline for and some milestones in both topics, also the interrelation between ICP-MS and (Flemish) environmental legislation is discussed.

## 1.1. SOME MILESTONES IN THE ENVIRONMENTAL LEGISLATION OF HEAVY METALS IN FLANDERS

*"Why has it seemed that the only way to protect the environment is with heavy-handed government regulation?" Gale Norton (United States Secretary of the Interior, 2001-2006)*

The first legislation in Flanders aimed at protecting the environment against the harmful effects of polluting industries (unhealthy or offensive odour), the oldest "Environmental Law" was established by the Imperial Decree of October 15th, 1810 [4,5].

By decision of the Regent on February 11th, 1946, Titles I and II of the General Regulations for Labour (ARAB) were established. The ARAB bundled various laws and decrees relating to occupational safety, occupational hygiene and environmental protection in a code. Title I provided a classification of hazardous, unhealthy or nuisance-causing establishments subjected to an environmental license requirement [4].

In 1977, Belgium got a first written warning from the European Union for failing to implement a European directive dating from 1975 on waste [6]. This delay was caused by the Belgian state reform that was in progress. With the Institutional Reform Act of August 8th, 1980, the management of the environment in Belgium became a task of the regions (Flemish, Walloon and Brussels Capital Region). The regions were therefore entitled to their own devices to implement a policy on environmental nuisance [5]. 1980 is also the starting point of the timeline in the emergence of the Flemish environmental legislation, as shown in Figure 1.

Shortly after the Belgian state reform in 1980 and under pressure of the proliferation of landfills, the actions of the environmental movement and the exhortations of the European Court, the issue of waste is discussed on one of the first meetings of the Flemish Council [6]. On July 2nd, 1981, the decree "concerning the prevention and management of waste-materials" - simply "**Decree on Waste"**- sees the light of day. The Flemish waste policy objectives are: 1) waste prevention, 2) promotion of reuse, recovery and recycling, 3) organization of the disposal of generated waste. To reach these goals, the **Public Waste Agency of Flanders (OVAM)** was founded. In 1982, the Belgian Nuclear Research Centre (SCK) starts to act as reference laboratory for OVAM.

A new policy on nuisance-causing establishments was announced with the Decree of the Flemish Council of June 28th, 1985, concerning Environmental Licenses [5]. This environmental decree entered into force on September 1st, 1991, with the first implementation order: the Order of the Flemish Government of February 6th, 1991, establishing the Flemish regulations concerning

environmental Licenses (**Title I of VLAREM**). This order deals with the various procedures and the list of establishments and activities that are classified as nuisance.

In 1991, the European Commission (EC) issued a nitrate directive (91/676/EEC) concerning the protection of water against contamination by nitrates from agricultural sources [7]. To meet the EC directive, the application of manure and fertilizers has been restricted in Flanders by **the Decree on Manure** (1991). The **Flemish Land Agency (VLM)**, founded in 1988, helps farmers to reach these goals.

The Flemish environmental policy was extremely fragmented and to rationalize and simplify the Environmental law, an "Interuniversity Commission Review of the Environmental Law" was established in 1989 (the so-called "Bocken Commission")[6]. In 1994, this Commission proposes a report: all sub-regulations should be integrated into a system of licensing and this initiated the Flemish environmental code.

A subsequent implementation order, the Order of the Flemish Government of June 1st, 1995, concerning General and Sectoral provisions relating to Environmental Safety (**Title II of VLAREM**) included the environmental conditions under which an establishment may be operated [4]. The use of Best Available Techniques (BAT) and the setting of environmental quality standards were the starting points in the Flemish environmental regulation.

The **Flemish Institute for Technological Research (VITO),** founded in 1991, takes over the role of reference laboratory for OVAM from the Belgian Nuclear Research Centre (SCK) with respect to the disciplines soil and waste. In 1994 VITO takes over the role of reference laboratory from the Belgian Institute of Hygiene and Epidemiology (IHE) for the disciplines water and air.

On February 22nd, 1995, the Flemish Parliament approved the Decree for soil remediation [6]. This soil remediation legislation had also been prepared by the Interuniversity Commission for the Revision of Environmental Law ("Bocken Commission"). A year later, the implementation decisions were bundled in the Order of the Flemish Government of March 5th, 1996, concerning the establishment of the Flemish regulations on Soil Remediation (**VLAREBO**). These texts created a legal framework to address soil problems in Flanders. In VLAREBO, standard values were defined for background values (unpolluted soils) and for soil remediation values, depending on the destination type of the soil (housing, industry). The most severe soil remediation values form a balance between a limited enrichment relative to the natural background composition of the soil on the one hand and the maximum protection of human health and the ecosystem from direct exposure on the other.

On December 17th, 1997, the Flemish Government approved the Decision establishing the Flemish regulations relating to waste prevention and management (**VLAREA**)[5]. VLAREA introduced the concept of secondary raw material for several applications, *e.g.*, as fertilizer, soil conditioner, construction material or soil. It is assumed that the main impact to the environment by using secondary raw materials is caused by the leaching of inorganic contaminants (*e.g.*, *heavy metals*) into the underlying soil and groundwater. The basic principle is the "marginal soil load", *i.e.,* a very limited enrichment of the underlying soil layer by inorganic contaminants.

In 1998, the European Commission (EC) issued Council Directive 98/83/EC on the quality of water intended for human consumption (adopted as Decision of the Flemish Government in 2002)[8,11]. The directive is intended to protect human health by laying down healthiness and purity requirements which must be met by drinking water within the European Community. About 340 billion litre of drinking water is produced yearly in Flanders by 15 drinking water suppliers [8]. The quality of the drinking water in Flanders is controlled by the **Flemish Environmental Agency (VMM)** in cooperation with the drinking water suppliers [9].

In the 1990s, the European Commission (EC) recognized the need for further action to avoid long term deterioration of the quality and quantity of freshwater resources and it called for a program of actions to be implemented by the year 2000, aiming at sustainable management and protection of freshwater resources [10]. These considerations coincided with the request made by the European institutions to the Commission to come forward with a proposal for a Directive, establishing a framework for a European water policy; this resulted in the adoption of the **Water Framework Directive** (WFD) 2000/60/EC on October 23rd, 2000. The Water Framework Directive has put forward a challenging legislative framework, establishing "good status" environmental objectives for all waters – surface, coastal, transitional, and ground waters – to be achieved by the end of 2015.

The EU regulatory Groundwater Framework on the protection of groundwater against pollution caused by certain dangerous substances that has been developed at the end of the 1970s (Directive 80/68/EEC) will be repealed by December 21th, 2013, under the Water Framework Directive. In the field of emission limit value legislation (waste water), the Dangerous Substances Directive (2006/11/EC) and its Daughter Directives on various individual substances were adopted in 2006.

The Flemish soil remediation decree of 2007 replaced the old decree of 1995 [6]. The simpler decree regulates soil certificates and remediation of contaminated soil. The decree of 1995 mainly had an effect on companies in operation and on transfer of ownership of (contaminated) grounds. Abandoned or unused areas that were no longer used because of soil contamination, called brownfields, remained unaffected. The new decree of 2007 aims to protect the available green spaces and to upgrade contaminated areas.

In 2008, The European commission adopted a new **Air Quality Framework Directive** 2008/50/EC, in which most of the existing legislation related to air quality (including the first air quality framework directive of 1996) was merged into a single directive with no change to existing air quality objectives [13]. The Fourth Daughter Directive (Directive 2004/107/EC), including target values for arsenic, cadmium and nickel in ambient air, entered into force in 2013.

In 2010, the Flemish Government approved, as part of the integral water policy, new environmental quality targets for surface water and groundwater and environmental quality standards for sediments and biota, based on the European **Water Framework Directive** (Directive 2008/105/EC). This Directive marks an important step in the use of sediments and biota as matrices for assessing long term trends and chemical status in the integral water policy [14]. In 2011, the associated Directive 2009/90/EG of the Commission, laying down technical specifications for chemical analysis and monitoring of water, was adopted as well (*e.g.*, instead of total elemental concentrations, dissolved elemental concentrations are to be determined in surface water).

In 2011, a decision of the Flemish Government establishing the regulations for recognition related to Environmental monitoring (**VLAREL)** is adopted [4]. This decision provides regulations on the recognition of professional qualifications and technical specifications for chemical analysis and monitoring of the Environment. Herein, it is mentioned that the **Flemish Institute for Technological Research (VITO)** is (re)designated as reference laboratory for Flanders.

In 2011, the Flemish Parliament approved the new **Decree on Materials** [6]. This represents the final part of sustainable materials management in Flanders. It implements the European Framework Directive (EC) 2008/98 for waste management and anchors the sustainable materials management and replaces the waste decree of 1981. The decree requires that a comprehensive look at the material chain is essential for a lasting solution to the issue of waste. The objectives of the new legislation are: 1) environment-friendly and sustainable waste management, 2) reducing the harmful effects of materials throughout the life cycle and 3) counteracting the depletion of resources.

Parallel to the decree, a new legislation that completely replaces the VLAREA, the Flemish regulations for the sustainable management of material cycles and waste (**VLAREMA**), was approved in 2012. This regulation not only includes the European end of waste approach, but also the successor of the *secondary raw material* approach, which is now referred to as *raw material*. As the handling of waste has an influence on soil and groundwater quality, a scientific and policy inter-correlation was needed between the VLARE(M)A (waste) and VLAREBO (soil, groundwater) codes. New risk-based limits for mineral materials were derived, based on safe concentrations in soil and groundwater [12]. Risk-based limit values indicate that experimental data obtained using the leaching test method on the mineral substance (waste), do not exceed safe concentrations in soil and ground water.

In summary, during the last 30 years, different Flemish regulations for the protection of our environment have been implemented. The last years, this legislation was amended many times, mostly under the influence of **new European environmental legislation** : Water Framework Directive, Ground Water Directive, Air Quality Directive…. a notable absentee in this list is soil. The soil directive has languished since it was first introduced in 2006. Some member states stymied the proposed legislation, claiming it was not the EU's prerogative to dictate policies on land use.

Also, a shift from "environmental protection" to "**environmental sustainability**" is being introduced (*i.e.*, Sustainable material management in Flanders). Implementing a more sustainable approach to the consumption and production of chemicals would not only benefit Europe's environment, but also reduce the detrimental effects arising in other parts of the world (see also § 3.3, e-waste).

**Interesting links :**

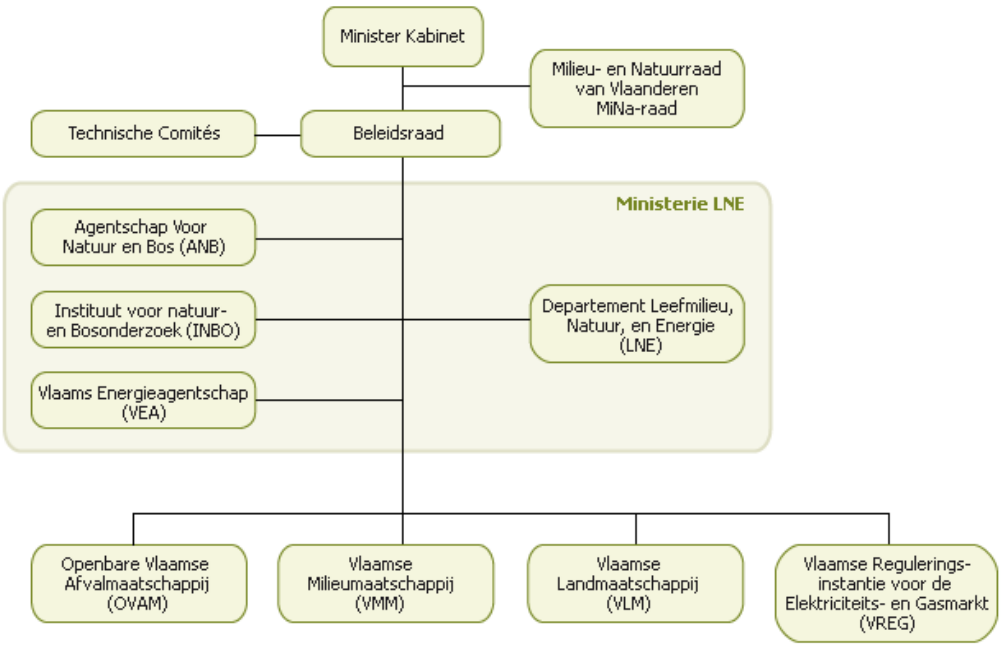
- The **Navigator Environment, Nature and Energy**, is a unique instrument that gives the updated and consolidated version of the Flemish environmental legislation. A clear structure and a sophisticated search engine allows finding the desired legislation http://navigator.emis.vito.be/milnav-consult/
- **EUR-Lex** provides free access to European Union law and other documents considered to be public. The website is available in the 23 official languages of the European Union : http://eur-lex.europa.eu/en/tools/about.htm
    - Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by **nitrates** from agricultural sources
    - Council Directive 98/83/EC of 3 November 1998 on the quality of **water intended for human consumption**
    - Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of **water policy**
    - Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on **ambient air quality a**nd cleaner air for Europe
    - Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on **environmental quality standards** in the field of water policy
    - Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on **waste**

## 1.2. WHO IS IMPLEMENTING THE ENVIRONMENTAL POLICY IN FLANDERS?

*"Nothing is more destructive of respect for the government and the law of the land, than passing laws which cannot be enforced."(A. Einstein)*

The Flemish Minister for Environment implements the environmental policy. For the preparation and implementation of the policy, the minister can count on the collaboration of the **Environment, Nature and Energy Department (LNE)** and a number of agencies from the Environment, Nature and Energy policy domain:

- The Public Waste Agency of Flanders **(OVAM**) is responsible for **waste management** and **soil remediation** in Flanders. It is a public Flemish Institution, established after the decree of July 2nd, 1981, covering waste management and prevention. Waste removal and soil remediation were included as well. In 1995, Flanders got a more specific legislation on soil remediation: the soil remediation decree. The soil remediation decree provides the Flemish government with an instrument to fight historical as well as recent soil pollution. One of its objectives is to remediate historical soil pollution within a period of 40 years. The soil remediation decree equally offers a range of possibilities to prevent new soil pollution or to remediate right away.
- The Flemish land agency (**VLM**), founded in 1988, is responsible for the organization and management of the open space in Flanders. Furthermore, it contributes to shaping rural policy in Flanders. The VLM contributes to meeting the environmental targets set in the Nitrates Directive, by actively guiding the farmers, stimulating them to practice sustainable agriculture and monitoring a correct implementation of the manure legislation. Its field of activity comprises the rural areas and the peri-urban open space in Flanders.
- The mission of The Flemish Environment Agency (**VMM)**, established in 1991, is to contribute to the realization of the environmental policy objectives by **reporting on the state of the environment** and by preventing, limiting and reversing harmful impacts on **water systems** and pollution of the **atmosphere**, and to the realisation of the integrated water policy objectives. VMM also produces the Flanders State of the Environment Report **(MIRA)**. MIRA describes, analyses and evaluates the state of the Flemish environment, discusses the environmental policy pursued and looks ahead at the future environment.




(organizational chart courtesy of http://www.lne.be/organisatie/organogrammen)

**Interesting links :**

- A special website was devoted to the **30th anniversary of the Public Waste Agency** (2011), with a 'virtual exhibition', a timeline, a collection with hundreds of photos, video clips and testimonials: http://www.30jaarovam.be/index.php/

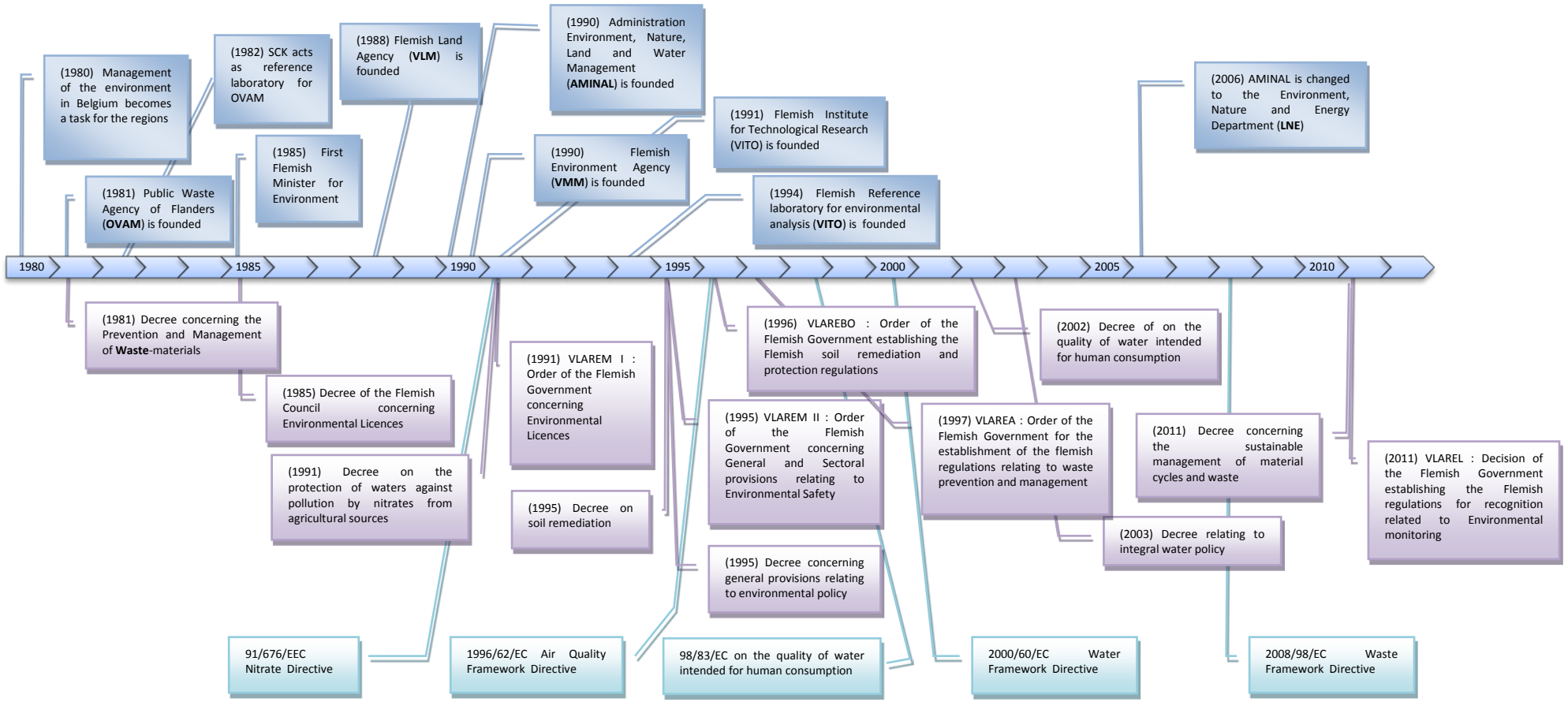



Figure 1: Timeline (1980 – 2012) showing the founding of Flemish agencies related to environmental issues (upper part) and milestones of important Flemish/European environmental legislation (lower part).

## 1.3. WHICH METHODS ARE USED FOR REGULATORY ENVIRONMENTAL MONITORING OF HEAVY METALS?

Given the significance of manmade dispersion of *heavy metals* in our environment, major legal acts in the EU (*e.g.,* Water Framework Directive, Air Quality Directive, see §1.1) have included monitoring programs in order to report on the state of our environment. In this paragraph a brief overview will be given on the decision-making process leading to the analytical methods to be used for regulatory monitoring. The emphasis will be on the determination of heavy metals in general and, in particular, on the use of ICP-MS (see § 1.4.1).

In the Decision of the Flemish Government of June 29th 1994 (and revised in 2011 in VLAREL), it is mentioned herein that the **Flemish Institute for Technological Research (VITO)** acts as reference laboratory for Flanders for the disciplines water, air, soil, waste and manure. Besides, this decision provides regulations on the recognition of professional qualifications and technical specifications for chemical analysis and monitoring of the Environment.

In support of the implementation of the environmental policy (see §1.2) and since 1994, VITO started to provide reference methods for the analysis of the different environmental matrices:

- **WAC**: compendium for sampling and analysis of water
- **LUC**: compendium for sampling and analysis of air
- **CMA**: Compendium for sampling and analysis in support of the material and soil remediation decrees
- **BAM**: compendium for sampling and analysis of manure, animal feed and soil in support of the manure decree
- **BOC**: Compendium for sampling and analysis in the context of soil protection

The Compendia of Flemish reference methods for environmental analysis can be found via the following link: http://www.emis.vito.be/referentielaboratorium (last accessed on 20/01/2013).

Especially for *heavy metals* - and in more general terms, inorganic parameters - the Flemish reference methods are nowadays based on European standards developed by the **European Committee for Standardization** (CEN) [35]. These standards have a unique status since they also are national standards in each of its 32 European member states. With one common standard in all these countries and every conflicting national standard withdrawn, comparison between analytical results becomes more feasible.

The national organisations responsible for drafting and publication of European standards in, *e.g.*, France (AFNOR), the Netherlands (NEN), Germany (DIN), work with national committees, consisting of national experts, where comments can be formulated on European standards. These comments made by national committees often include much more than just scientific argument (*e.g.*, proposals for which acid digestion to be used are strongly related to methods that have been historically used in the country).

At Belgian level, NBN - the Belgian Bureau for Standardisation - is the national organisation responsible for the drafting and publication of standards. However, since 1980, the management of the environment in Belgium became a task for the regions (Flemish, Walloon and Brussels Capital Region). Since then, there has hardly been consultation or discussion between the regions as to which reference methods to use for environmental analysis.

As the development of European standards with respect to environmental monitoring were strongly linked to the European Directives, VITO in consultation with LNE and OVAM (see §1.2) started to consistently introduce European standards as Flemish reference methods since 2002. Besides, technical committees with Flemish recognised laboratories were organised, to discuss the practical implementation of the analytical reference methods.

A similar trend has been observed in the Walloon Region and was also recently (2012) initiated by the Brussels Capital Region. In some way, the European Committee for Standardization has led to a "rapprochement" in the internal Belgium situation. Still, structural consultation between the regions in this respect would be desirable. The European Committee for Standardization (CEN) only accepts comments from the Belgian Bureau for Standardisation (NBN), but often no unanimous comments are formulated because of the absence of a common Belgian environmental policy.

CEN closely cooperates with its international counterpart, the International Organisation for Standardization (ISO) in the fields of soil and water. With respect to ICP-MS, the following **EN standards** have been published so far (2012) by different CEN technical committees in the context of Environmental analysis:

CEN/TC 230 - Water analysis

- EN ISO 17294-2:2004 Water quality - Application of inductively coupled plasma-mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements (ISO 17294-2:2003)
- EN ISO 17294-1:2006 Water quality - Application of inductively coupled plasma-mass spectrometry (ICP-MS) - Part 1: General guidelines (ISO 17294-1:2004)

CEN/TC 264 - Air quality

- EN 14385:2004 Stationary source emissions. Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V
- EN 14902:2005 Ambient air quality. Standard method for the measurement of Pb, Cd, AS, and Ni in the PM 10 fraction of suspended particulate matter
- EN 15841:2009 Ambient air quality - Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition

CEN/TC 400 Horizontal standards in the fields of sludge, biowaste and soil

- CEN/TS 16171:2012 Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma-mass spectrometry (ICP-MS)

CEN/TC 292 Characterization of waste

- EN 16192:2012 Characterization of waste - Analysis of eluates
  (a reference is made to EN ISO 17294-1:2006 and EN ISO 17294-2:2004)
- EN 15192:2006 Characterization of waste and soil - Determination of Chromium(VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection
  (a note is made that hyphenated methods with ion chromatographic separation and detection techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS) may be used)

The lag in the publication of EN standards related to ICP-MS (starting in 2004) is somewhat in contrast with the first United States Environmental Protection Agency (US EPA) standard related to ICP-MS that was already published in 1990 for the determination of trace elements in water (US EPA 200.8). This US EPA procedure was updated in 1994 to address improved sensitivity and detector modifications and in 2005, guidance on the use of collision/reaction cell technology was introduced. US EPA also pioneered in 1997 with the first standard method using ion chromatography coupled to inductively coupled plasma-mass spectrometry (Bromate in Drinking Water, US EPA 321.8) and in 2007 with a standard method for elemental and speciation isotope dilution mass spectrometry (US

EPA 6800). According to the US National Environmental Methods Index (NEMI), 18 standard methods for the analysis of water using ICP-MS are available to date.

In Flanders, ICP-MS was introduced for the first time as a Flemish reference method in the compendium for sampling and analysis in support of the **waste and soil** remediation decrees in 2006 (CMA, see also Figure 9). The selection of the ICP-MS method as a reference method was the result of a round robin test that was organized by VITO in commission of OVAM in 2004 to evaluate the analytical performance of laboratories for the determination of Ba, Cd, Cr, Mo, Sb and Se in eluates with ICP-AES and ICP-MS [36]. Nineteen laboratories (from Flanders/Belgium and the Netherlands) with recognized expertise for eluate analysis participated in this round robin test and analyzed four samples spiked with the elements at relevant concentration levels. Based on these results, it was concluded that for the elements Mo, Ba, Cr and Cd accurate and reproducible data were obtained, independent of the technique applied (ICP-MS or ICP-AES). For the determination of the elements Sb and Se, the ICP-MS technique is the method of choice, especially when concentrations in the lower µg/L-range have to be determined with minimum measurement uncertainty. The results of this round robin test were also used as validation data for the introduction of ICP-MS in the EN standard for the analysis of eluates (EN 16192:2012).

The development of EN standards is governed by the principles of consensus and national commitment and this process can sometimes take a long time as illustrated in the next example. Project HORIZONTAL started in 2002 with the aim to develop harmonised European standards in the field of sludge, soil, and treated biowaste. These standards were needed in order to facilitate the regulation of these major streams in the multiple decisions related to different uses and disposal governed by EU Directives. The work started with desk studies to evaluate the feasibility of the development of a horizontal standard. Drafts of horizontal technical specifications (CEN/TS) were submitted to CEN/TC 400, a project committee especially devoted to this project. CEN/TC 400 decided in 2010 that the horizontal technical specifications (CEN/TS) from the Project HORIZONTAL were not sufficiently validated in the course of previous interlaboratory comparisons and should be upgraded to European standards by generating new reliable validation data [37]. A new validation was organised in 2013, in which a **soil**, a **sludge** and a **biowaste** material were distributed among different European laboratories and in which elements were determined after digestion/extraction of the materials according to the following European standards (EN) and technical specifications (CEN/TS):

- EN 16173:2012 Sludge, treated biowaste and soil - Digestion of nitric acid soluble fractions of elements
- EN 16174:2012 Sludge, treated biowaste and soil - Digestion of aqua regia soluble fractions of elements
- CEN/TS 16170:2012 Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma-optical emission spectrometry (ICP-OES)
- CEN/TS 16171:2012 Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma-mass spectrometry (ICP-MS)
- CEN/TS 16172:2013 Sludge, treated biowaste and soil - Determination of elements using graphite furnace atomic absorption spectrometry (GF-AAS)
- CEN/TS 16175-2:2013 Sludge, treated biowaste and soil - Determination of mercury - Part 2: Cold vapour atomic fluorescence spectrometry (CV-AFS)

To date (2013), the technical specifications (CEN/TS) for the determination of elements have not been published as European standard yet and the example illustrates the time lapse in the development of EN standards. It is worth to mention that along with this new validation study, a comparison was made between CEN/TS 16171 (ICP-MS) and CEN/TS 16175-2 (CV-AFS) for the determination of Hg in the digestion solutions. A good correlation was found between both

determination methods at these low levels of mercury and it is to be expected that Hg will be included in the scope of CEN/TS 16171 as one of the elements determinable by ICP-MS. This will certainly favour the use of ICP-MS for soil, sludge and biowaste analysis in the future, as no separate Hg determination (with, *e.g.*, CV-AFS) will be needed. Moreover and under impulse of the national standardisation organisations of the Scandinavian countries, nitric acid is being promoted as the sole acid to be used for environmental sample digestion. This would further play into the hands of ICP-MS as the method of choice for monitoring. However, countries such as Germany and the Netherlands have historically used *aqua regia* digestion and it remains to be seen whether they will agree with this proposal.

For the analysis of elements in **water** in the context of environmental regulatory monitoring, a study was performed by VITO in 2006 to evaluate the different analytical methods available for selection as reference method [38]. It was recommended that ICP-MS should be included in the compendium for sampling and analysis of water (besides ICP-AES and AAS) and this was done in the revision of the compendium in 2009. At the same time, the reference methods for the analysis of waste water as defined in VLAREM II were updated (annex 4.2.5.2, until 2009 only atomic absorption spectrometry and polarography were defined as reference methods). In 2011, by decision of the Flemish Government (in line with Directive 2009/90/EG and in support of the European Water Framework Directive), ICP-MS became the only method of choice for chemical analysis and monitoring of dissolved elements in surface water (with the exception of Hg, which is not included in EN ISO 17294, and for which a separate determination with, *e.g.*, CV-AFS is still needed).

For the analysis of elements in **air** in the context of environmental regulatory monitoring, the first version of the compendium for sampling and analysis of air (LUC) became available in 2012. In this compendium, a reference to ICP-MS, ICP-AES and AAS is made. In the same year, the reference methods for the analysis of elements in emissions as defined in VLAREM II were updated and a reference to the compendium was included (annex 4.4.2, until 2012 only AAS, ICP-AES, DCP-OES and XRF were defined as reference methods).

Currently, there is a greater appreciation of the importance of metrology in analytical chemistry with many environmental laboratories accredited to international standards such as ISO 17025. However, with increasing standardization and accreditation of professional qualifications, a critical comment can be formulated that possibly too much emphasis is placed on achieving uniform end results of an analysis rather than on understanding the analytical measurement within the context of the sample (obtaining an accurate value).

The assumption of standardization and accreditation in a regulatory context is that only one or a few constituents of a sample - usually the analytes of interest - play a role in the measurement result that is obtained. Though, this assumption is usually not true for environmental samples. When applying standardized procedures in routine, users tend to have as little concern as possible about which other species in the sample might yield a false response or whether the method is applicable to all samples in the measurement run. Also policy makers have an ambiguous relation to the concept of measurement uncertainty and how to deal with it in a regulatory context. This approach of using standardized procedures has been referred to “the chemical analysis of things as they are not” and chemists were classified as “Determinators”, while more traditional analytical chemists can be categorized as “Analysts” [39]. Determinators’ primary interest is how the analytical result pertains to a particular system and this is also often the assumption in the current routine use of environmental reference methods.

In some way, the increasing standardization and accreditation of professional qualifications that is introduced in the environmental regulatory monitoring has led to a false impression that also the understanding of the analytical measurement within the context of the sample was increased. One

must be aware that a breakdown of the monitoring chain (*i.e.*, drafting the sampling plan, sampling, sample preparation, sample analysis, data interpretation) into different entities / persons increases the risk of losing an overview on the real environmental issue. Unfortunately and under pressure of economic competition, an inverse relationship is being created in the (commercial) environmental laboratories between standardization and accreditation on the one hand and understanding and knowledge of the analytical measurement within the context of the sample on the other. It is to be expected that with increasing juridical issues in environmental regulatory monitoring, *environmental analysts* will become more and more *environmental determinators*. This is especially true when one takes into account that, from a regulatory point of view, strict compliance with the reference measurement methods is considered more important than obtaining an accurate value.

On the other hand, it is observed that with each introduction of new environmental legislation, not only the number of analytes of interest is increased, but also physicochemical properties of the sample are considered to acknowledge the issue of (bio)availability (*e.g.,* in WFD, the water quality criteria for Cd in surface water depends on hardness and pH, see § 2.5), the issue of geochemical characteristics (*e.g.*, soil remediation standards for *heavy metals* depends on the pH, clay and organic carbon content of the soil, see § 2.2) or the issue of toxicity (*e.g.*, hexavalent chromium in waste leachates, see § 3.3).

Hopefully, this trend will give rise to a better understanding of the analytical measurement within the context of the sample itself and will lead to joined forces between *environmental analysts and determinators* for the correct interpretation of the actual environmental situation.

Another negative side-effect of harmonisation and standardisation of analytical methods is that new and innovative monitoring / screening methods face difficulties of acceptance and use in a regulatory context. This is also related to the concept of measurement uncertainty (especially using screening methods) and how to deal with it in a regulatory context, *i.e.*, the translation of probabilistic data (analytical data) into boolean data (environmental issue? yes/no). While from a scientific point of view, it is believed that a combined monitoring methodology using on-line and/or screening monitoring methods in combination with standardised methods would lead to a more cost-effective and better understanding of local or regional environmental issues.

**Interesting links :**

- **Institut scientifique de service public (ISSeP)** is the reference laboratory for the Walloon region: http://www.issep.be
- **Brussels instituut voor milieubeheer (BIM)** is the reference laboratory for the Brussels Capital Region, http://www.leefmilieubrussel.be/
- The analytical methods used for environmental monitoring can be hazardous to the environment and to human health. Greener analytical methods use fewer hazardous solvents, use safer chemicals, prevent waste, and conserve energy during the sample preparation and analysis. Greenness profiles for many of the monitoring methods are available in the **(US) National Environmental Methods Index (NEMI)**.The greenness profiles, based on four criteria, give guidance for selecting a method that has a less negative impact on the environment : https://www.nemi.gov/
- Extended search engine for standards developed by The **European Committee for Standardization (CEN)**: http://esearch.cen.eu/esearch/

## 1.4. THE ATOMIC SPECTROMETRY TIMELINE IN ENVIRONMENTAL ANALYSIS

In the following section (§ 1.4.1), ICP-MS will be discussed with emphasis on the different components on the one hand and on how the different types of (commercially available) instruments cope with spectral interferences, the Achilles' heel of ICP-MS, on the other. In the context of this dissertation, quadrupole-based ICP-MS units (ELAN 6000 and NEXION 300S, Perkin Elmer) and a sector-field ICP-MS unit (Element II, Thermo Fisher Scientific) were used (see Figure 2).

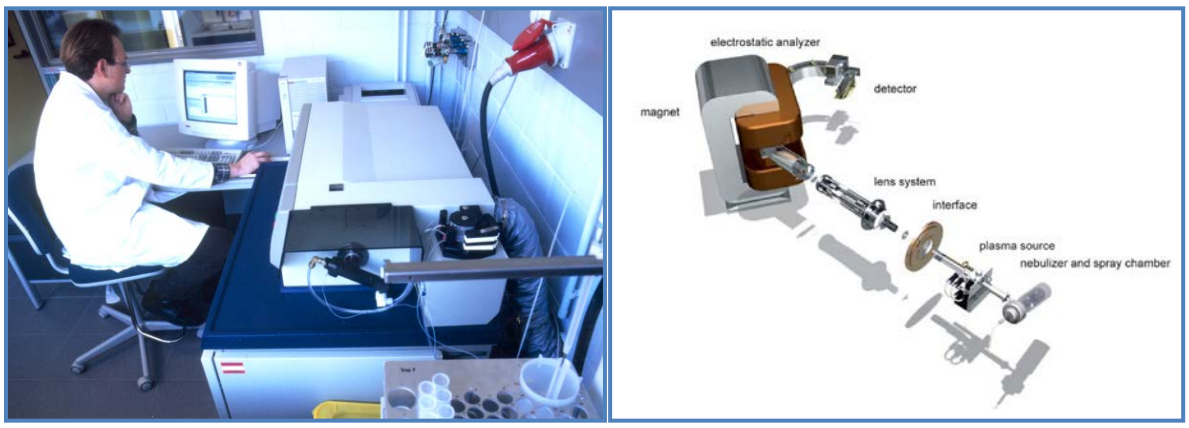



Figure 2: (left) Young scientist operating a Perkin Elmer Elan 6000 quadrupole-based ICP-MS instrument (1999); (right) schematic representation of a sector field ICP-MS instrument (Element II), Thermo Fisher Scientific.

Thereafter (§ 1.4.2), the emergence of ICP-MS in environmental analysis since 1980 and some milestones of important Flemish/European/US standard methods based on ICP-MS for the determination of elements in environmental matrices are described (see also § 1.3). Sample preparation is discussed in § 1.4.3, as this is usually needed in environmental analysis to convert analytes to a more suitably detectable form or to separate them from the sample matrix.

### 1.4.1. ICP-MS INSTRUMENTATION

An ICP-MS instrument combines a high-temperature inductively coupled plasma (ICP) ion source (temperature of around 6000-10000 K) with a mass spectrometer [15-17]. The ICP source converts the atoms of the elements in the sample into ions; these ions are then separated from one another according to their mass-to charge ratio and detected by the mass spectrometer (the different components are visualised in Figure 3).

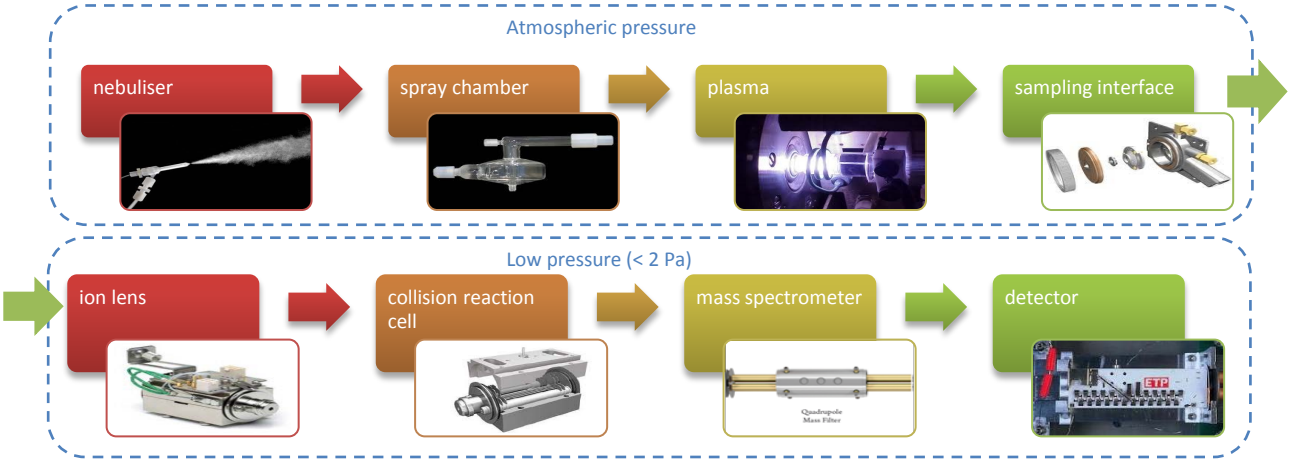



Figure 3: General scheme of an ICP-MS instrument with indication of different components.

### → The different components of an ICP-MS instrument [15-17]

The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a **nebulizer-spray chamber** or by using a laser to directly convert solid sample into an aerosol. Once the sample aerosol is introduced into the **ICP torch**, it is completely desolvated. The molecules set free out of the solid particles thus formed are atomized and these gaseous atoms are then ionized towards the end of the plasma. From a physical point of view, a plasma is nothing else than the fourth state of matter besides solid, liquid and gas (most of the matter in our universe exists in the state of a plasma)[19]. The ions formed in the ICP are typically positive ions, $M^+$ or $M^{2+}$, therefore, elements that prefer to form negative ions, such as Cl, Br, F, *etc.*, are very difficult to determine via ICP-MS. The sample matrix may affect the degree of ionization that will occur in the plasma or give rise to ionic species that may interfere with analyte determination. Argon is commonly used as plasma gas.

Once the elements in the sample are converted into ions, they are brought into the mass spectrometer via the **interface cones** [21]. The interface region in the ICP-MS transmits the ions travelling in the argon stream at atmospheric pressure into the low pressure region of the mass spectrometer (<2 Pa). This is done through the intermediate vacuum region created in-between the two interface cones, the sampler and the skimmer. The sampler and skimmer cones are metal disks with a small hole (~1mm) in the centre. The purpose of these cones is to sample the centre portion of the ion beam coming from the ICP torch. Due to the small diameters of the orifices in the sampler and skimmer cones, ICP-MS has some limitations as to the amount of total dissolved solids allowed in the samples. Generally, it is recommended that samples have no more than 0.2% total dissolved solids (TDS) for best instrument performance and stability. If samples with very high TDS levels are run, the orifices in the cones will eventually become blocked, causing decreased sensitivity and detection capability and requiring the system to be shut down for maintenance. This is why many sample types, including digested soil and rock samples must be diluted before ICP-MS analysis (see also § 2.2).

The ions from the ICP source are then transported to the mass spectrometer by the **electrostatic lenses** in the system. Different types of ICP-MS systems have different types of lens systems. The simplest employs a single lens, while more complex systems may contain as many as 12 ion lenses. Each ion optic system is specifically designed to work with the interface and mass spectrometer design of the instrument.

Once the ions enter the **mass spectrometer**, they are separated according to their mass-to-charge ratio. Different types of mass analyzers are being used in commercially available ICP-MS instruments, *i.e.,* quadrupole mass analyzers, sector-field mass analyzers and time-of-flight (TOF) analyzers.

The most commonly used type of mass spectrometer is the **quadrupole mass filter (ICP-QMS)**. A quadrupole mass filter consists of 4 rods, AC and DC voltages are applied to the two diagonally opposed pairs of the rods. The two pair of rods thus obtained, show DC voltages of opposite signs, while the sinusoidal AC voltages (RF frequency) show a 180° phase difference. The result is that an electrostatic filter is established that only allows ions of a single mass-to-charge ratio (m/z) to pass through the setup to the detector at any given time. The quadrupole mass filter is a sequential filter, with the settings being changed to select another m/z. However, the voltages on the rods can be switched at a very high rate. This high scanning speed is why the quadrupole ICP-MS is often considered to have (quasi) simultaneous multi-elemental analysis properties. Very recently, a new type of quadrupole-based ICP-MS instrument has been introduced onto the market [22]. This instrument is referred to as a triple quadrupole or an ICP-QQQ set-up by the manufacturer (Agilent), although the terminology “triple quadrupole” is not entirely correct, as in-between the two quadrupole analyzers, an octopole-based collision/reaction cell is located. The first quadrupole

prevents all off-mass ions from entering the cell, allowing more controlled and efficient interference removal in reaction mode (see further, Figure 5), regardless of sample type.

Conventionally, quadrupole ICP-MS instruments provide approximately unit mass resolution. High mass resolution of **sector-field instruments (ICP-SFMS)** is a feature which depends on the geometry of the electric and magnetic sector, and the slit configuration. In this type of instrument, a combination of a magnetic sector and an electrostatic sector are used to separate and focus the ions. Such an arrangement is called a double-focusing high resolution mass spectrometer. In ICP-MS, reverse Nier-Johnson geometry - where the magnetic sector is located before the electrostatic sector - is commonly used in order to decouple the electric fields in the electrostatic sector from any electric field originating by the ICP RF generator (*e.g.*, ELEMENT ICP-SFMS, Thermo). The resolution of sector-field instruments can be changed by adjusting the width of the entrance and exit slits before and after the MS. Typical ICP-SFMS instruments have resolving powers up to $10^4$ and are operated at pre-set resolution settings for low, medium or high-resolution to make their operation easier for the user. Unfortunately, for every 10-fold increase in resolving power, there is a concomitant decrease in signal intensity. Recently a sector-field mass spectrometer with Mattauch-Herzog geometry became commercially available (Spectro MS). The advantage of this geometry over the Nier-Johnson geometry is that the ions of different masses are all focused onto the same plane and offers truly simultaneous detection of all isotopes (Li to U) as a result of a semiconductor-based multi-channel detector, albeit at low mass resolution only.

Another method of mass spectrometry is based on the measurement of the time-of-flight of ions of known energy over a known distance. The **time-of-flight mass analyzer (ICP-TOFMS)** is a pseudo-simultaneous detection type device, which can accomplish a full mass spectrum in approximately 30 µs. In this technique, ions are subjected to a pulsed electric field which, ideally, imparts the same kinetic energy (KE) on all ions in the packet. These ions are then directed to a field-free region (*i.e.*, drift tube) where the differences in velocities spatially and temporally separate ions of differing m/z. The KE attained by each ion will be product of the ion's charge and strength of the electric field.

Once the ions have been separated according their mass-to-charge ratio, they must then be detected or counted by a suitable **detector**. The fundamental purpose of the detector is to translate the number of ions striking the detector into an electrical signal that can be measured and related to the number of atoms of that element in the sample via the use of calibration standards. Most detectors use a high negative voltage on the front surface of the detector to attract the positively charged ions to the detector. Once the ion hits the active surface of the detector, a number of electrons is released, which then in turn strike the surface of the detector, amplifying the signal. In the past years, the continuous dynode channel electron multiplier (CEM), which was used on earlier ICP-MS instruments, has been replaced with discrete dynode type detectors. Discrete dynode detectors generally have wider linear dynamic ranges than CEMs, which is important in ICP-MS, as the concentrations analyzed may vary from sub-µg/L to high mg/L. Both detector types can be run in two modes, pulse-counting and analog, which further extend the instrument's linear dynamic range and can be used to protect the detector from excessively high signals. A second type of ICP-SFMS instrument is also available that uses multiple detectors, this type is called multi-collector ICP-SFMS or MC-ICP-SFMS [16]. These instruments are generally designed and developed for the purpose of performing high-precision isotope ratio analyses. Since an array of 5-10 detectors can be positioned around the exit slit of a double-focusing system, the isotopes of a single element can generally all be determined simultaneously, leading to the technique's high-precision. MC-ICP-MS instruments tend to use simpler, less expensive Faraday cup type detectors, as these have the ability to deal with the very high count rates common with magnetic sector instruments and do not suffer from dead time effects. However, these detectors do not have the flexibility, necessary for quadrupole ICP-MS instruments.

**Interesting You tube links on the principles of ICP-MS** :

- Agilent, ICP-MS (collision cell) : http://www.youtube.com/watch?v=MQqtV2oiC6U, last accessed on 08/01/2013
- Agilent, ICP Triple Quad : http://www.youtube.com/watch?v=b9BfKcxmltI&feature=relmfu, last accessed on 08/01/2013
- Perkin Elmer, ICP-MS (collision and reaction cell) : http://www.youtube.com/watch?v=L-FYh2z9mi0&feature=related, last accessed on 08/01/2013.
- Spectro, MC-ICP-SF-MS : http://www.youtube.com/watch?v=75uMtzyo844, last accessed on 08/01/2013

## → How to cope with spectral interferences? [17]

Spectral interferences are often considered as the Achilles' heel of ICP-MS. Several strategies on how to cope with spectral interferences were used in the context of this dissertation and are described in the following section.

Spectral interferences in ICP-MS are caused when ions generated from the plasma, the sample, entrained air or a combination thereof carry a nominal mass-to-charge ratio that is identical to that of the analyte ion. Whether or not an interfering ion signal present at mass m ± Δm will be separated from an analytical signal present at mass m depends on the mass difference Δm and the resolution of the instrument. Mass resolution R is generally defined as R = m/Δm, where Δm is the mass difference necessary to achieve a valley of 10% between two neighbouring peaks of identical intensity at mass m and m ± Δm as shown in Figure 4.

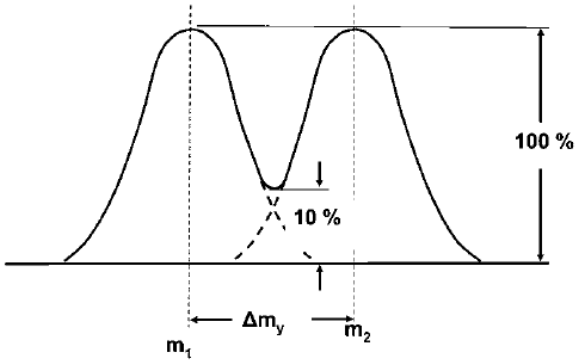



Figure 4: Illustration of 10% valley definition of mass resolution (courtesy of [17]).

Quadrupole mass spectrometers as used in ICP-MS provide peak widths between 0.7-1.0 amu. For most environmental applications, and especially for elements in the mass region 40-80 amu (Cr, Cu, Ni, Zn, As), this resolution is not sufficient to separate the overlapping signal from a molecular or isobaric ion from that of the nuclide of interest.

Spectral interferences may be subdivided into several groups, as they can be attributed to the presence of isobaric atomic ions, multiply charged ions and polyatomic ions of various origins.

**Isobaric overlap** exists when the signals of nuclides of different elements coincide at the same nominal mass. Since the mass difference between isobars is in general very small, resolutions between $10^4$ and $10^8$ are required for their separation. The maximum mass resolution setting of commercial ICP-SFMS instruments (about $10^4$) is by far insufficient to overcome interferences of this kind. Therefore, an alternative approach to cope with this problem is used. For each element - with the only exception of indium - at least one isotope is free from isobaric overlap and can be monitored

instead, but in many cases this will not be the most abundant one. This strategy is often successful. If more complex samples are analysed, the number of analyte signals disturbed by other kinds of interferences is drastically increased in the mass range below 100 amu. Since isobaric interferences are usually easily predictable, they can also be corrected for mathematically by relying on natural isotopic abundances.

**Multiply charged ions** will be found in the mass spectrum at a position m/z (m is the nominal mass and z is the ion charge), *i.e.*, doubly charged ions are for instance found at half of their nominal mass. Multiply charged ions usually have a lower formation rate in an ICP and occur mainly in the medium mass range. Doubly charged ions of the main matrix constituents are frequent contributors.

**Polyatomic ions** cause the most severe spectral interference problems in environmental analysis and thus, their origin shall briefly be discussed. Polyatomic interferences are less predictable and depend on the sample composition (analytes and matrix) and the operational parameters of the ICP-MS system. Therefore, it is difficult and sometimes impossible to mathematically correct for them. These interferences require mass resolutions of $10^3$ to $10^4$ for their resolution up to mass 70 and sometimes more than $10^4$ at higher masses. Polyatomic interferences may find their origin in the sample itself, such as oxide ions which, owing to their high bond strength, have a real chance of 'surviving' the passage through the hot zones of the plasma. They may also arise from the discharge gas, contaminants, entrained air, the reagents and solvents used and the matrix of the sample. They might become extremely complex in organic matrices. The formation of cluster ions from the dominant species in the plasma (Ar, H, O, C, N) is a major source of polyatomic ions that do not only arise in the plasma, but can also be formed during the extraction process [18]. The formation of interferences is governed by thermodynamics (exothermic and endothermic processes) and is possible if the energy which is needed for the process is provided by the plasma or the excess reaction heat. The product molecule usually has a binding energy which is high enough to survive the short passage through the plasma and the interface as the exposure time of particles in the plasma is only about 2 ms.

Proper optimization of the instrument is the very first step towards overcoming interferences. Nonetheless, there are several strategies to cope with residual interferences (besides the use of high mass resolution), which will be described shortly in the following sections. The common $^{40}Ar^{35}Cl^+$ interference - argon from the plasma and chloride from the sample matrix combine to form a polyatomic species, $^{40}Ar^{35}Cl^+$, which carries the same nominal mass as the arsenic isotope (m/z 75) - will be used as an example to demonstrate how the different strategies cope with spectral interferences.

***Mathematical correction procedures***

Mathematical correction is usually applied in case of relatively simple situations (isobaric interferences) or if all other measures fail. In the case of an isobaric interference, another nuclide of the interfering element is measured and the contribution of the interference to the analyte signal is calculated relying on the abundances of the isotopes of the interfering element.

The situation is more complicated for polyatomic interferences as their occurrence are not easily predictable and depends on the operational parameters as well as on the matrix. Therefore, the formation probability has to be estimated using external matrix-matched solutions or the same ion has to be observed at a different m/z and its intensity used for further correction.

This is demonstrated via the following example: $^{75}As^+$ suffers from a spectral interference in Cl-containing solutions as a result of the occurrence of the $^{40}Ar^{35}Cl^+$ ion. As a consequence, the following mathematical strategies can be used: The $^{40}Ar^{35}Cl^+$ interference is measured along with the $^{35}Cl^+$ (or

$^{37}Cl^+$) signal in pure matrix solutions, containing only the matrix and Cl of increasing concentration, but no As. The ratio $^{40}ArCl^+/^{35}Cl^+$ is calculated from these solutions and an average ratio is further used as correction factor. Now, the signal on mass 75 is measured in the solution along with the signal of $^{35}Cl^+$ on mass 35 (or $^{37}Cl^+$ on mass 37). The $^{35}Cl^+$ (or $^{37}Cl^+$) signal is now multiplied with the previously calculated factor, providing an estimate for the interference of $^{40}Ar^{35}Cl^+$ on mass 75. The remaining signal is most probably the As signal. Unfortunately, the solution isn't always this simple: $^{75}As^+$ also suffers from the polyatomic interference $^{40}Ca^{35}Cl^+$ in calcium-containing samples (*e.g.*, soil). Another possibility would be that the $^{40}Ar^{37}Cl^+$ signal on mass 77 is measured along with the signal on mass 75. Via the isotopic abundances of Cl, the $^{40}Ar^{35}Cl^+$ signal can be calculated from the $^{40}Ar^{37}Cl^+$ signal. Again, the remaining signal is most probably the requested As signal. Nonetheless, we can observe an additional problem: we also find $^{77}Se^+$ on mass 77, where we expect our $^{40}Ar^{37}Cl^+$ interference. Therefore prior to calculating the $^{40}Ar^{35}Cl^+$ contribution from the $^{40}Ar^{37}Cl^+$ signal, we have to subtract the signal of $^{77}Se^+$. We can estimate the contribution of $^{77}Se^+$, relying on the isotopic abundances of Se and using, *e.g.*, the $^{82}Se^+$ signal intensity. Nonetheless, we have to consider that we find an isobaric interference of $^{82}Kr^+$ on mass 82. Not to consider any $^{40}Ar_2{}^1H_2{}^+$ interference.

It is obvious that this strategy only leads to satisfying results when a relatively high analyte concentration and low matrix concentration are occurring. As good practice, it is always recommended to monitor more than one isotope (if possible), even if the other isotopes are less abundant.

***Sample introduction systems***

Among various strategies discussed over many years, the appropriate selection of a sample introduction system best suited for the analytical problem can already help to overcome much solvent- and matrix-based spectral interferences. Cooled spray chambers are applied to reduce the amount of water vapour transferred to the plasma. These systems use heating/cooling devices in order to first vaporize the solvent and subsequently condense and drain the solvent. Advanced systems use desolvation systems to significantly reduce interferences. Solvent molecules can pass through membranes and are removed by a counter stream of Ar, whereas the dried aerosol is transported to the plasma (oxide formation rates can be reduced by some orders of magnitude compared to conventional introduction systems) [23]. Depending on the temperature programmes chosen for electrothermal vaporization, solvent-based interferences can be reduced prior to the analysis of the trace elements. Dissolution of solid samples and thus interferences caused by mineral acids can be avoided if laser ablation is chosen as a sample introduction device, even though other matrix-based interferences can still occur.

***Sample/matrix separation***

One straight chemical method to avoid formation of interferences is the direct separation of the analytes of interest from the matrix. Even spectral interferences from samples with a high level of dissolved salts can be avoided if, *e.g.*, hydride or cold vapour generation is applied for trace/matrix separations. The analytes of interest can be separated from the interfering matrix by chromatography as well. This is accomplished either by using a batch process or by direct coupling of chromatography to ICP-MS (see also § 3.2 )[24].

***Cool/cold plasma technique***

A number of interfering ions are formed inside the inductively coupled plasma or at the sampling cone surface in contact with the plasma. Thus, changing the working conditions of the plasma is a powerful tool, especially for the reduction of argon-based interferences. This approach was realised in the 'cool/cold plasma' technology. Cool/cold plasma conditions are obtained by increasing the

nebulizer gas flow rate or addition of an additional gas to the central channel of the torch, along with the reduction of the RF-generator power. In this operation mode, the risk of secondary discharges is high. The breakthrough was achieved once effective plasma shielding was developed by appropriate induction coil grounding or application of a plasma shield. The cold plasma technique helps to reduce argon-based spectral interferences such as $Ar^+$, $ArC^+$, $ArO^+$, $ArCl^+$, $Ar_2^+$. This can be used for an improvement of limit of detections (LODs) for elements such as Ca, K, Cr, and Fe, which are difficult to determine at low levels, *e.g.*, in the electronic industry. These advantages have to be paid for under the form of many additional spectral interferences coming from water clusters (combinations with $H_2O$ and $H_3O^+$) and increased oxide formation [19]. Additionally, a loss in sensitivity for all elements with first ionization energy above 8 eV have been observed and even worse, a loss of robust plasma conditions causing elevated matrix effects hampers its application. As a consequence, this mode is mainly used for relatively pure samples with low salt content.

***Collision and reaction cell technology***

Among all approaches for overcoming spectral overlap, those based on instrumental improvements have been most successful and in particular, the application of collision and reaction cells in front of a low resolution quadrupole mass analyser have changed the whole spectrum of applications in ICP-QMS. In current cell technologies, a pressurized cell, equipped with an ion guide (which – depending on the instrument – is an RF-only band-pass quadrupole, a hexapole or an octopole) is used to overcome a number of prominent spectral interferences by gas phase reactions with a reaction gas (reaction cell) or by application of a retarding field in combination with a non-reactive collision gas (collision cell). In the latter case, molecular polyatomic species are expected to lose more kinetic energy by collisions with a buffer gas then atomic ions. With application of a retarding field, the polyatomic ions can be selectively discriminated against (kinetic energy discrimination). The KED mode of operation in the Agilent 7700 series ICP-MS is represented below (figure by courtesy of Agilent).

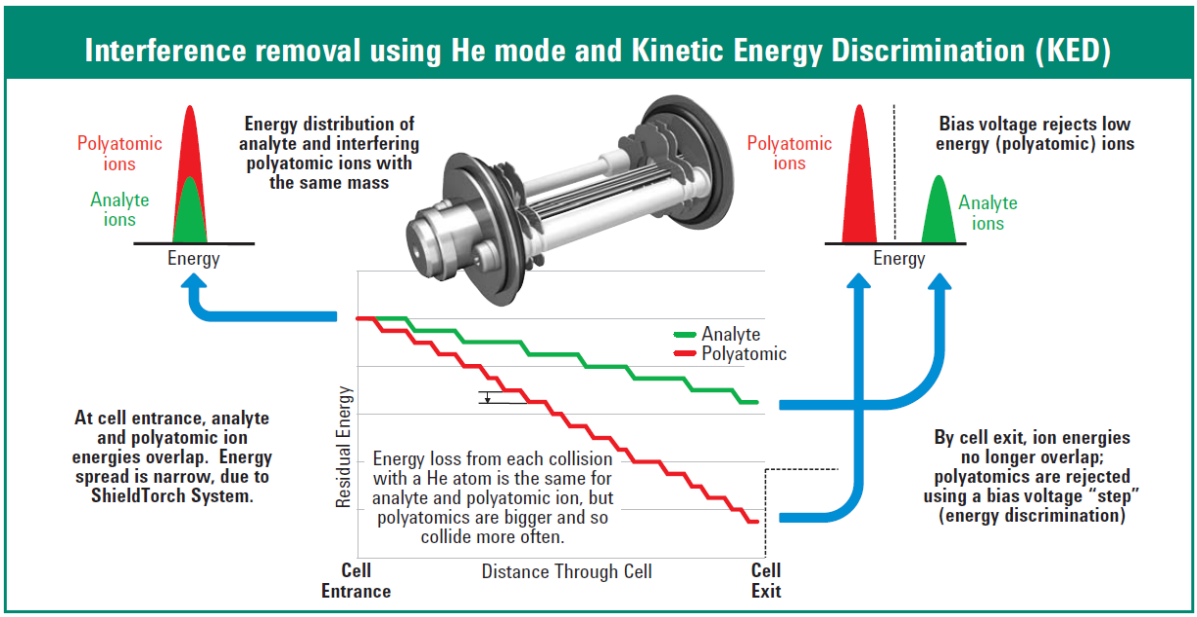



Figure 5: The KED mode of operation in the Agilent 7700 series ICP-MS (courtesy of Agilent).

Reaction gas technology is based on the formation of different molecular ions form the interfering polyatomic species (*e.g.*, $2\ ArAr^+ + H_2 \rightarrow 2\ ArArH^+$), neutralisation of interferences (*e.g.*, $ArCl^+ + NH_3 \rightarrow ArCl + NH_3^+$) or by shifting the analyte of interest to a higher mass (*e.g.*, $As^+$ will be converted to $AsO^+$ and the mass will be shifted from mass 75 to 91 using $O_2$ as reaction gas). Usually, reaction gas

technology is advantageous to be coupled with an ion filter in order to exclude newly formed interferences. Whether a reaction will proceed or not can be predicted by thermodynamics, nevertheless optimization is usually done empirically. Unfortunately, also no single reaction or collision gas or application of the combination of a buffer gas and a retarding field is able to overcome all possible interferences from polyatomic species and most often, the interfered element has to be determined in a separate run to achieve the best sensitivities for as many elements as possible. Moreover, the matrix dependence of the reaction/collision cell technology is not fully elucidated. Nonetheless, the technology has no inherent limitations, in contrast to high resolution ICP-SFMS where the maximum resolution is $10^4$.

***Mass resolution***

Conventionally, quadrupole ICP-MS instruments provide approximately unit mass resolution. Typical sector-field ICP-MS instruments have resolving powers up to $10^4$ and are operated at pre-set resolution settings for low, medium or high-resolution to make their operation easier for the user. Unfortunately, for every 10-fold increase in resolving power, there is a concomitant decrease in signal intensity.

Most polyatomic species can be separated from the nuclide of interest by application of high mass resolution ($m/\Delta m < 10^4$). In most of the relevant examples of spectral interference, a resolution of about 4000 (most often called medium resolution) would be by far sufficient for separation. Only in special cases, some polyatomic species are observed, which require a higher mass resolution ($4000 < m/\Delta m < 10\,000$). In the example given for $^{75}As^+$, a resolution of about 8000 is sufficient to overcome this problem.

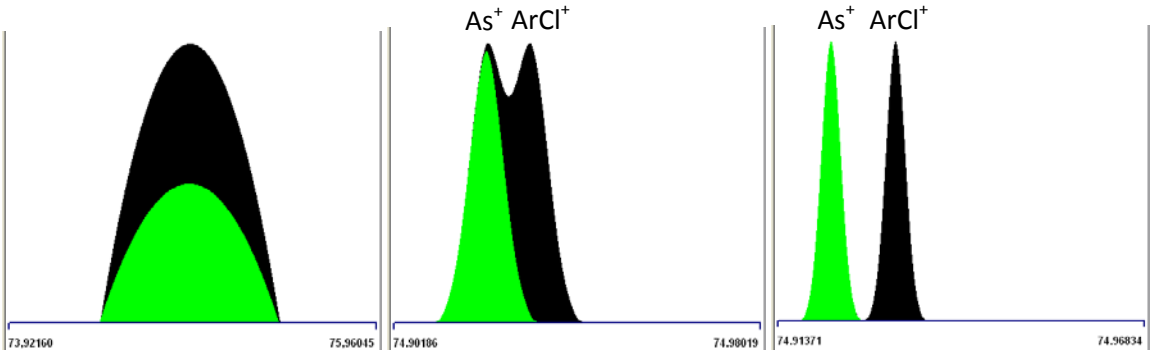



Figure 6: Effect of measuring in the different resolution modes (low (~ quadrupole), medium and high resolution, respectively) on the separation between the $^{75}As^+$ (green) and $^{40}Ar^{35}Cl^+$ (black) signals.

Of course, high mass resolution is not a panacea against all spectral interferences. As mentioned already, isobaric interferences are far beyond the scope of most commercially available devices. $MO^+$ ions, where oxygen is a constituent of many mineral acids and water, can be resolved from the corresponding analyte signals in the mass range below 100 and above 140 amu (a resolution of less than $10^4$ is sufficient for a complete separation). In the mass range between 100 and 140 amu, a resolution of up to $10^6$ would be necessary. The required resolution exceeds by far the resolution attainable with commercially available instrumentation. This is a crucial point for, *e.g.*, low level rare earth element (REE) determination if formation of oxides is not prevented by other means. This example demonstrates that high mass resolution is a very powerful approach to overcome many, but not all of the spectral interferences occurring in routine applications.

### 1.4.2. ATOMIC SPECTROMETRY TIMELINE

One of the most successful analytical plasma sources in emission as well as in mass spectrometry, is the inductively coupled plasma. The analytical inductively coupled plasma (ICP) was described in 1964 by Greenfield and later introduced for analytical applications in atomic emission spectroscopy (AES) [17]. The first commercial ICP-AES instrument was constructed in 1974. In 1978, Houk started to couple an ICP to a quadrupole-based mass analyzer. First results were already published in 1980, the official birth year of ICP-MS (see also timeline, Figure 9)[1,25].

In the 1980s, a transition from Flame Atomic Absorption Spectrometry (FAAS) to Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) as a workhorse in environmental laboratories was driven by a commercial necessity for higher sample throughputs with a higher degree of automation. In the 1990s, many water laboratories shifted to ICP-MS as the technique promised to offer the throughput capabilities of ICP-AES, coupled with the sensitivity of Electrothermal Atomic Absorption Spectrometry (ETAAS). The higher detection power offered by ICP-MS, compared to that of ICP-AES, led to its rapid acceptance by the Environmental and Earth Science Communities [26].

The main trend in water analysis since then has been the gradual decline and replacement of FAAS with ICP-AES, and the rise and fall of ETAAS as a competitor from ICP-MS. AAS is still heavily used throughout the world due to its low relative cost and usefulness for cross-checking results from other instruments. Most of the advances in AAS and ICP-AES now are front-end modifications; advances in the instruments themselves seem to be mostly increased computerisation with automatic set-up of conditions. One of the limiting factors for AAS is that it is essentially mono-elemental; attempts have been made to create fast sequential instruments to speed up analysis or perform simultaneous multi-element ETAAS (*e.g.* continuum source atomic absorption spectrometry [27]). Some of the more important innovations in ICP-AES include the introduction of dual view instruments and the adoption of Echelle spectrometers coupled with array detectors [28].

However, it is argued in a recent 25-year retrospective spectrometry update that the most important advance in water analysis has been the development of ICP-MS from a research curiosity into a robust, precise and sensitive analytical tool that now can detect most elements in fresh and drinking waters without any or after minor sample pretreatment [26,29]. Routine methods for the elemental analysis of drinking water were published in 1990 (see §1.3). By the early 1990s, the capability of ICP-MS as an element-specific HPLC detector was being increasingly exploited for speciation analysis (see §3.1). Sensitivity improvements were gained using similar strategies to those employed with ICP-AES, such as the use of ultrasonic nebulisers.

Figure 7 shows the elements traditionally determined by ICP-MS and their approximate Instrumental Detection Limit (IDL). Care should be taken to note that IDLs are calculated as 3 times the standard deviation of a blank measurement and represent the best possible detection capability of the instrument. In real life, the Method Detection Limit (MDL) will generally be (sometimes) higher than the IDL and will depend upon many factors, including: laboratory and instrument background levels, sample matrix, sample collection and preparation methods, and operator skill level (see also monitoring studies, CHAPTER 2). However, the IDL can be used as a general guide as to the relative capabilities of the ICP-MS technique as compared to other analytical techniques.

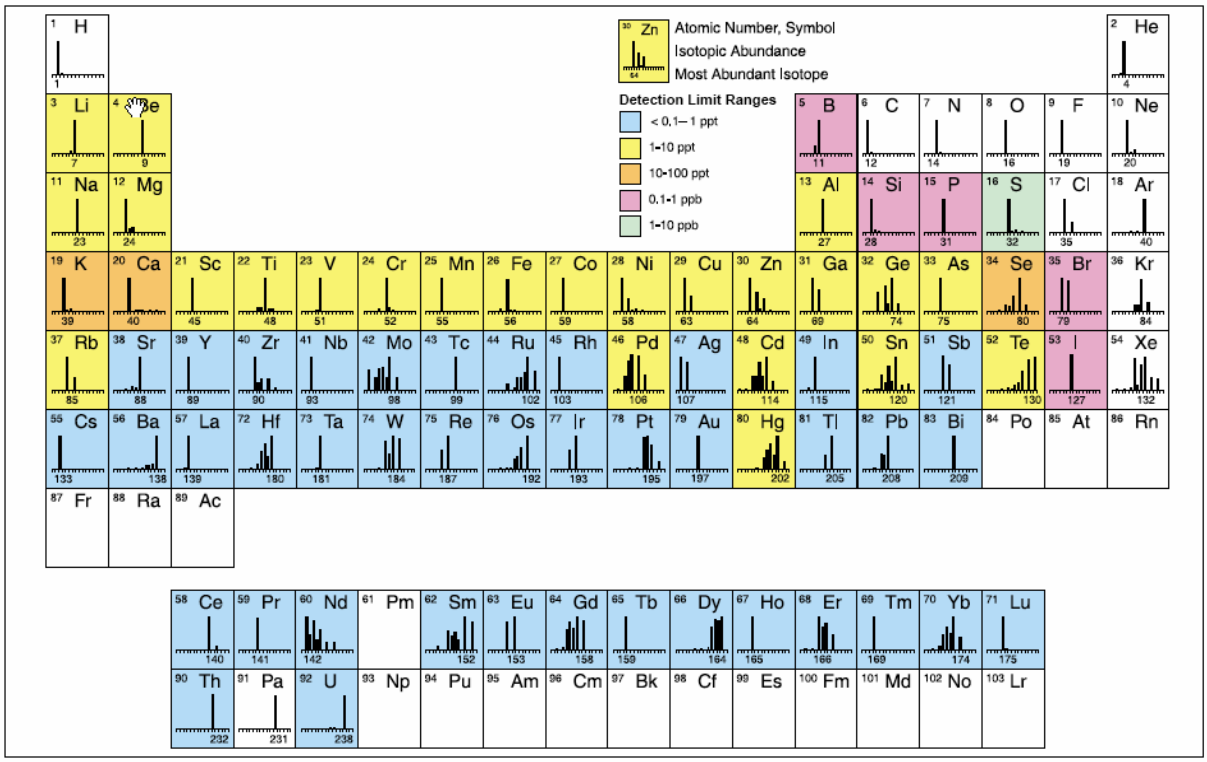



Figure 7: Approximate detection capabilities of the ELAN 6000 quadrupole ICP-MS (Courtesy of PerkinElmer, Inc.).

It should be noted that for several elements including S, Se, B, Si, P, Br, I, K, and Ca, ICP-MS shows fairly high detection limits. In the case of I and Br, this is due to the fact that very few positive ions are formed in the ICP plasma for these elements. For elements such as S, Se, P, K, and Ca, isobaric and molecular interferences from either the sample matrix or plasma species interfere with the primary isotope. This means that less abundant isotopes with less interference (if available) must be used for determination of these elements, which will degrade detection capabilities for these elements.

Sensitivity improvements due to instrument design were obtained when sector-field mass spectrometers were used with the ICP ion source [17]. Single-collector sector-field ICP-MS instruments were designed to offer higher sensitivity than quadrupole-based systems. When they became available commercially in 1989, their use tended to be restricted to facilities where applications necessitated high mass resolution or enhanced sensitivity. The use of such instruments has not spread widely to other environmental laboratories, partly due to cost considerations, but mostly because the needs of these laboratories were satisfied by the performance of quadrupole-based systems. Spectral interferences remained an issue with quadrupole-based systems and necessitated the development and frequent checking of computer algorithms to correct for interferences from major element-containing polyatomic ions, particularly for trace elements with an m/z of ≤ 80. Many analysts also modified their dissolution protocols, sometimes detrimentally, in order to produce a final solution in dilute nitric acid because of the contribution of other mineral acids to the formation of significant polyatomic interferences.

In the 2000 Atomic Spectrometry Update-Environmental analysis of JAAS, the first collision cell instrument with a hexapole cell was described; however, the boom in the literature describing the use of these instruments occurred during the period covered by the 2003 review, and by the 2005 review, a themed issue of JAAS focusing on the use of collision and reaction cell techniques in atomic mass spectrometry has appeared [26]. Nowadays, collision and reaction cell technology is included in practically all commercially available quadrupole-based ICP-MS instruments.

The dash to ICP-MS has however not consigned FAAS, ETAAS and ICP-AES to museums. For laboratories undertaking analysis of environmental matrices and focusing attention to a couple of elements and/or applications only, such techniques remain competitive. This is illustrated in the figure below, providing an overview of the catalogue prices of the different commercially available instruments (year 2012, prices by courtesy of Thermo, Agilent, Spectro and Perkin Elmer). The vast majority (around 90%) of ICP-MS systems sold worldwide use a quadrupole mass spectrometer, with alternative configurations (*e.g.*, double-focusing sector-field, time-of-flight) making up the remainder [31].

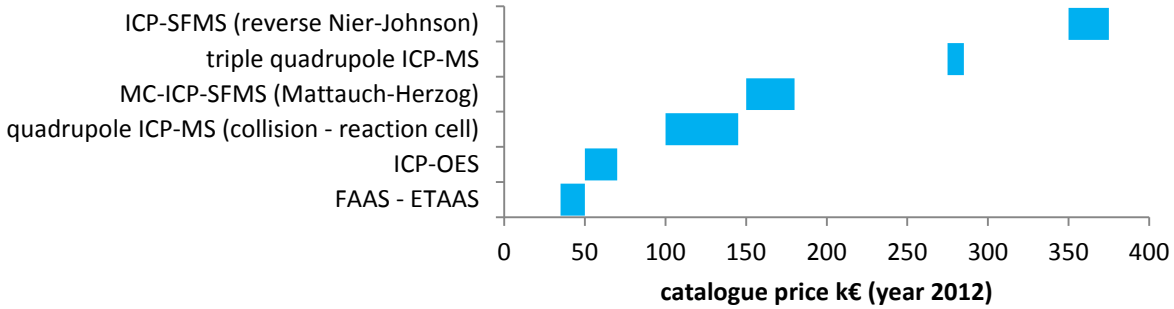



Figure 8: Catalogue prices of commercially available atomic spectroscopy instruments (year 2012).

In summary, in the sixties of last century, commercial Atomic Absorption Spectrometry (AAS) instruments were introduced, followed by inductively coupled plasma-atomic emission spectrometry instruments (ICP-AES) in the seventies and inductively coupled plasma-mass spectrometry instruments in the eighties (ICP-MS). It is clear from Figure 10 that since its introduction in 1980, ICP-MS applications have continuously increased. The papers on ICP-MS as a speciation tool start appearing in 1986 and represent 20 % of the total published papers on ICP-MS during the last 10 years. The papers on ICP-MS in environmental research also started to appear in 1987 and represent 15 % of the total number of published papers on ICP-MS during the last 10 years. Of all papers published in the field of ICP-MS in environmental research, approximately ¼ is dedicated to speciation analysis.

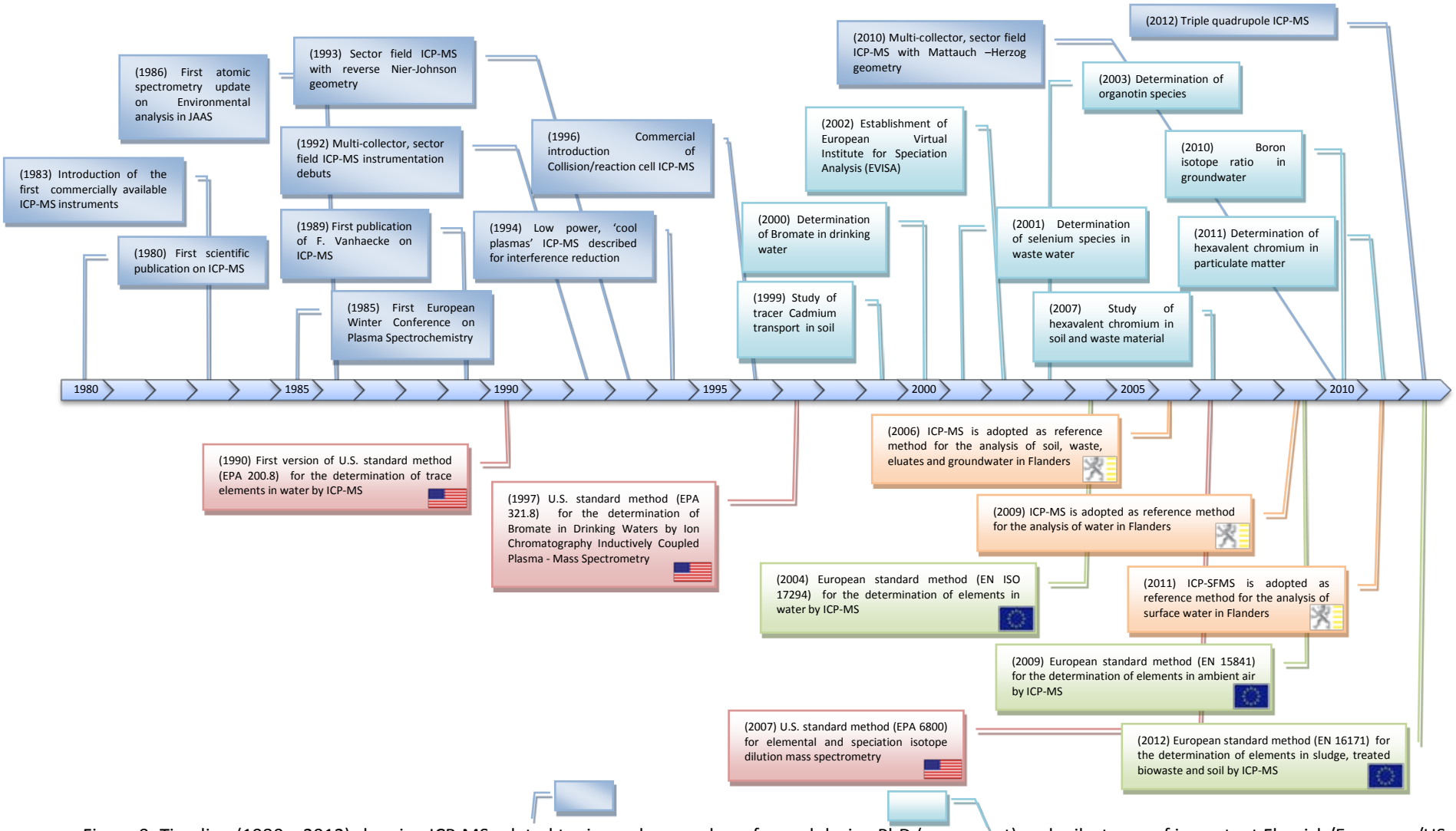



Figure 9: Timeline (1980 – 2012) showing ICP-MS related topics and research performed during PhD (upper part) and milestones of important Flemish/European/US standard methods for the determination of elements in Environmental matrices (lower part) [28,29].

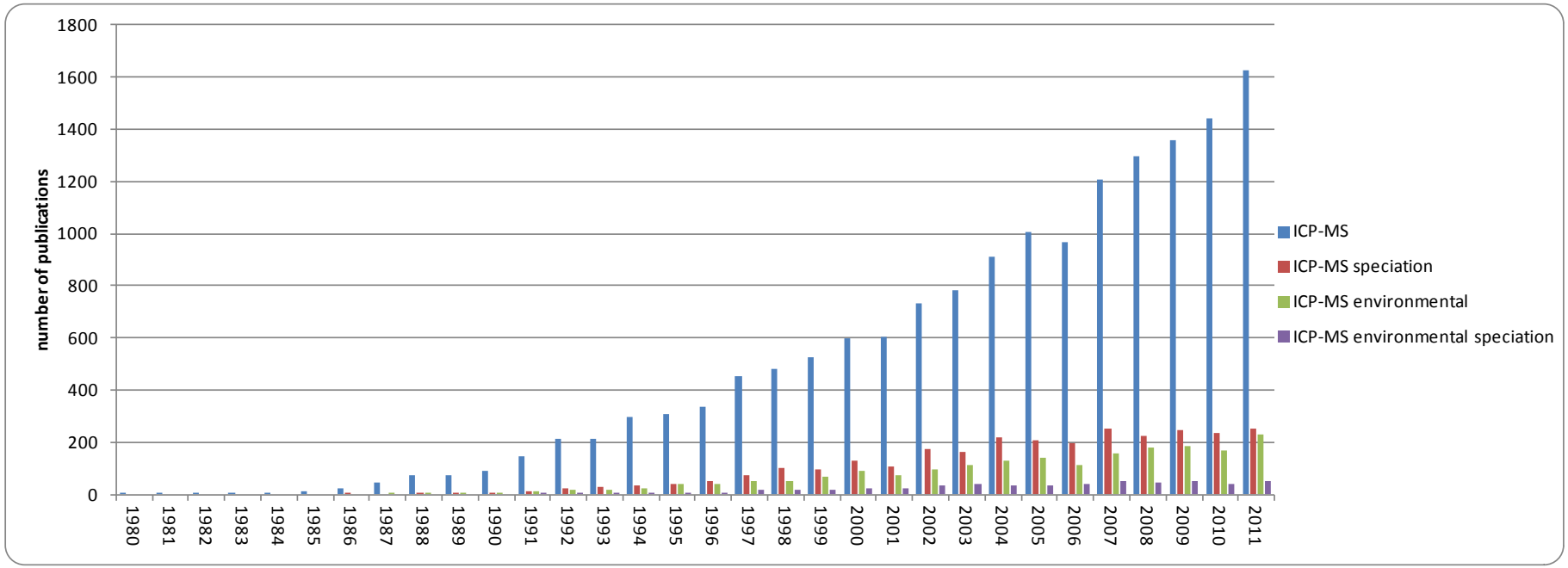



Figure 10: Number of published papers/year from 1980 to 2011 on" ICP-MS"," speciation using ICP-MS"," ICP-MS in environmental topics" and "speciation using ICP-MS in environmental topics" (web of science).

### 1.4.3. ACID DIGESTION OF ENVIRONMENTAL MATRICES

Sample preparation is usually needed in chemical analysis to convert analytes to a more suitably detectable form, to separate them from the sample matrix or to concentrate species for trace analysis [32]. This step is often pointed out as the Achilles' heel in chemical analysis, in view of the risks of analyte losses, sample contamination and incomplete sample decomposition or analyte extraction. In addition to these sources of systematic errors, sample preparation is often the most time-consuming step in analytical procedures. This contrasts with the impressive development of modern instrumental techniques that significantly improved detectability and reduced the analysis time. In spite of this development, sample treatment is still needed to improve selectivity, to minimize matrix effects and to avoid deleterious effects on the instrument (*e.g.*, clogging of nebulizers and irreversible retention of substances in chromatographic columns).

For most environmental analysis, acid digestion procedures are employed to completely transfer the analytes of interest from the matrix into solution, so that they can be introduced into the determination step (ICP-MS, ICP-AES, AAS) in liquid form. The goal of every digestion process is therefore the complete dissolution of the analytes and the complete decomposition of the matrix, while avoiding loss of or contamination with analytes. In this context, wet chemical digestions utilizing various mineral acids are carried out in either an open system, that is, under atmospheric pressure, or in closed vessels. Further, the samples may be heated in convection or microwave ovens. Below, the acids (or combination of acids) typically used for environmental regulatory analysis are summarized. The cost of the acid increases with the required purity grade. For most environmental applications, the cost of the acid solution varies between 40 – 150 €/l acid. However, for ultra-trace element determination the price of the highest purity grade acids vary between 300 to 800 €/l (year 2012, prices by courtesy of Merck, Fisher Scientific and Baker).

| | use |
|---|---|
| **Nitric acid ($HNO_3$)** | Oxidizing agent $(CH_2)_n+2\ HNO_3 \rightarrow CO_2+2NO+2H_2O$<br>Frequently mixed with $H_2O_2$ or HCl, HF<br>Forms soluble nitrates with most elements |
| **Hydrochloric acid (HCl)** | Non-oxidizing acid<br>Forms soluble chlorides with most elements |
| **Hydrofluoric acid (HF)** | Non-oxidizing acid<br>Decomposition of silicates $SiO_2+6HF \rightarrow H_2SiF_6+2H_2O$ (excess required, otherwise loss of *e.g.* $BF_3$, $SiF_4$, $SeF_4$).<br>Complexing required to mask fluorides prior to further use: $H_3BO_3+4HF \rightarrow HBF_4+3H_2O$ |
| **Hydrogen peroxide ($H_2O_2$)** | In combination with nitric acid, increased oxidation potential $2H_2O_2 \rightarrow 2H_2O+O_2$<br>Reoxidizes $NO_x$ into $NO_3^-$ (and suppresses the formation of the yellow nitrous oxides typical of nitric acid) |
| **Nitro hydrochloric acid (*aqua regia*)** | $HCl:HNO_3 = 3:1$<br>Forms NOCl and releases chlorine as the active component: $2NOCl \rightarrow 2NO+Cl_2$<br>Digestion of precious metals, sulphides |

Considering that *Aqua regia* digestion was said to be "discovered" around 800 AD by the Persian alchemist Jabir ibn Hayyan (Geber), little has changed the last 30 years in terms of acid mixtures employed and the degree of total decomposition achieved [26]. Nevertheless, sample preparation has always been one of the great challenges in environmental analysis, mainly because of the highly refractory nature of some mineral phases. Beginning in the 1970s, microwave radiation has been successfully used to speed up heat transfer and to improve both safety conditions and control of chemical reactions at high pressures and temperatures [32]. In addition to more efficient decomposition, microwave-assisted procedures have contributed to minimize the consumption of toxic reagents and, consequently, the amount of residues. Due to improvements in the reaction

flasks, with the development of safer, more resistant materials and designs, it was possible to perform sample decompositions at higher temperatures and pressures. In these conditions, the oxidizing power of $HNO_3$ greatly increases and dangerous reagents (*e.g.*, $HClO_4$) are not required, not even to decompose samples with high carbon content. High-performance closed vessel microwave-assisted digestion systems are now the norm in many trace elemental laboratories. It must be noted however that performance of such systems has taken twenty or so years to evolve to the current level of maturity. Further advances are on the way with the next generation of microwave-assisted high-pressure autoclave systems, which will offer even superior performance.

*Aqua regia* leaching of soils remains the standard approach. Here, given that such work is generally carried out in commercial laboratories, sample throughput is a key issue and as such, hot block digestion techniques remain dominant. High sample throughputs remain an issue for microwave digestion systems. The emerging dominance of inductively coupled plasma-mass spectrometry (ICP-MS) as the technique of choice meant that fusions were no longer fashionable because the high dissolved solids content of the resulting solution, even after dilution, led to cone blockage. With improved tolerance to high TDS in ICP-MS, fusion procedures are now, once again, in routine use in geochemical and environmental laboratories when complete dissolutions are required [30].

At present, awareness of green aspects has led analytical chemists to consider key indicators (*e.g.*, operation time, safety, volume/concentration of solvents and energy consumption) when developing new sample preparation methods. A drawback of sample preparation is the generation of large amounts of toxic wastes, because classical procedures consume large amounts of acids (for sample decomposition) and organic solvents (for analyte extraction and sample clean-up). Indeed, sample treatment is usually the analytical step that yields most residues and demands most energy [32]. These wastes need to be suitably managed and treated in order to avoid environmental contamination, so taking time and increasing the cost of analysis. In the context of green analytical chemistry, ultrasound-assisted solid-sample pretreatment and digestion using solely nitric acid is being increasingly evaluated. The same holds true for speciation analysis, where soft extraction under mild conditions is generally necessary [33,34].

# CHAPTER 2 ICP-MS APPLICATIONS IN ENVIRONMENTAL REGULATORY MONITORING

## 2.1. PERSPECTIVE ON ELEMENTAL ANALYSIS

Given the importance of clean water, air and soil for human use and environmental quality, it is not surprising that major chemical pollution issues have been important drivers for research in environmental chemistry [41]. Large issues driving environmental research since the beginning of the "environmental era", starting in 1960s, were nutrient over enrichment of lakes (eutrophication), the proliferation of pesticides (DDT), acid rain (or acid deposition), atmospheric transport of mercury, harmful disinfection by-products in drinking water, e-waste disposal, ….

The term *heavy metals* is commonly used to address adverse effects of elements in our environment. Although IUPAC (International Union of Pure and Applied Chemistry, *i.e.*, the world authority on chemical nomenclature) explicitly criticized the use of the term *heavy metals* as ambiguous and pointless, this has not banned the term itself in popular and scientific literature [42]. The oldest recorded scientific use of the term dates back to 1936 (related to elemental density), but today it represents an ill-defined umbrella term for various elements (primarily transition metals, *e.g.*, Cr, Ni), but also some non-metals (*e.g.*, Se, As). Because of this ambiguity, the term *heavy metals* will be written in italics in the following paragraphs and considered as a term which is simply defined as a set of elements frequently used in legislation without a widely accepted scientific rationale.

*Heavy metals* have unique characteristics that should be considered when assessing their environmental risks. Unlike most organic substances, *heavy metals* are neither created nor destroyed by biological or chemical processes. Rather, they are transformed from one chemical form into another. Because *heavy metals* are naturally occurring, many organisms have evolved mechanisms to regulate their accumulation and storage. Moreover, some elements are essential nutrients, so, when they are not present in sufficient concentrations, growth, survival and reproduction of the organisms can be affected. Table 1 summarizes the essentiality status for some environmentally relevant elements [43]. These features, along with the fact that elements naturally occur as inorganic forms in environmental compartments and are cycled through the biotic components of an ecosystem, complicate the evaluation of toxicity data for inorganic substances.

| Essential | Non-essential |
|---|---|
| Cr, Co, Cu, Fe, Mn, Mo, Ni, Se, Zn | As, Sb, Cd, Pb, Hg, Tl, Ag, Sn |

Table 1: Essentiality of elements to living organisms.

Generally spoken, manmade dispersion of *heavy metals* in the environment takes place via discharges in the air in the form of dust particles, as a result of discharge into the surface water or soil and via accidental spill. *Heavy metals* end up on (and in) the soil as a result of atmospheric deposition, by dumping waste or through the use of fertilizers. Once present in the soil, they can permeate down into the groundwater. However, binding processes delay the movement of elements into the soil to a significant extent. They can pollute the surface water as a result of run-off. *Heavy metals* in the surface water can quickly settle in the watercourse sediment, where they may be released into the surface water again over a long period.

Given the significance of manmade dispersion of *heavy metals* in our environment, major legal acts in the EU (*e.g.,* Water Framework Directive, Air Quality Directive) have included monitoring programs in order to report on the state of our environment. In the context of risk assessment however, one must keep in mind that *heavy metals* are naturally occurring constituents of our environment that vary in concentrations across geographic regions. In other words, as *heavy metals* are naturally present in our environment, knowledge of (regional) ambient background concentrations is needed to provide baseline data for pollution and risk assessment studies.

Along with the implementation of the regulatory monitoring requirements in the different European member states, the use of analytical methods developed by the **European Committee for Standardization** (CEN) was recommended (see also § 1.3). With one common standard in all these countries and every conflicting national standard withdrawn, comparison between analytical results becomes more feasible. A beneficial side-effect, taking into account that since 1980, the management of the environment in Belgium became a task for the regions, is that the European environmental regulatory monitoring requirements not only triggered a harmonisation among the different European member states, but also led to a "rapprochement" in the internal Belgium situation.

As a case study, the impact of the European environmental regulatory monitoring requirements in Flanders will be discussed in this chapter (see Figure 11). As far as available, only monitoring studies using European Standard methods (EN) based on ICP-MS instrumentation were considered.

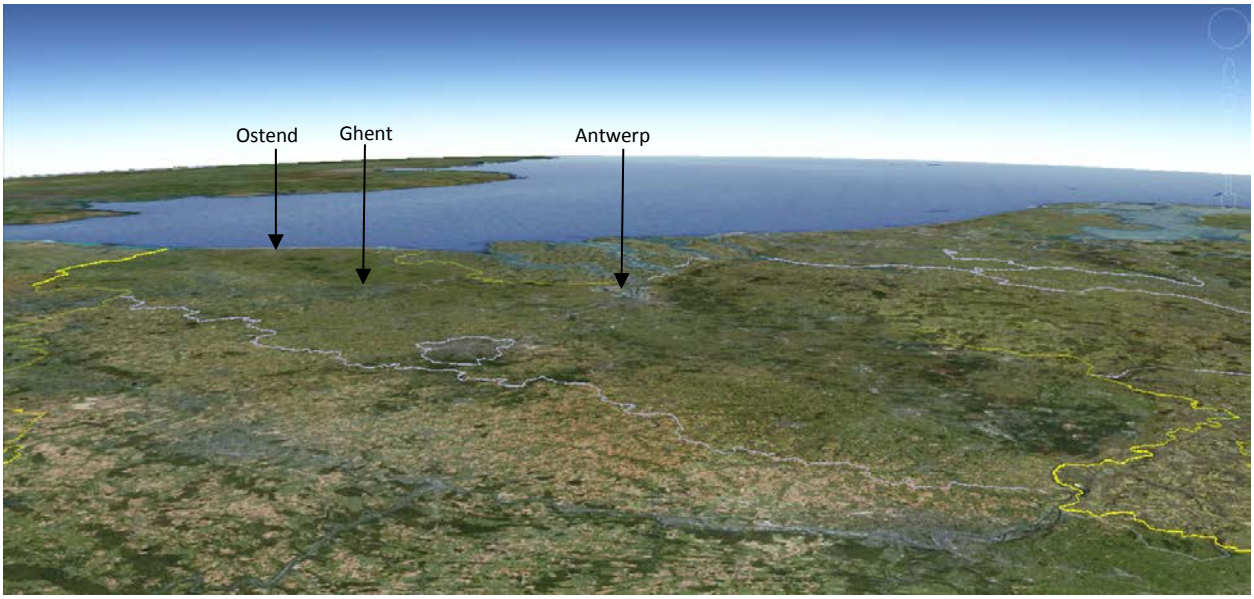



Figure 11: Map situating Flanders with placemarks of some important cities (courtesy of Google Earth).

The question "*How low is low and how low do we need to go?"* can be adequately answered by ICP-MS in environmental regulatory monitoring of elements [44](see also § 1.4.2). It is argued that the risk of sample contamination nowadays represent a far greater challenge than adequate instrumental limits of detection for regulatory environmental monitoring. In analogy with speciation analysis, the measurement itself is often no longer the limiting step, but the sampling and sample pretreatment (*e.g.*, extraction, leaching, digestion) are considered the most critical steps for accurate trace environmental monitoring. Moreover, it is argued that hindrance to the implementation of the European monitoring requirements is not the technical feasibility of analysis at these concentration levels, but rather communication, knowledge exchange and harmonization among laboratories [45].

In the following paragraphs, an inventory of regulatory monitoring studies (courtesy of VMM and OVAM) on trace elements in the Flemish environment (soil, water, air) is provided. All of these measurements were carried out with the aim to define Flemish regulatory environmental limits or to investigate the Flemish environmental situation with respect to European regulatory environmental limits. For the derivation of ambient background concentrations of *heavy metals*, only rural (non-polluted) background locations were selected. Only for soil the monitoring study was performed at VITO, for the other compartments, the monitoring studies were performed or commissioned by VMM.

In summary, the focus in this chapter is on the analysis (of acid digests) of environmental samples using European Standard methods (EN) based on ICP-MS instrumentation. These examples will show that the sensitivity combined with multi-element capabilities of ICP-MS played (and still plays) an important role in this context.

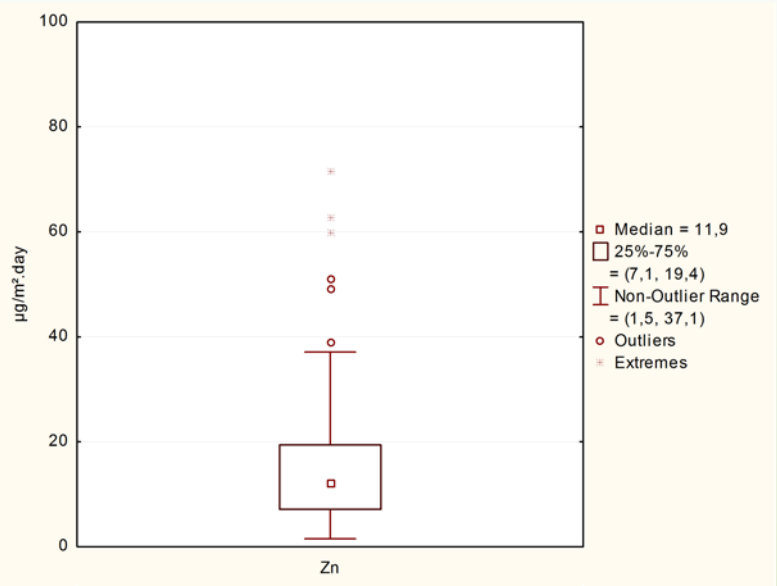
**Interesting links:**

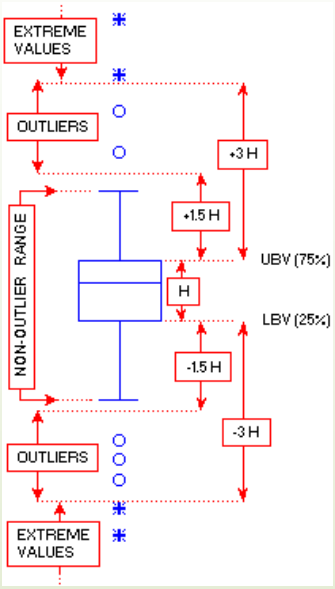
- **MIRA** - Flanders Environment Report - offers an overview of the state of the environment in Flanders divided into different environmental themes [40] (since 1994): http://www.milieurapport.be/
- The **European Environment Agency** (EEA) coordinates the European environment information and observation network by providing information on the different environmental issues since 1994: http://www.eea.europa.eu/themes

**Statistics :**

Box-and-whisker plots were used for visualizing the background concentration ranges that were determined in the different monitoring studies. Box-and-whisker plots display differences between populations without making any assumptions of the underlying statistical distribution: they are non-parametric. The median/quartile/range type of plots used in the dissertation were computed using Statistica (StatSoft, Inc. (2011), STATISTICA (data analysis software system), version 10. www.statsoft.com) and are a convenient way of graphically depicting background concentration ranges.

As an example, the median/quartile/range plot of ambient background concentrations of Zn in wet atmospheric deposition in 75 samples collected at Koksijde during 2010-2011 and analysed after acid digestion with ICP-MS are visualized below.




The median/quartile/range plot describes the central tendency of the variable (Zn) in terms of the median of the values (represented by the smallest box in the plot). The spread (variability) in the variable values is represented by the quartiles (the 25$^{th}$ and 75$^{th}$ percentiles, larger box in the plot, height = H) and the non-outlier range (the "whiskers" in the plot). The non-outlier range is the range of values that fall below the upper outlier limit (*i.e.*, + 1.5 * the height of the box, H) and above the lower outlier limit (*i.e.*, -1.5 * the height of the box, H). The upper value of the box in the box plot (*i.e.*, the 75$^{th}$ percentile) is indicated as UBV, the lower value of the box in the box plot (*i.e.*, the 25$^{th}$ percentile) is indicated as LBV.

The spacings between the different parts of the box help to indicate the degree of dispersion (spread) and skewness in the data, and identify outliers and extremes. Values "far" from the middle of the distribution are referred to as outliers and extreme values if they meet the conditions specified below.

A data point is considered to be an outlier value if the following conditions hold (the diagram on the right illustrates the ranges in the box and whisker plots) :
data point value > UBV + 1,5*(UBV - LBV) or data point value < LBV – 1,5*(UBV – LBV).

A data point is considered to be an extreme value if the following conditions hold:
data point value > UBV + 3 *(UBV - LBV) or data point value < LBV – 3 *(UBV - LBV).

## 2.2. AMBIENT BACKGROUND CONCENTRATION OF ELEMENTS IN SOIL IN FLANDERS

Soil is defined as the top layer of the earth's crust. It is formed by mineral particles, organic matter, water, air and living organisms. As interface between the earth, the air and the water, the soil performs many vital functions: food and other biomass production, storage, filtration and transformation of many substances including water, carbon, nitrogen. Soil has a role as a habitat and gene pool, serves as a platform for human activities, landscape and heritage and acts as a provider of raw materials [46].

Trace metals in surface soils are derived from both parent materials and anthropogenic activities. Because of the latter, it is often difficult to quantify the natural background concentrations of metals in soils [47-49]. In fact, it can be argued that natural background no longer exists on this planet because of human influence, and this is particularly true for densely populated and industrialised regions like the Flemish region of Belgium. Therefore, the usual, or ambient, concentration of a metal in soil consists of both a natural geochemical fraction and an anthropogenic fraction [50]. The anthropogenic fraction refers to moderate diffuse inputs into the soil, not the inputs from local point sources that generally result in a much elevated concentration.

At the moment, only nine EU member states have specific legislation on soil protection (especially on contamination) [46]. Different EU policies (for instance on water, waste, agriculture) are contributing to soil protection. But as these policies have other aims and other scopes of action, they are not sufficient to ensure an adequate level of protection for all soil in Europe. In anticipation of a European Soil Framework Directive with the objective to protect soils across the EU, the Flemish Government pioneered in 1996 with the first order of the Flemish Government establishing the soil remediation and protection regulations (VLAREBO, 1996). In this context, soil quality reference values were needed to be developed as a basis to identify and assess soil contamination processes at regional level. Hence, there was a need to establish levels of trace elements currently found in common (clean) soils.

For the first soil remediation and protection regulation (VLAREBO, 1996), data on soil characteristics and total trace element contents of soils in Flanders were compiled from various sources [47,51]. The derived median ambient background concentration of trace elements (determined as aqua regia extractable amounts) in Flemish soil are summarized in Table 2 (see column top soil (0-20 cm) VLAREBO 1996)[47]. Baseline values for a standardized soil (*i.e.*, 10 % clay, 2 % organic material) were derived as the 90$^{th}$ percentile of the top soil measurements and were included in the VLAREBO legislation of 1996 (see column baseline values VLAREBO 1996).

In 2002, the Public Waste Agency of Flanders (OVAM), responsible for waste management and soil remediation in Flanders, decided to harmonise the acid digestion procedure for waste and soil analysis. For the acid digestion of soil, it was decided to use the same digestion method as for waste, *i.e.*, Flemish reference method CMA/2/II/A.3 (see also § 1.3), which is based on European standard EN 13656, developed by CEN/TC 292 (Characterization of waste)[52].

As this reference method included the use of HF (besides $HNO_3$ and HCl), there was a need for revision of the baseline values for *heavy metals* as defined in VLAREBO (1996), which were derived as aqua regia extractable amounts (only $HNO_3$ and HCl). The choice of an acid digestion procedure can have an effect on the accuracy and precision attainable in the multi-elemental analysis of soil [54,55]. In the case of aqua regia digestion, complete solubilization of refractory minerals is not achieved (*e.g.*, illustrated for Cr, see Figure 13, where only ~ 80 % is recovered as compared to full recovery with the supplementary use of HF).

The following paragraphs describe how the (current) baseline values for *heavy metals*, as defined in the soil remediation decree of 2007, were derived.

### → Background sampling locations

For the determination of the baseline values for elements according to acid digestion reference method CMA/2/II/A.3 (EN 13656), 45 top soil samples (0-20 cm and 50-100 cm) and 45 subsoil samples (tertiary geological period) were collected in Flanders in 2006 (see Figure 12)[53].


Figure 12: Locations of soil sampling sites used for the determination of baseline values (courtesy of Google Earth).

### → European regulatory monitoring method

The methods used for the determination of elements in soil were based on:

- EN 13656:2003 Characterization of waste – Microwave-assisted digestion with hydrofluoric (HF), nitric ($HNO_3$) and hydrochloric (HCl) acid mixture for subsequent determination of elements in waste
- EN 13657:2002 Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements (EN 16174:2012 Sludge, treated biowaste and soil - Digestion of aqua regia soluble fractions of elements)
- CEN/TS 16171:2012 Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma-mass spectrometry (ICP-MS)
- CEN/TS 16170:2012 Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma-optical emission spectrometry (ICP-OES)
- CEN/TS 16175-2:2013 Sludge, treated biowaste and soil - Determination of mercury - Part 2: Cold vapour atomic fluorescence spectrometry (CV-AFS)

The concentrations of As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, V and Zn in these soil samples were determined after microwave extraction according to the European standard digestion methods EN 13656 (HF/ HCl /$HNO_3$) and EN 13657 (HCl /$HNO_3$).

In short, standard procedure EN 13656 (translated as Flemish reference method CMA/2/II/A.3) involves sieving of the soil sample with a 2 mm sieve, drying and milling. About 0,5 g of the sample is weighed in a digestion vessel; 6 ml of 12 M HCl, 2 ml of 16 M $HNO_3$ and 4 ml of 29 M HF are added

and the sample is subsequently digested in a microwave system. At the end, 44 ml of 4% (m/v) boric acid is added (boric acid masks fluorides prior to further analysis, $H_3BO_3 + 4\ HF \rightarrow HBF_4 + 3\ H_2O$), the digestion solution is transferred to a volumetric flask of 100 ml and made up to volume.

The digestion according to EN 13657 involves the addition of 6 ml of 12 M HCl and 2 ml of 16 M $HNO_3$ (aqua regia). In the case of aqua regia digestion, complete solubilization of refractory minerals is not achieved (*e.g.*, for Cr, see Figure 13), but trace element concentrations can be determined without severe matrix interferences in a 1/5 dilution of the digestion solution by ICP-MS.

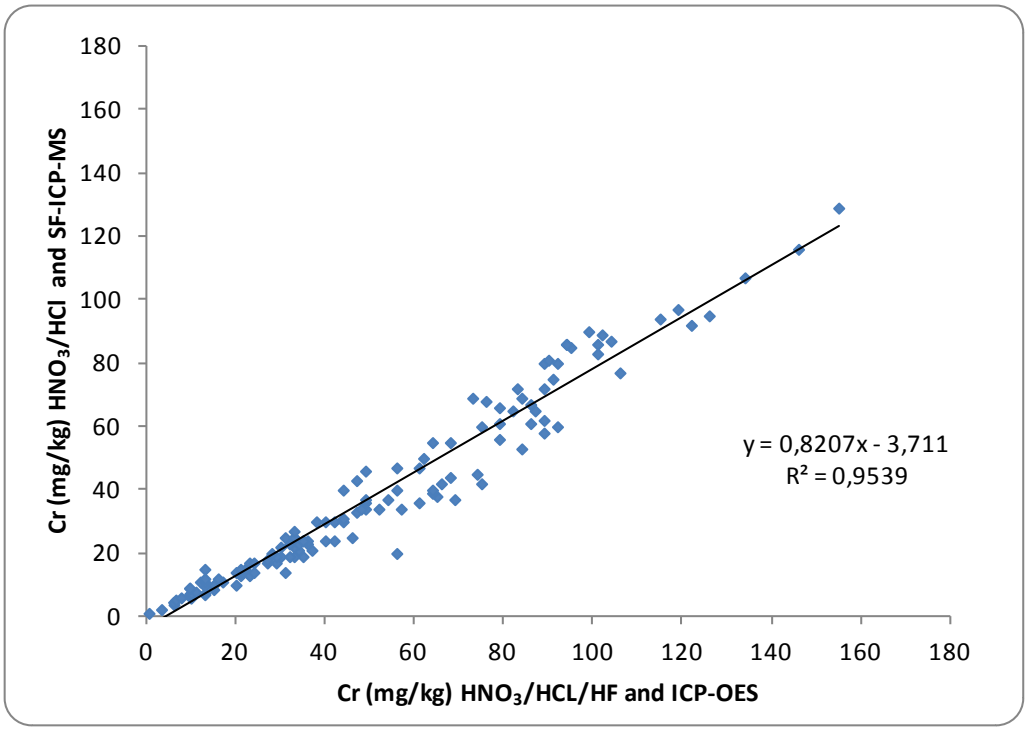



Figure 13: Comparison between determination of Cr in soil after aqua regia and $HNO_3$/HCl/HF digestion (data courtesy of OVAM [53]).

In the case of $HNO_3$/HCl/HF digestion and when using ICP-MS, the dilution factor needed to suppress matrix effects due the high salt content (boric acid) is so large that sensitivity becomes comparable with a (matrix-)robust technique such as ICP-AES. In ICP-MS procedures, it is generally recommended to keep the level of total dissolved solids below 0.2 % (2000 mg/l) to minimize deposition of solids in the sample introduction system, the plasma torch or the cone apertures of the ICP-MS instrument. For this reason, the determination of elements in the top and subsoil samples following $HNO_3$/HCl digestion was realized by ICP-SFMS and following $HNO_3$/HCl/HF digestion by ICP-AES.

The ICP-SFMS procedure involves a 1/5 dilution of the aqua regia digestion solution prior to analysis. The elements As, Se and Zn were measured in high resolution mode, the remainder of the elements in medium resolution mode. Detection limits were in the order of 10 – 50 µg/kg soil (calculated as 3 x s on 10 procedure blank solution analyses and corresponding to an actual measurement of 10 – 50 ng/L in the diluted digestion solution) [53].

The trueness of the method was controlled by checking the elemental concentrations with the reference values for the aqua regia soluble concentration certified reference material BCR-141R (Trace elements in calcareous loam soil), BCR-144R (Sewage Sludge) and BCR-146R (Sewage sludge). The recovery for the certified elements (Cr, Co, Ni, Cu, Cd, Pb and Zn) ranged between 94 and 103 %, which is in line with other reported ICP-MS data on these reference materials [56].

The precision expressed as 95 % confidence interval is dependent on the concentration level in soil analysis. According to multiple soil analyses within the context of validation of CEN/TS 16171 (Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma-mass spectrometry), a median precision of 7 % in the range > 10 mg/kg, 12 % in the range 1-10 mg/kg and 18 % in the range < 1 mg/kg was derived [57].

### → Background concentration of elements in soil

The median concentration of elements determined in Flemish soil after $HNO_3$/HCl digestion followed by sector-field ICP-MS analysis and after $HNO_3$/HCl/HF digestion followed by ICP-AES analysis are summarized in Table 2 for the 45 top soil samples (0-20 cm and 50-100 cm) and 45 subsoil samples (tertiary geological period) [53]. As soil type has a major influence on the concentrations of elements, statistical analyses on the soil geochemical data (pH, clay content, organic carbon content, effective cation exchange capacity) were performed with the aim of estimating local or soil-type specific ambient background concentrations for the trace elements.

As the reference digestion method includes the use of HF since 2002, baseline values for a standardized soil (*i.e.,* 10 % clay, 2 % organic material) were derived in Flanders as the 90$^{th}$ percentile of the top soil measurements using $HNO_3$/HCl/HF digestion and these were included in the VLAREBO legislation of 2007 (see Table 2)[53]. For the first soil remediation and protection regulation (VLAREBO, 1996), the baseline values were derived as the 90th percentile on trace elements determined as *aqua regia* extractable amounts in Flemish soil [47]. For comparison, also median values for total concentration of elements in European topsoil (0-20 cm) from the Forum of European Geological Surveys (FOREGS) Geochemical Baseline Mapping Programme are represented [58].

| | Top soil (0-20 cm) VLAREBO 2007 | | Top soil (50-100 cm ) VLAREBO 2007 | | Subsoil (tertiary) VLAREBO 2007 | | Top soil (0-20 cm) VLAREBO 1996 | European topsoil | Baseline values VLAREBO 2007 | Baseline values VLAREBO 1996 |
|---|---|---|---|---|---|---|---|---|---|---|
| | $HNO_3$/HCl ICP-SFMS | $HNO_3$/HCl/HF ICP-AES | $HNO_3$/HCl ICP-SFMS | $HNO_3$/HCl | $HNO_3$/HCl ICP-SFMS | $HNO_3$/HCl/HF ICP-AES | $HNO_3$/HCl | | $HNO_3$/HCl/HF | $HNO_3$/HCl |
| | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg |
| As | 7 | 11 | 5.9 | 12 | 8.7 | 7.6 | 7 | 7 | 16 | 19 |
| Cd | 0.3 | <0.5 | 0.1 | <0.5 | 0.05 | <0.5 | 0.18 | 0.15 | 0.7 | 0.8 |
| Co | 5 | 7 | 5 | 6 | 7 | 6 | 0.05[b] | 7.8 | | |
| Cr | 25 | 34 | 24 | 40 | 62 | 82 | 24.6 | 60 | 62 | 37 |
| Cu | 11 | 16 | 5 | 9 | 3 | 5 | 9.6 | 13 | 20 | 17 |
| Hg | 0.06[a] | 0.06[a] | 0.03[a] | 0.03[a] | 0.01[a] | | 0.17[c] | 0.04 | 0.1 | 0.55 |
| Mo | 0.4 | 2 | 0.1 | 2 | 0.3 | 1.5 | | 0.62 | | |
| Ni | 7 | 9 | 11 | 10 | 12 | 14 | 3.5 | 18 | 16 | 9 |
| Pb | 26 | 34 | 8.25 | 17 | 6.1 | 3.4 | 21.5 | 23 | 31 | 40 |
| Sb | 0.5 | <2 | 0.1 | <2 | 0.3 | <2 | | 0.6 | | |
| Se | 0.3 | <5 | 0.1 | <5 | 0.3 | <5 | | | | |
| V | 37 | 48 | 26 | 34 | 62 | 70 | | 60 | | |
| Zn | 56 | 60 | 22 | 37 | 29 | 34 | 34.5 | 52 | 77 | 62 |

Table 2: Median ambient background concentration and regulatory baseline values (90$^{th}$ percentile) for trace elements in soil.

[a] cold vapour-AFS was used for the determination of Hg according to CEN/TS 16175-3.
[b] for Co a large discrepancy was observed between the median value (0.05 mg/kg) and the average value (0.42 mg/kg)[47].
[c] a baseline level of 0.1 was derived in Flemish soils according to ref. 51.

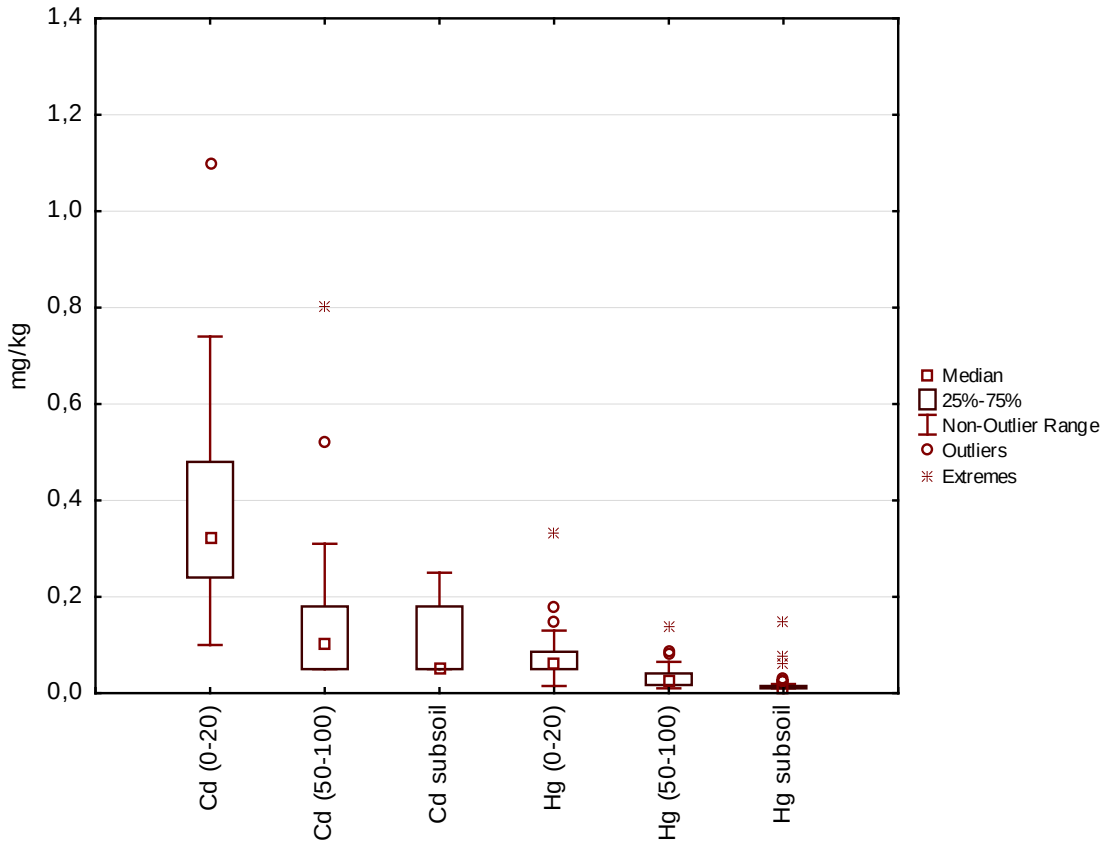
Top soil (0-20 cm) VLAREBO 2007: median elemental concentrations in 45 Flemish top soil samples (0-20 cm) following $HNO_3$/HCl digestion and analysis by sector-field ICP-MS and $HNO_3$/HCl/HF digestion and analysis by ICP-AES [53].
Top soil (50-100 cm) VLAREBO 2007: median elemental concentrations in 45 Flemish top soil samples (50-100 cm) following $HNO_3$/HCl digestion and analysis by sector-field ICP-MS and $HNO_3$/HCl/HF digestion and analysis by ICP-AES [53].
Subsoil (tertiary) VLAREBO 2007: median elemental concentrations in 45 Flemish subsoil samples (50-100 cm) following $HNO_3$/HCl digestion and analysis by sector-field ICP-MS and $HNO_3$/HCl/HF digestion and analysis by ICP-AES [53].
Top soil (0-20 cm) VLAREBO 1996: median elemental concentrations in Flemish top soil samples (0-20 cm) following $HNO_3$/HCl digestion and analysis by flame atomic absorption [47].
European topsoil (0-20 cm): median values for total concentrations in the European topsoil (0-20 cm)[58].
baseline values (VLAREBO 2007): baseline values ($90^{th}$ percentile) for a standardized soil (*i.e.,* 10 % clay, 2 % organic material) using $HNO_3$/HCl/HF digestion.
baseline values (VLAREBO 1996): baseline values ($90^{th}$ percentile) for a standardized soil (*i.e.,* 10 % clay, 2 % organic material) using $HNO_3$/HCl digestion.

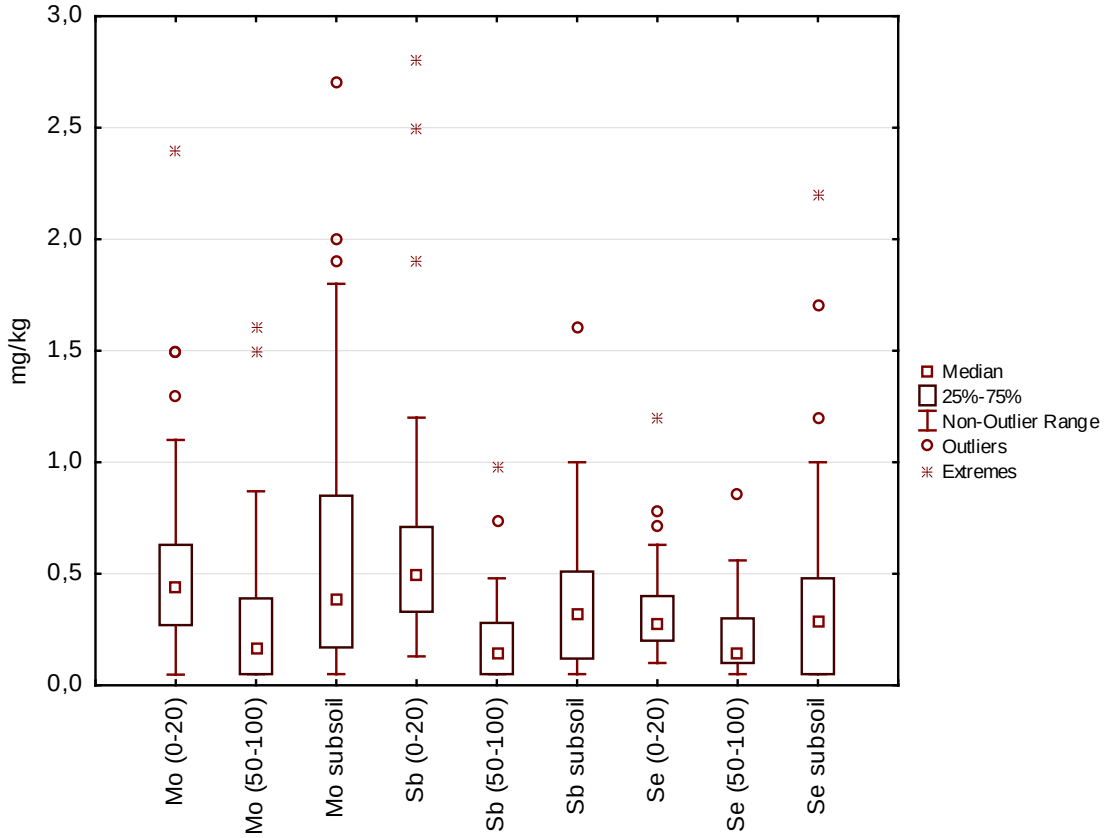
A regression and correlation analysis was performed on the data for each element obtained upon $HNO_3$/HCl digestion and ICP-SFMS analysis on the one hand and $HNO_3$/HCl/HF digestion and ICP-AES analysis on the other (e.g. see Figure 13). For the elements Mo, Sb, Cd and Se, the majority of the concentrations were below the quantification limit of ICP-AES. For this reason, no baseline values were defined for Mo, Sb and Se. For Cd, the baseline value of 0.7 mg/kg was derived as the $90^{th}$ percentile of the soil measurements (using $HNO_3$/HCl/HF digestion) with a concentration level above the detection limit of the ICP-AES method.

With the current soil digestion method (CMA/2/II/A.3, EN 13656), the determination of baseline values with ICP-AES or ICP-MS is difficult due to severe matrix effects caused by the high salt content of the acid digestion solution. When using aqua regia digestion, this matrix effect is less pronounced and soil background concentrations of elements such as Cd, Sb and Se can be easily determined with the superior sensitivity of ICP-MS as compared to ICP-AES.

As mentioned in § 1.3, it is to be expected that Hg will be included in the revised version of CEN/TS 16171 as one of the elements that can be determined with ICP-MS. This will certainly favour the use of ICP-MS for soil, sludge and biowaste analysis in the future, as no separate Hg determination (with *e.g.*, CV-AFS) will be needed. Moreover and under impulse of the Scandinavian countries, nitric acid is being promoted as the sole acid to be used for environmental sample digestion. This would further play into the hands of ICP-MS as the method of choice for environmental regulatory monitoring.

The elemental concentrations in Flemish soils following $HNO_3$/HCl digestion and analysis by sector-field ICP-MS are represented in the figures below.


1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
mg/kg
Cd (0-20)
Cd (50-100)
Cd subsoil
Hg (0-20)
Hg (50-100)
Hg subsoil
Median
25%-75%
Non-Outlier Range
Outliers
Extremes


3,0
2,5
2,0
1,5
1,0
0,5
0,0
mg/kg
Mo (0-20)
Mo (50-100)
Mo subsoil
Sb (0-20)
Sb (50-100)
Sb subsoil
Se (0-20)
Se (50-100)
Se subsoil
Median
25%-75%
Non-Outlier Range
Outliers
Extremes

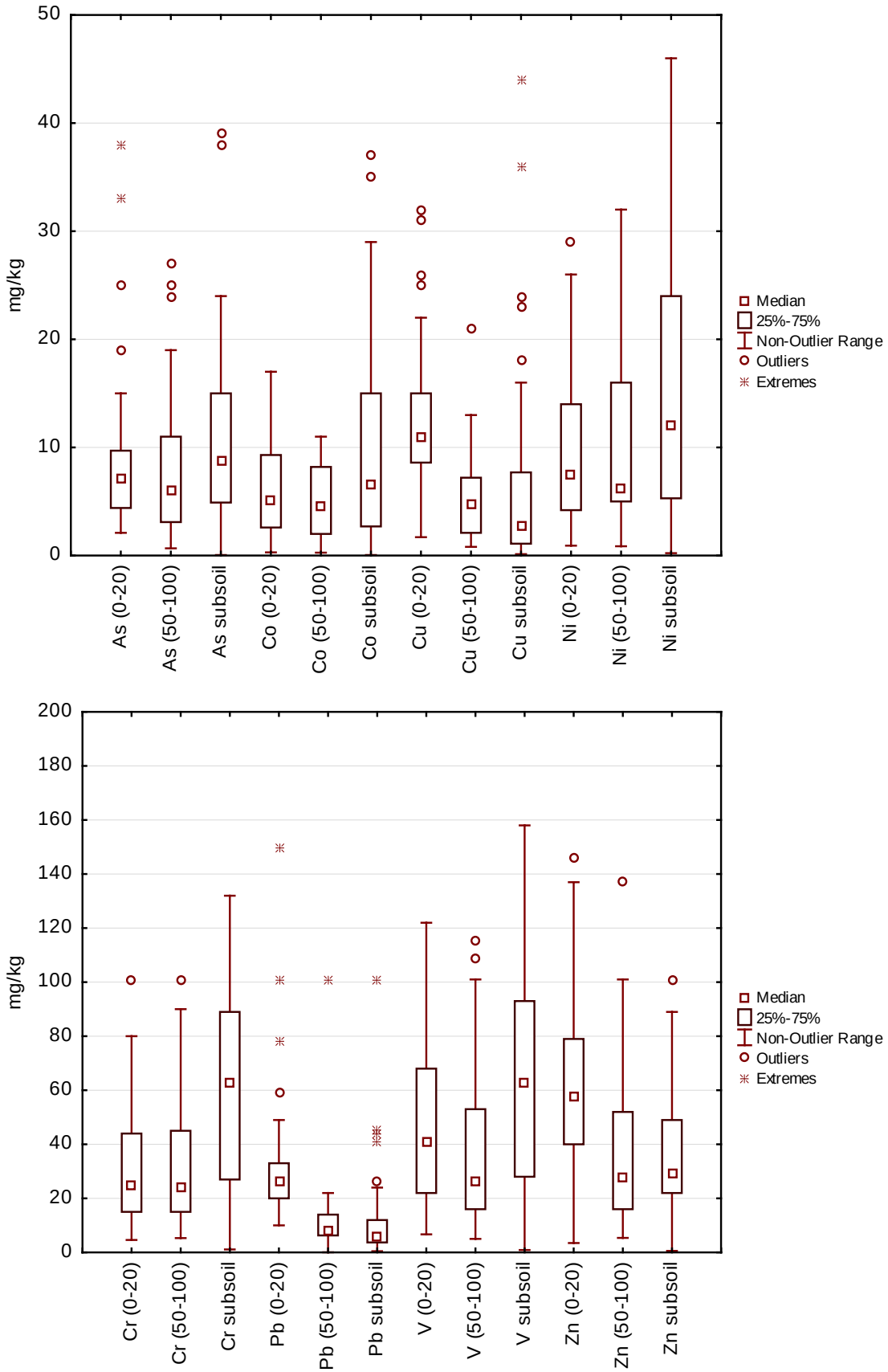



Figure 14: Elemental ambient background concentration in Flemish soils following $HNO_3$/HCl digestion and analysis by sector-field ICP-MS (45 top soil samples (0-20 cm and 50-100 cm) and 45 subsoil samples (tertiary geological period), collected at different locations in 2006, see Figure 12 (data courtesy of OVAM [53]).

As can be derived from the median values of European geochemical baseline values taken from the FOREGS Geochemical database, the concentrations of Cd in the top soil in Flanders are elevated in comparison with the European median value (see also Table 2 and § 4.2)[58]. This is also visualized in the map below, representing a geostatistical analysis of the FOREGS Geochemical database.

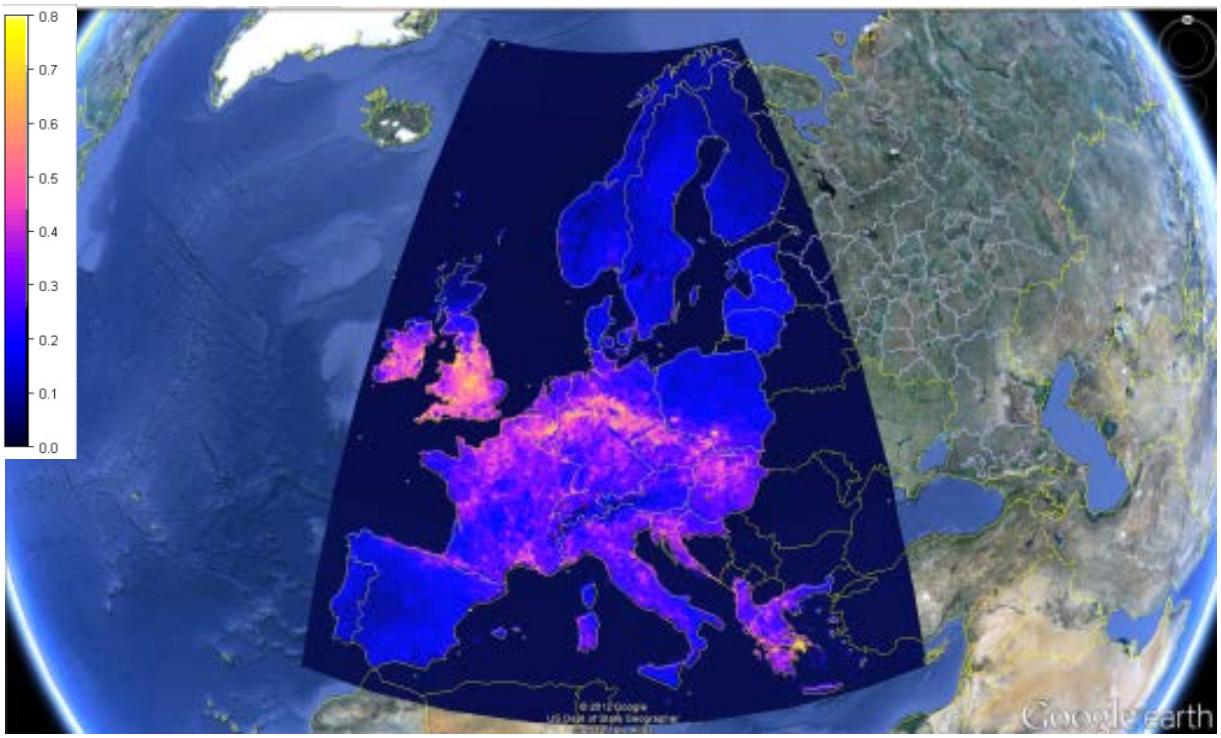



Figure 15: Map of Cd in topsoil samples in Europe from the FOREGS Geochemical database (concentrations mg/kg) (courtesy of Google Earth)[58].

The assessment of risks to human health and the environment, related to exposure of chemicals in agricultural soil and grazing land soil, is one of the requirements of the REACH regulation (Registration, Evaluation, Authorisation and Restriction of Chemical substances). In order to provide harmonised geochemical data of arable land and land under permanent grass cover at the European scale, the GEMAS (Geochemical Mapping of Agricultural Soils of Europe) project was started in 2007 [59]. This geological survey was performed in 34 European countries, covering an area of approximately 5.6 million $km^2$ at a sample density of 1 site per 2500 $km^2$, collecting one sample from arable land (0–20 cm) and land under permanent grass cover (0–10 cm) each. Soil samples were digested following $HNO_3$/HCl digestion and analysed by ICP-MS (the final report and data set will be freely available in December 2013)[59]. On average, there is a factor 6 difference in the median concentrations of the elements among the countries sampled. Several elements (*e.g.*, Ni) show an even substantially larger difference up to a factor of more than 100. At the continental scale, the occurrence of ore deposits and geology play the key role in determining the element distribution patterns. When defining background value for any one element in future European soil legislation, this will be an important factor to consider.

**Interesting links:**

- **Heavy metals in European soils,** a geostatistical analysis of the FOREGS geochemical database using **Google Earth**. The maps present results of mapping concentrations of eight critical heavy metals (arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc) using the 1588 georeferenced topsoil samples from the FOREGS Geochemical database. The concentrations were interpolated over the 26 European countries that contributed to the database : http://eusoils.jrc.ec.europa.eu/library/Data/Foregshmc/index.htm
- **GEMAS** aims to provide harmonised geochemical data of arable land and land under permanent grass cover at the European scale (final report and data set will be freely available in December 2013) : http://www.bgs.ac.uk/gbase/GEMAS.html
- The **Geochemical atlas of Europe**, http://weppi.gtk.fi/publ/foregsatlas/maps_table.php

## 2.3. AMBIENT BACKGROUND CONCENTRATION OF ELEMENTS IN AMBIENT AIR IN FLANDERS

A clean air supply is essential to our own health and that of the environment. But since the industrial revolution, the quality of the air we breathe has deteriorated considerably - mainly as a result of human activities. Increasing industrial activity and energy production, the burning of fossil fuels and the dramatic rise in traffic on our roads all contribute to air pollution in our cities which, in turn, can lead to serious health problems [60,64].

### 2.3.1. AMBIENT BACKGROUND CONCENTRATION OF ELEMENTS IN FINE PARTICULATES IN FLANDERS

The issue of air quality is still a major concern for many European citizens. It is also one of the areas in which the European Union has been most active. Since the early 1970s, the EU has been working to improve air quality by controlling emissions of harmful substances into the atmosphere, improving fuel quality, and by integrating environmental protection requirements into the transport and energy sectors. As the result of EU legislation, progress has been made in tackling air pollutants such as sulphur dioxide, lead, nitrogen oxides, carbon monoxide and benzene [65]. However, despite a reduction in some harmful emissions, air quality continues to cause problems.

Fine particulates present a health risk which is of increasing concern in Flanders. It is therefore important to identify the sources and causes of this type of pollution. To do so, the Flemish Environment Agency (VMM) has carried out several particulate matter (PM) chemical characterization studies, where hot spots and rural background sites were monitored [70,71,72]. The following paragraphs describe how ambient background concentrations of elements were derived in ambient air for Flanders.

#### → Background sampling locations

A monitoring campaign consisting of element characterization in $PM_{10}$ (particles with an aerodynamic diameter less than 10 µm) was organized by VMM on different industrial and background locations. Once a week, $PM_{10}$ samples were collected during 2008-2009 at the background locations Moerkerke, Aarschot and Retie and during 2010 at Retie (250 filter samples were collected in total).

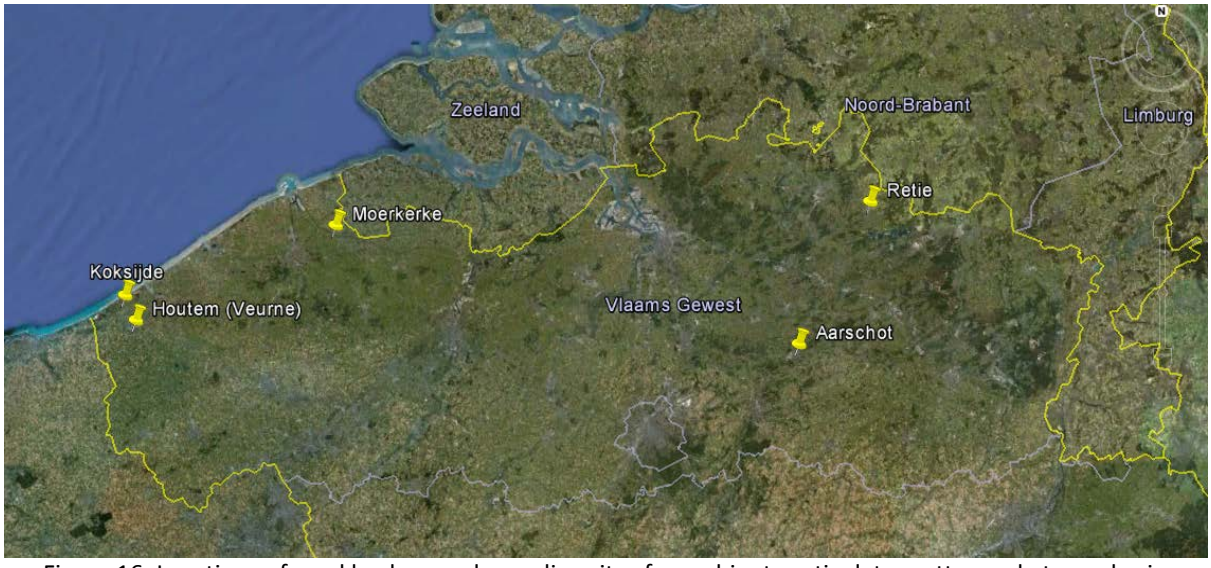



Figure 16: Locations of rural background sampling sites for ambient particulate matter and atmospheric deposition in Flanders (courtesy of Google Earth).

### → European regulatory monitoring method

The method used for the determination of elements in $PM_{10}$ was based on:

- EN 14902:2005 Ambient air quality - Standard method for the measurement of Pb, Cd, As, and Ni in the PM 10 fraction of suspended particulate matter

Ambient air samples are typically collected for TSP (airborne particles or aerosols less than 100 µm), $PM_{10}$ (particles with an aerodynamic diameter less than 10 µm), or $PM_{2.5}$ (particles with an aerodynamic diameter less than 2.5 µm) analysis. Samples are collected using an apparatus that incorporates an inlet, sample collection media, and air-sampling pumps intended to collect air for a specified time period. Sampling inlet size and flow rate generally define the size of the particles collected on the sampling medium. During sample collection, air is drawn through the sampling device and particle matter is collected on filter media. Due to the generally low concentrations of elements in air, it is critical to evaluate filter media for elemental content. Thus, a "blank" filter must always be analyzed in conjunction with the air samples collected.

In Flanders, $PM_{10}$ sampling is performed by sampling of 55 m³ air through a quartz filter (Ø 47mm) over a period of 24 hours. On return to the lab, the filters are weighed to determine the total $PM_{10}$ concentration. Subsequently, the filter (or parts of it) is (are) analyzed for trace elemental composition by ICP-MS after $HNO_3/H_2O_2$ digestion or elemental composition is measured on the whole filter directly with X-ray fluorescence spectroscopy (XRF) [74-76].

According to EN 14902, the filter (or parts of it) is transferred into a microwave sample vessel, 8 ml of 16 M $HNO_3$ and 2 ml of 10 M $H_2O_2$ are added, while ensuring complete submersion of the filter in the digestion acid. The microwave is programmed so that the acid mixture reaches approximately 180 °C within 20 min. Subsequently, the temperature is slowly increased to up to approximately 220 °C and then held for about 20 min. After the digestion procedure, the vessels are allowed to cool down to room temperature. The digestion solutions are transferred into labelled volumetric flasks of 100 ml and diluted to the mark with ultrapure water.

The ICP-(SF)MS procedure involves a direct analysis of the digestion solution. In a validation study of EN 14902 performed at VITO using ICP-SFMS, the elements As, Se and Zn were measured in high resolution mode, the remainder of the elements in medium resolution mode [66]. Detection limits calculated as 3 x s on 24 procedure blank solution analyses were in the order of 5 – 50 ng/filter (corresponding to ~ 0.01 to 0.1 ng/m³) for Cd, Ag, V, As, Mn, Co, Mo, Cr, Ni, Sn, Sb, Tl and 50-500 ng/filter (corresponding to ~ 0.1 to 1 ng/m³) for Ba, Cu, Pb, Se, Zn, Fe and 5000 ng/filter (corresponding to ~ 10 ng/m³) for Al. These instrumental detection limits cover possible contamination during the acid digestion procedure and instrumental sensitivity. In order to verify the possible contribution of the type of filter, 10 blank Teflon® and 10 blank quartz filters were digested and analysed. When using Teflon® filters, no significant contribution was observed. However, when using quartz filters, contamination was observed for Ni (30 ng/filter), Mn (60 ng/filter), Cr (130 ng/filter), Zn (700 ng/filter), Ba (1200 ng/filter) and Fe (1900 ng/filter).

The trueness of procedure EN 14902 has been controlled by checking the recovery of elements in NIST 2584 - Trace Elements in Indoor Dust [66,67]. EN 14902 stipulates that the average recovery for Cd and Pb should be between 90-110 % and for As and Ni between 85 – 115%. These requirements were fulfilled for the average recovery of 30 analyses of NIST 2854 for Cd (98%), As (100%) and Pb (93%), but not for Ni (66%). The value for Ni in NIST 2854 is an indicative value (not a certified one), however the average recovery of Cr also amounts to 72% only, indicating that refractory elements may not completely solubilise using the $HNO_3/H_2O_2$ digestion and that the supplementary use of, *e.g.*, HF for complete recovery of Ni from $PM_{10}$ is needed [68]. The average recovery for other

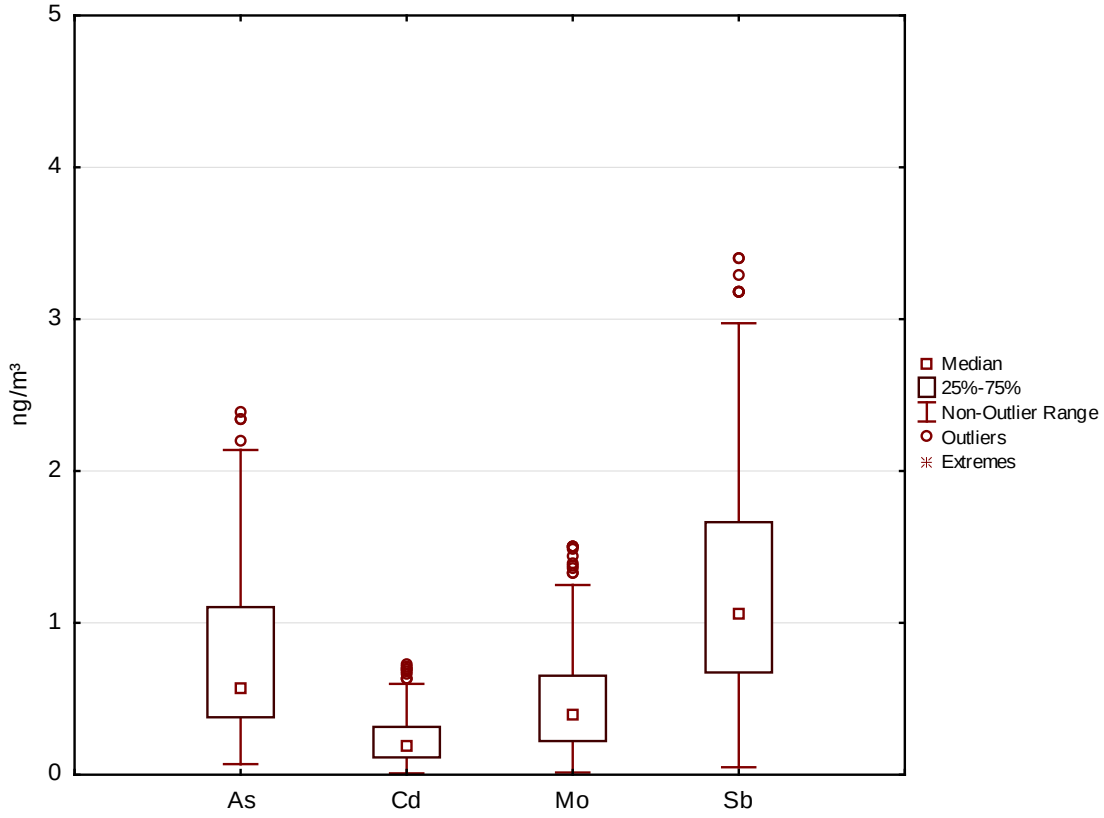
elements with indicative values amounted to: Mo (80%), V (80%), Mn (83%), Co (87%), Cu (92%), Sb (29%), Ba (87 %), Zn (99%) and Se (102%)[66].

For comparison purposes, NIST 2854 was also brought into solution via microwave-assisted digestion using $HNO_3$ and HF (with addition of $H_3BO_3$ at the end) and measured by ICP-AES according to EN 14385 [69]. This European Standard specifies a reference method for the determination of the mass concentration of specific elements in exhaust gases from hazardous and municipal waste incinerators. The recovery for all elements was in the range 90-110 %, underlining the influence of the acids used in the digestion procedure [66].

The precision expressed as 95 % confidence interval on $PM_{10}$ is dependent on the concentration level. Based on multiple analysis of NIST 2854 (n=30) according to EN 14902, a precision in the range of 10 to 20 % can be derived for all elements, with the exception of Sb (32%)[66]. These results are in line with reported performance characteristics of method EN 14902 based on a European interlaboratory comparison exercise [76].

### → Background concentration of elements in $PM_{10}$

The results of ambient background concentration of elements in $PM_{10}$ in Flanders, based on 250 filters measured after acid digestion with ICP-MS according to EN 14902:2005, are summarized below [71,72,73](data courtesy of VMM). The filters were collected at Moerkerke, Aarschot and Retie.



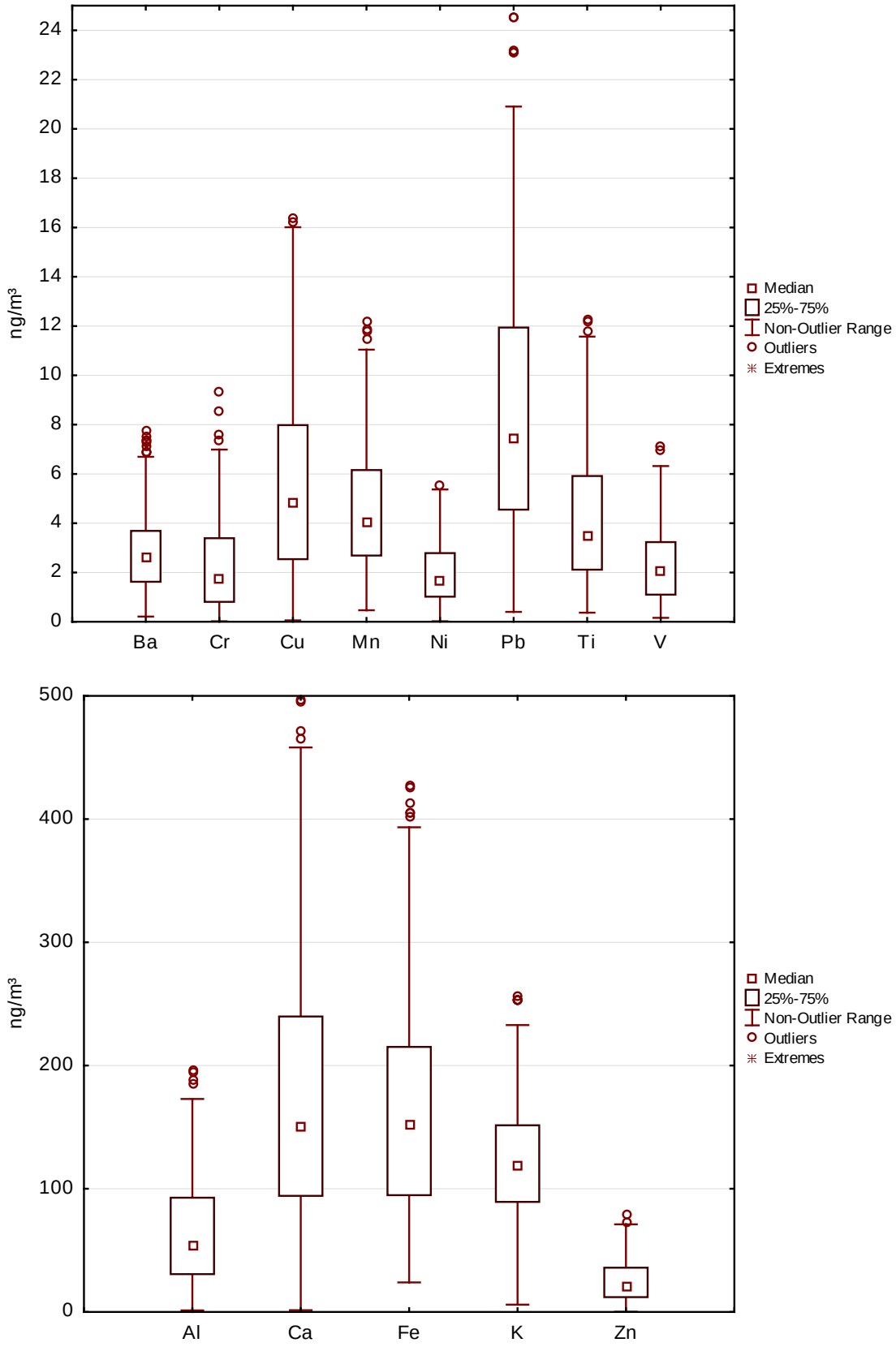



Figure 17: Ambient background concentration of elements in $PM_{10}$ in Flanders, determined with ICP-MS after acid digestion according to EN 14902 (250 $PM_{10}$ samples collected at 3 different locations in 2009-2010, Figure 16, data courtesy of VMM [71-73]).

The following median values can be derived for Flemish ambient background concentrations of elements in fine particulates. The yearly median $PM_{10}$ value at rural background sites in Flanders amounts to 20 µg/m³ (the annual European limit value for the protection of human health is 40 µg/m³) [71,72].

| | Al | As | Ba | Ca | Cd | Cr | Cu | Fe | K | Mn | Mo | Ni | Pb | Sb | Ti | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ng/m³ | | | | | | | | | | | | | | | | |
| Median | 57 | 0.61 | 2.7 | 160 | 0.20 | 2.0 | 5.0 | 160 | 120 | 4.3 | 0.44 | 1.8 | 8.1 | 1.1 | 3.6 | 2.2 | 22 |
| AQL | | 6[a] | | | 5[a] | | | | | | | 20[a] | 500[b] | | | | |

(a) Air Quality Limit measured as contents in $PM_{10}$, target value in force since 31/12/2012
(b) Air Quality Limit annual mean, measured as contents in $PM_{10}$, limit value in force since 1/1/2005

Table 3: Median ambient background concentrations of elements in $PM_{10}$ in Flanders (data courtesy of VMM [71-73]).

For baseline value determination of elements, the sensitivity of ICP-MS is needed, especially for the determination of cadmium. Detection limits attainable with EDXRF and WDXRF are in the order of 150 and 50 ng Cd/filter, respectively [62,74,75]. This corresponds to ~ 1 ng/m³ (WDXRF) and is a factor of 10 higher than the detection limit obtained according to method EN 14902 using ICP-SFMS (and well above the median background value of 0.2 ng Cd/m³). For the determination of the other elements for which European Air quality limits have been defined so far (As, Pb and Ni), the sensitivity of EN 14902 using ICP-SFMS or EDXRF are both fit for purpose. However, in analogy to soil digestion, the $HNO_3/H_2O_2$ digestion (EN 14902) may not completely solubilise refractory elements, *e.g.*, Ni, and the use of HF for complete recovery from $PM_{10}$ may be needed [68].

According to the Air quality in Europe report 2011 (European Environment Agency), the annual mean concentrations of Cd and As in $PM_{10}$ in Belgium seems elevated in comparison with that in other European member states (see Figure 18)[60]. However it must be noted that the monitoring stations in Belgium are a mix of traffic, industrial and rural or urban background areas. Differences in locations of the monitoring stations between member states are of concern and interpretation or comparison of the chemical status should therefore be done carefully.

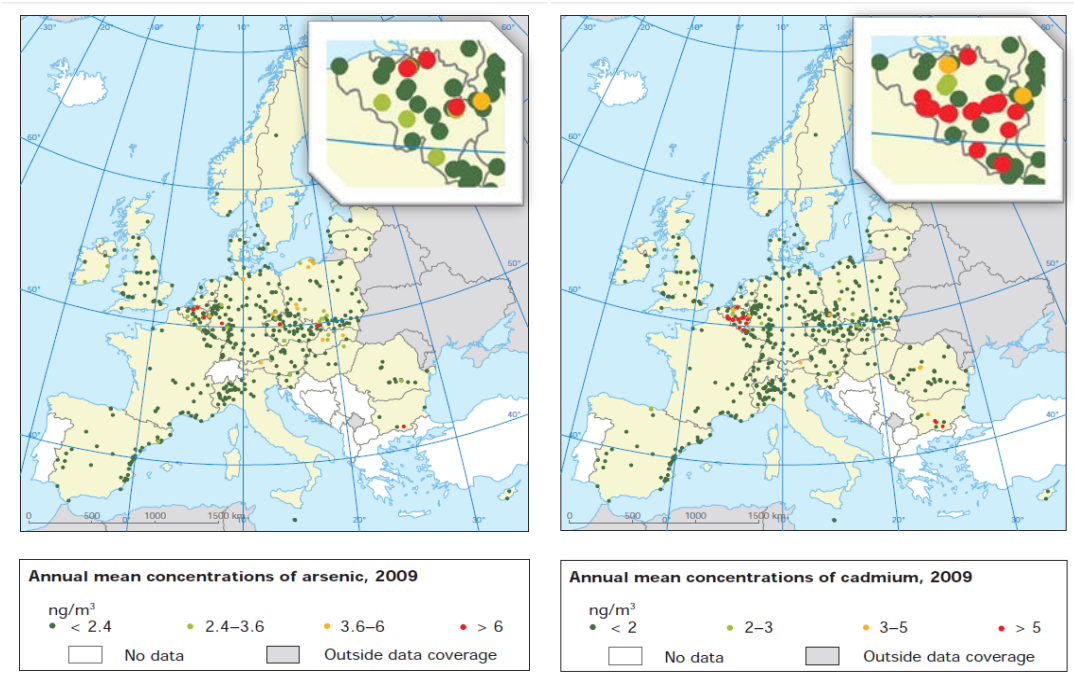



Figure 18: Annual mean concentrations of As (left) and Cd (right) in $PM_{10}$ in 2009 in Europe (figure courtesy of European Environment Agency [60]).

### 2.3.2. AMBIENT BACKGROUND CONCENTRATION OF ELEMENTS IN ATMOSPHERIC DEPOSITION IN FLANDERS

Total atmospheric deposition of elements, which is defined as the sum of wet and dry deposition, can be estimated using wet-only and bulk collectors [63]. The wet-only collector is designed to collect only sedimenting wet particles, while the bulk collector is designed to collect all sedimenting wet and dry particles.

As atmospheric mercury exists mainly in the form of elemental mercury vapour ($Hg^0$)(90 to 99%), besides particle-bound mercury (< 5%) and gaseous divalent mercury (*e.g.,* $HgCl_2$)(<5%), atmospheric deposition occurs mainly via dry deposition or wash-out of particle-bound and gaseous divalent mercury. Mercury in the form of elemental vapour ($Hg^0$) has a long atmospheric lifetime, which makes transport on hemispheric and global scales feasible. In the northern Hemisphere, anthropogenic emissions have increased the background concentrations of mercury in air by a factor of 2-3 since before industrialization. Within the context of the compulsory measurement CAMP (Comprehensive Atmospheric Monitoring Program) within the OSPAR Convention (Convention for the Protection of the Marine Environment of the North-East Atlantic), weekly measurements of Hg in wet deposition are carried out at different background locations in Europe [82].

The following paragraphs describe how ambient background concentrations of elements were derived in atmospheric deposition for Flanders.

#### → Background sampling locations

In Flanders, total atmospheric deposition of elements for ambient background concentration is estimated with wet-only collectors at Koksijde on a weekly basis and with bulk collectors at Koksijde and Bonheiden on a monthly basis (see Figure 16)[61]. Wet deposition of mercury is sampled on a weekly basis at Koksijde and background concentrations of total gaseous mercury are continuously monitored at Houtem (Veurne) with an automated mercury analyser [84].

#### → European regulatory monitoring method

The methods used for the determination of elements in atmospheric deposition were based on:

- EN 15841:2009, Ambient air quality - Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition
- EN 15853:2010, Ambient air quality - Standard method for the determination of mercury deposition
- EN 15852:2010, Ambient air quality - Standard method for the determination of total gaseous mercury

For bulk sampling, VMM is currently in transition to change to the European standard EN 15841, which slightly differs from the Belgian standard NBN T94-101 (1976)[78]. EN 15841 specifies methods for sampling wet-only and bulk deposition of As, Cd, Ni and Pb. The samples of the bulk and wet-only collectors are transferred to the laboratory in the sampling bottle and acidified with nitric acid (to 1 v/v %). A test portion is subsequently microwave-digested by adding suitable volumes of nitric acid and analysed by graphite furnace atomic absorption spectrometry (GF-AAS) or by ICP-MS. Since 2009, samples are analysed with ICP-MS by VMM [61].

Detection limits calculated as 3 x s on replicate measurements of blank collectors are in the order of 0.05 – 0.2 µg/m².day [62]. Based on duplicate sampling of bulk depositions at Koksijde, a precision (95 % confidence interval) of better than 20 % is achieved for all elements in 80 % of the monitored

depositions. However, in the other cases, a difference up to a factor of 4 was observed in the duplicate measurements, illustrating that contamination (*e.g.*, Cu, Zn) represents a challenge for accurate trace environmental monitoring.

Weekly measurements of Hg in wet deposition at Koksijde are carried out according to EN 15853. The (wet only) precipitation sample is stabilized with hydrochloric acid and transferred to the laboratory in the collection vessel. Mercury in the precipitation sample is oxidised using bromine monochloride and subsequently analysed by an atomic fluorescence spectrometer equipped with a gold amalgamation system for Hg preconcentration (Leeman Labs, Hydra AF) [82]. The method detection limit amounts to 0.001 µg/m².day with a precision (95 % confidence interval) of less than 10 %. Based on duplicate sampling, a combined uncertainty (ca. 95% confidence level) of 53 % was derived [82].

Background concentrations of total gaseous mercury are monitored according to EN 15852 (2010, Ambient air quality - Standard method for the determination of total gaseous mercury) with an automated mercury analyser, consisting of a gold amalgamation system coupled to an atomic absorption spectrometer [84].

### → Background concentration of elements in atmospheric deposition

The results for the bulk and wet-only collectors in 2010-2011 at background locations in Flanders, analysed after acid digestion with ICP-MS, are summarized in the figures below [61]. The median values of bulk and wet deposition in 2010-2011 at rural background sites in Flanders are summarized below.

| | As | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| | µg/m².day | | | | | | | | |
| **Median bulk deposition** | 0.37 | 0.10 | 0.94 | 4.6 | 160 | 23 | 1.1 | 4.6 | 21 |
| **Median wet deposition** | 0.21 | 0.06 | 0.40 | 9.0 | 21 | 8.1 | 0.67 | 1.4 | 12 |

Table 4: Median values of bulk and wet deposition at rural background sites in Flanders (data courtesy of VMM [61,62]).

Especially for cadmium and arsenic, the superior sensitivity of ICP-MS is needed for ambient background determination of these elements in atmospheric deposition. However, duplicate sampling of bulk depositions at Koksijde, where differences up to a factor of 4 were observed in 20 % of the duplicate measurements, underline that the risk of sample contamination (*e.g.*, Cu) may represent a far greater challenge than adequate instrumental limits of detection for regulatory environmental monitoring.

Based on the weekly measurements of Hg in wet deposition at Koksijde, the time-weighted average mercury deposition for the year 2011 at Koksijde amounted to 0.025 µg Hg /$m^2$.day [82]. The median background value of daily measurement of total gaseous mercury in 2011 amounted to 0.7 ng/m³ [84].

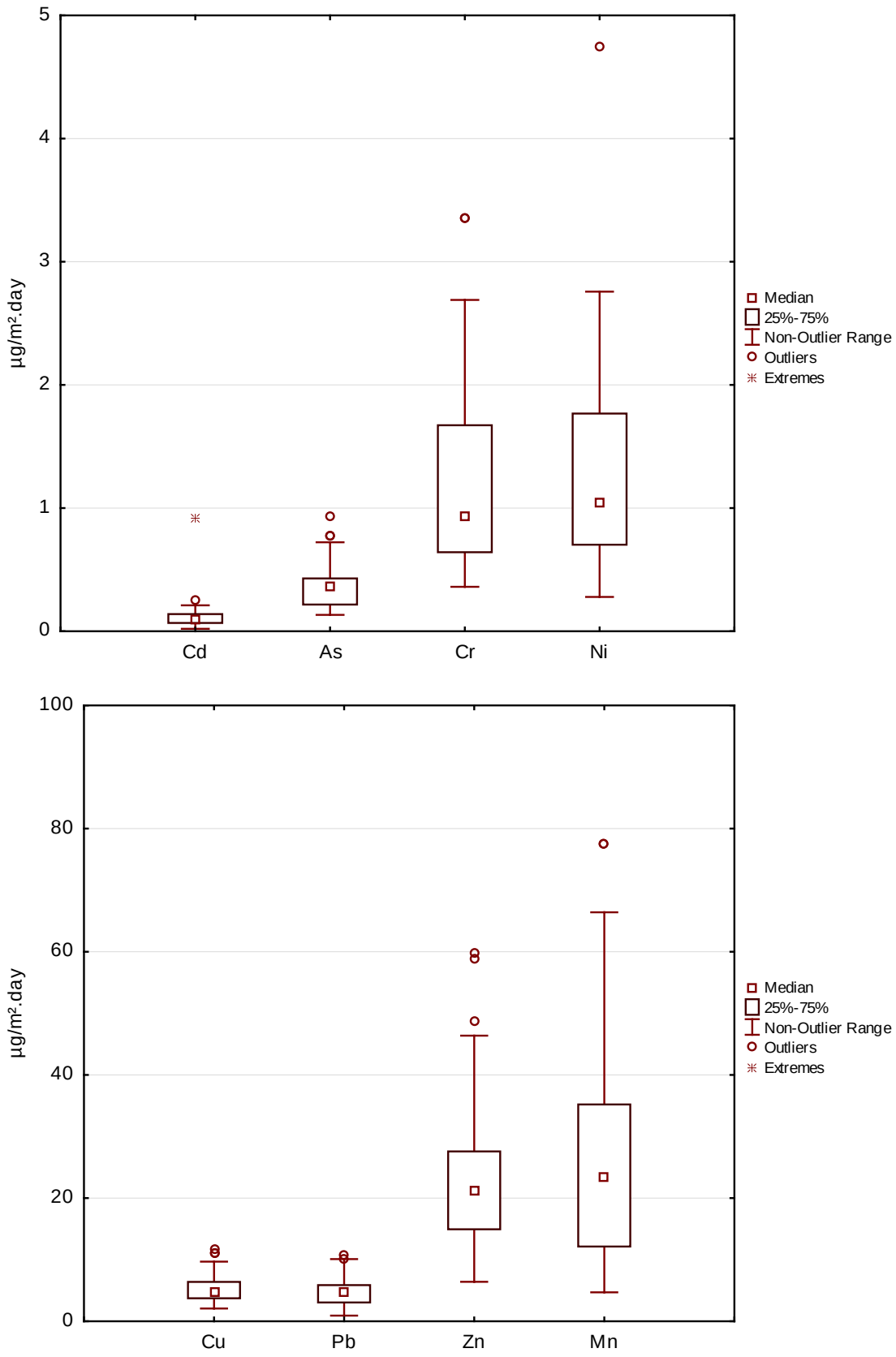



Figure 19: Ambient background concentration of elements in total atmospheric deposition in Flanders, analysed with ICP-MS after acid digestion (52 samples collected at Koksijde and Bonheiden in 2010-2011, data courtesy of VMM [61,62]).

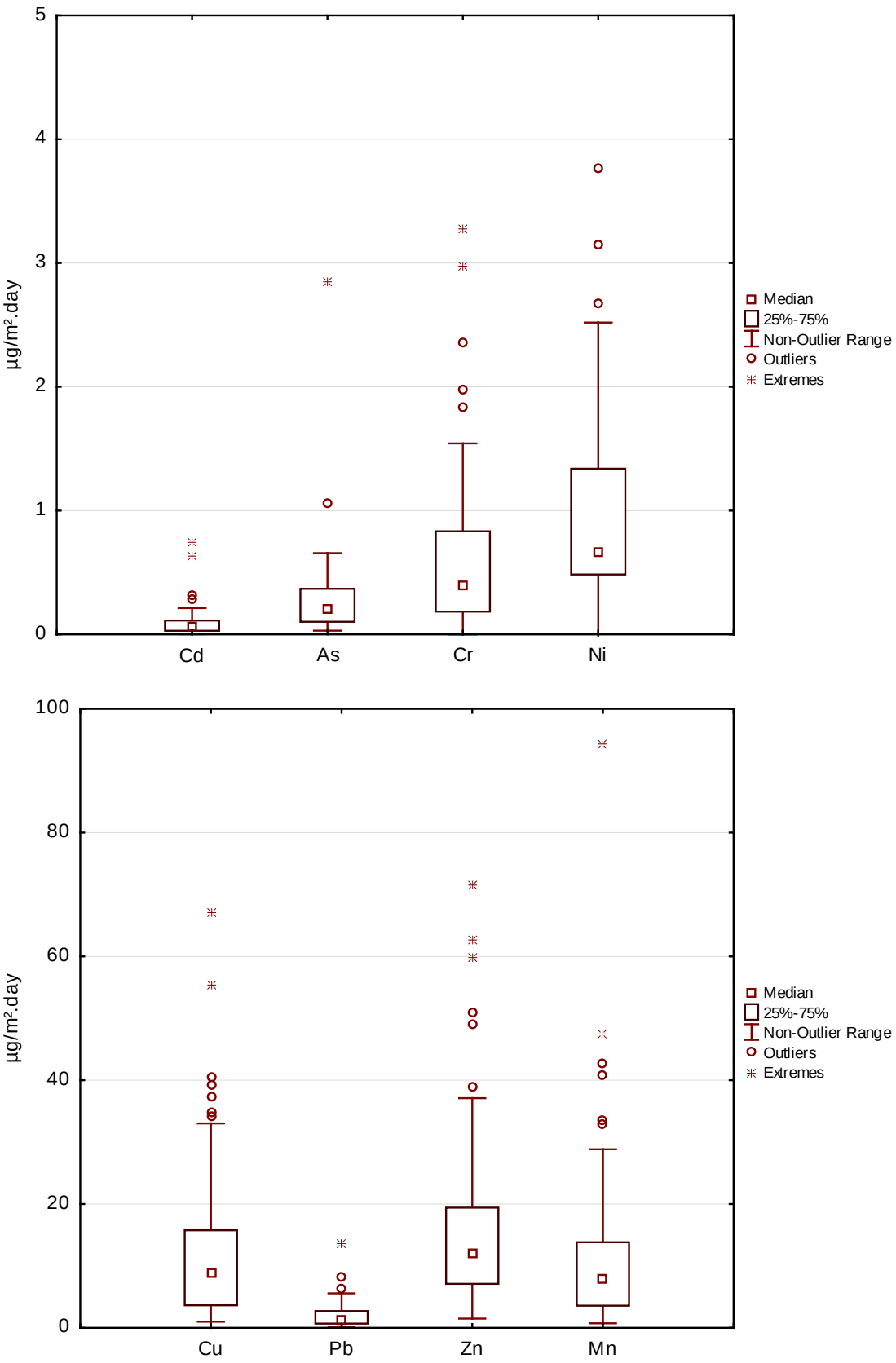



Figure 20: Ambient background concentration of elements in wet atmospheric deposition in Flanders, analysed after acid digestion with ICP-MS (75 samples collected at Koksijde in 2010-2011, data courtesy of VMM [61,62]).

In Figure 21, the total (dry and wet) deposition of cadmium across Europe in 2008 (g/km².year) is presented [85]. Cadmium is primarily produced as a by-product from the extraction, smelting and refining of zinc and other non-ferrous metals (see also § 4.2). It has predominantly been used in rechargeable nickel-cadmium batteries, although sales to consumers have now been banned in Europe, with the exception of certain uses. Cadmium is also used in the production of pigments, coatings and platings. Emissions of cadmium to air arise primarily from combustion processes in power plants and industry. For comparison, the median background value of bulk deposition for Cd of 0.1 µg Cd/m².day derived above, corresponds to 36.5 g/km².year.

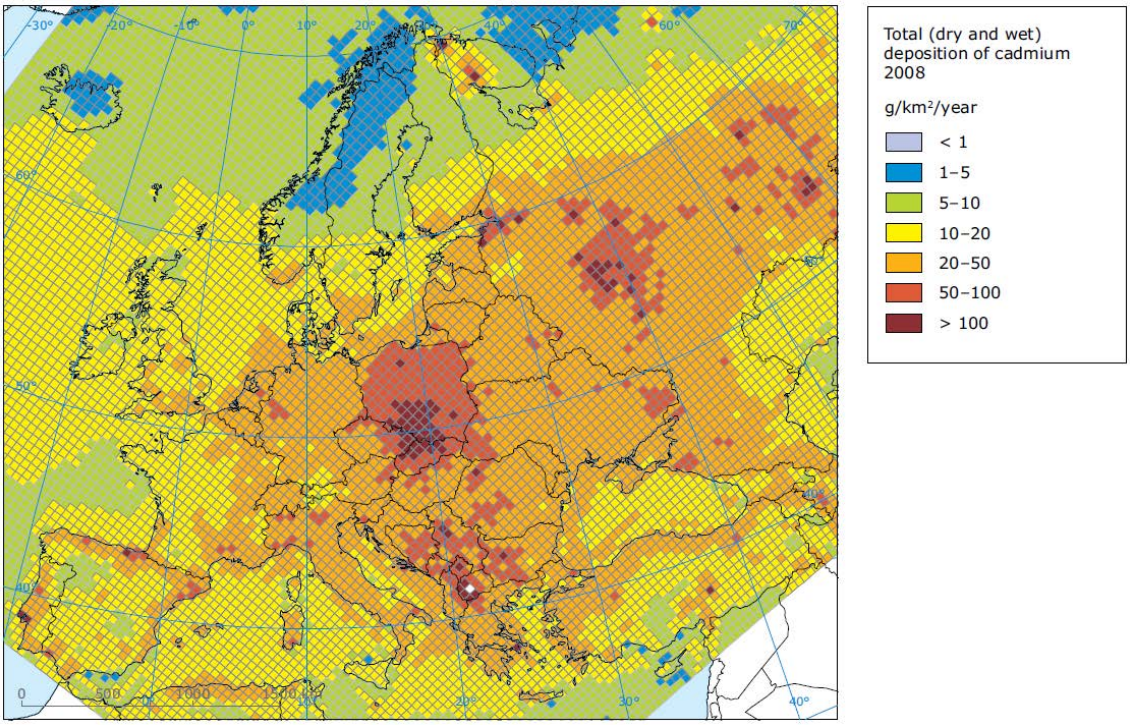



Figure 21: Total (dry and wet) deposition of cadmium across Europe in 2008 (g/km$^2$.year)(figure courtesy of European Monitoring and Evaluation Programme [85]).

Cadmium emissions to air are ultimately deposited onto land or directly into fresh and marine waters. Atmospheric deposition in urban areas will typically result in cadmium being washed from impervious surfaces, collected and discharged to a receiving water, either directly or via a wastewater treatment plant. Combined wet and dry deposition of cadmium across Europe is variable, generally ranging between 10 and 50 g/km$^2$.year but reaching in excess of 100 g/km$^2$.year in parts of central and south-eastern Europe (see Figure 21). Across the 32 European Economic Area member countries, emissions of cadmium to air have declined significantly over recent years — by about 58 % between 1990 and 2008 [85]. This decline reflects improvements in abatement technologies at industrial facilities and, in some countries, the closure of older plants as a result of economic restructuring.

## 2.4. AMBIENT BACKGROUND CONCENTRATION OF ELEMENTS IN RIVER SEDIMENT IN FLANDERS

Trace element concentrations in soils and sediments are mainly dependent on the nature of the parent material from which they are derived, but anthropogenic influences can also alter trace element concentrations in terrestrial and fluvial environments [89]. Consequently, the natural background concentration of trace elements in sediments (as in soils, see § 2.2) can be used as a reference value to estimate the contamination level of sediments. In the past, quantitative relationships between the bedrock and the surrounding soil and/or sediments have been established, but further development of the soil, weathering, erosion and transport processes can alter this relationship between the soil and the underlying lithology.

The occurrence of background concentrations of trace elements in soils and sediments is, besides the lithology, also influenced by their clay and organic matter content [47]. Therefore, clay and organic matter content are often used to calculate 'corrected' background values for trace metal concentrations in soils and sediments.

In an attempt to establish a regression model to explain trace element concentrations in Flemish soils, Tack *et al.* found a rather poor relationship between total *heavy metal* concentrations in soils and the clay- and organic matter content. This indicates that the independent variables (clay and organic matter content) are not sufficient to explain trace element background concentrations in soil and that the addition of other variables could probably improve the model. To overcome this drawback of the "clay fraction", data normalization towards "conservative elements" (Al, Fe, Li …) is often carried out. In many studies, Fe and/or Al are used as "normaliser" to account for the natural variability of trace elements in soils and sediments and a positive linear correlation between Fe and trace element concentrations has been found in several studies [89].

In Europe, stream sediments have been widely used as a sampling medium for geochemical mapping. Since 1985, the Forum of European Geological surveys (FOREGS) has been working on a geochemical atlas of Western Europe to deduce background geochemical information and to assess environmental pollution of floodplain and present-day river systems [90]. With the implementation of European Directive 2008/105/EQS, the use of sediments for assessing long term trends and chemical status was introduced in the European integral water policy [14].

Since 2000, the Flemish Environmental Agency is monitoring the sediment quality at 600 locations in Flanders in both navigable and unnavigable waters, according to the Triad approach. This Triad sediment quality assessment is an integrated investigation technique based on the analysis of physico-chemical, biological and ecotoxicological parameters [91]. For the evaluation of the physico-chemical parameters, a standardization to an organic matter content of 5% and a clay content of 11% is done for *heavy metals* and organic contaminants.

The following paragraphs describe how ambient background concentrations of elements were derived in river sediments for Flanders.

### → Background sampling locations

For the determination of median ambient background concentrations of trace elements, only those locations with no acute impact on benthic biota (= ecotoxicological class 1) and good biological quality (= presence of benthic macro invertebrates, biological class 1) were selected [92,93]. From the 228 river sediment locations sampled during the 2010-2011 monitoring campaign (and measured with ICP-MS by VMM), the selection criteria of no acute impact on benthic biota and good biological quality were met at only 22 locations and these are visualized below [94].

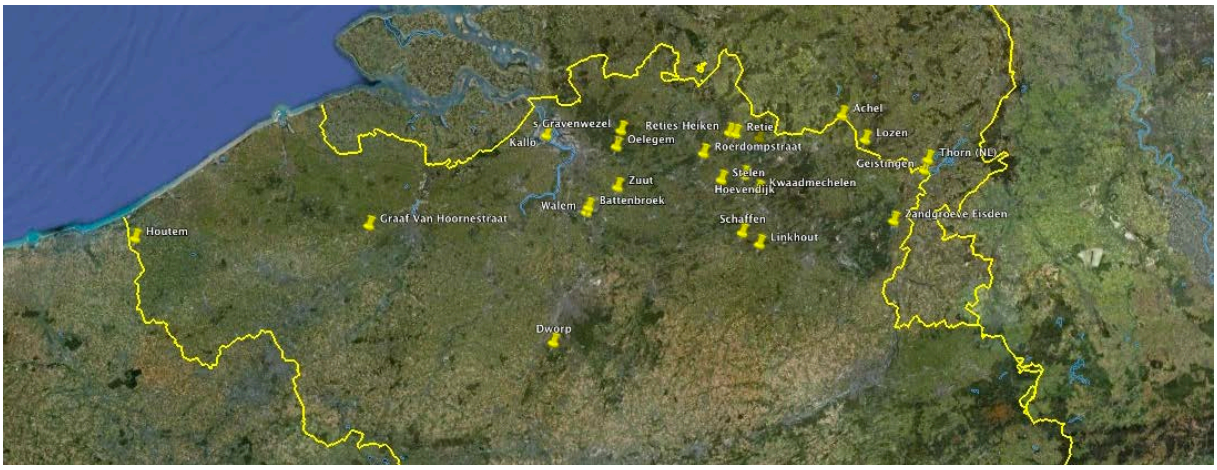



Figure 22: Locations of river sediment and surface water sampling sites used for the determination of ambient background values (courtesy of Google Earth).

### → European regulatory monitoring method

The methods used for the determination of elements in river sediment were based on:

- EN 16174:2012 Sludge, treated biowaste and soil - Digestion of aqua regia soluble fractions of elements
- CEN/TS 16171:2012 Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma-mass spectrometry (ICP-MS)
- EPA 7473:1998 Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry

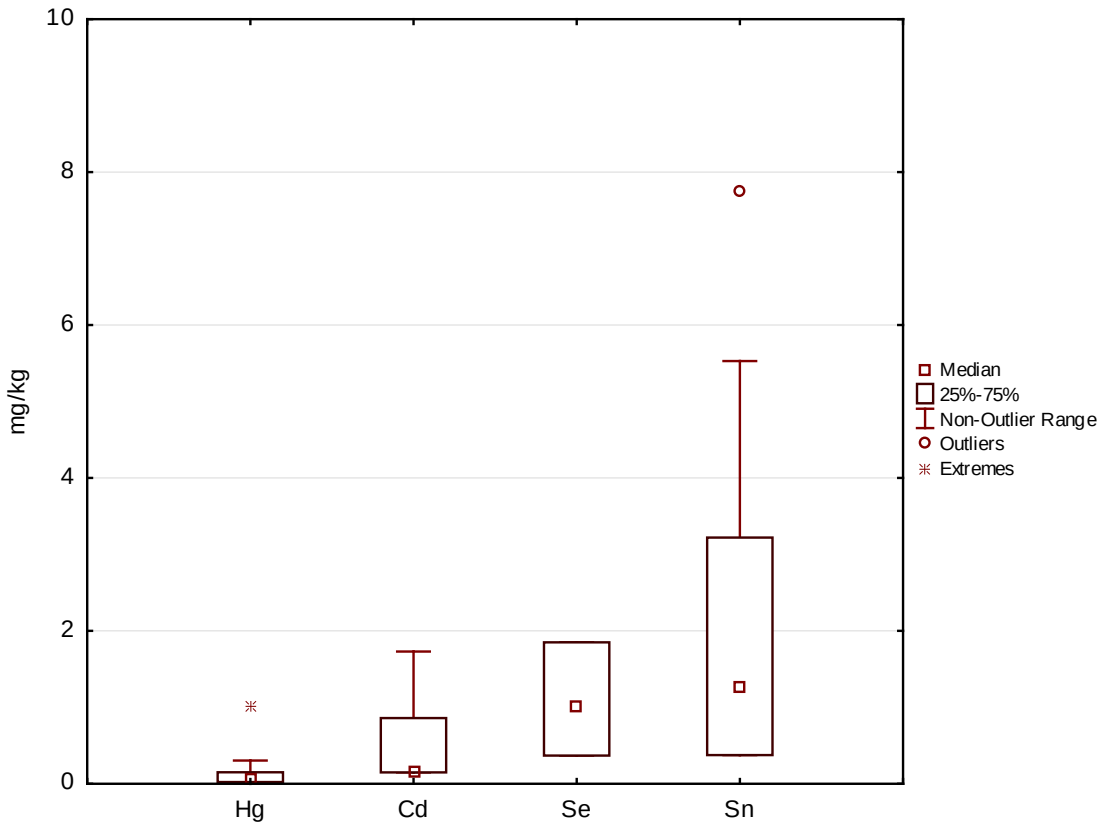
The determination of elements in river sediments was performed by the Flemish Environmental Agency (after aqua regia digestion) with ICP-AES until 2009, thereafter ICP-SFMS was used for the determination [92]. With a turn-over time of 4 years, the 600 locations are sampled [93].

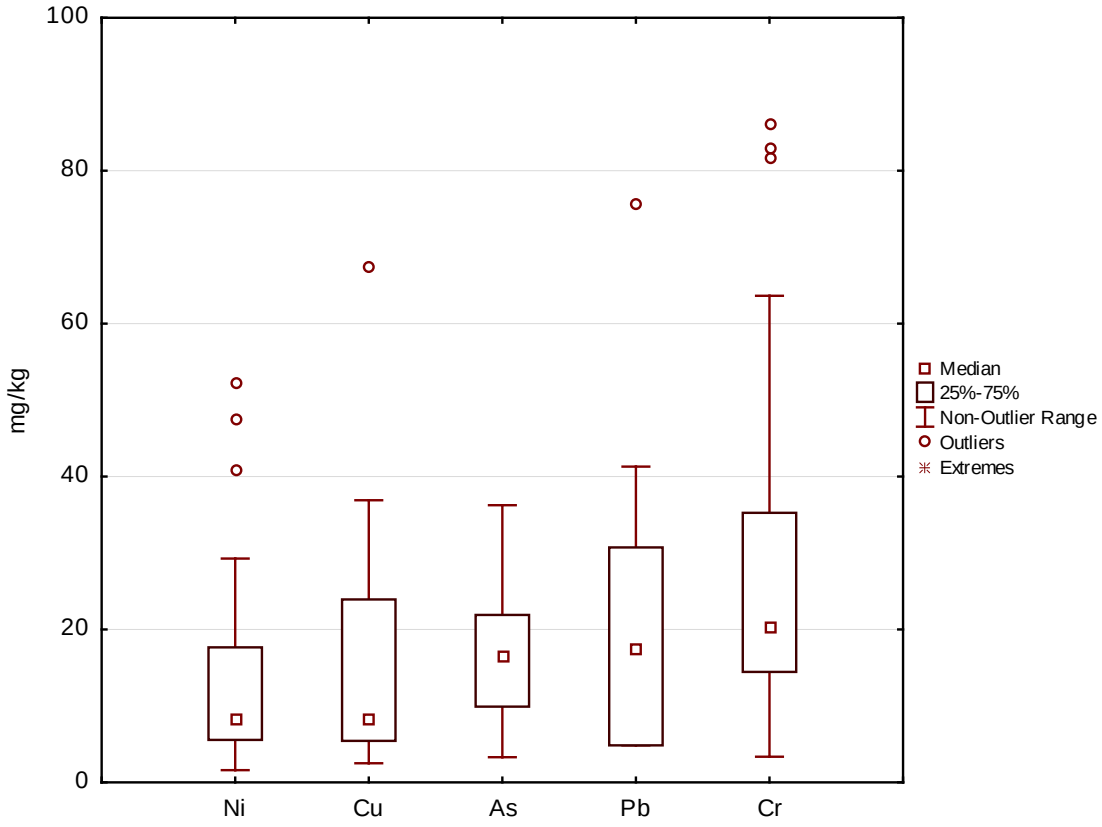
The trueness of procedure CEN/TS 16171 (ICP-MS) after aqua regia digestion was controlled by checking the recovery of elements spiked to river sediments. The average recovery for the elements checked, varied between 90-110 %. The precision of procedure CEN/TS 16171 after aqua regia digestion on river sediments, expressed as 95 % confidence interval, is dependent on the concentration level and in the range of 14-24 % for all elements [93].

### → Background concentration of elements in river sediment

Ambient background concentrations of elements in Flemish river sediment with no acute impact on benthic biota and good biological quality are summarized in the figures below. The median elemental background concentrations analysed by ICP-MS after aqua regia digestion during the 2010-2011 monitoring campaign are summarized in Table 5 [92,93].

Median values of elemental concentrations from the analysis of 105 river sediments in Flanders in 2006 are also summarised in Table 5 [89]. These analyses were performed to investigate the relationship between *heavy metals* (As, Cd, Cr, Cu, Hg, Pb, Ni, Sn and Zn) and major elements and the (geological) location. For comparison purposes, also the median values for aqua regia concentrations in European stream sediments from The FOREGS Geochemical Baseline Mapping Programme are represented [58].


10
8
6
4
2
0
mg/kg
Hg
Cd
Se
Sn
Median
25%-75%
Non-Outlier Range
Outliers
Extremes


100
80
60
40
20
0
mg/kg
Ni
Cu
As
Pb
Cr
Median
25%-75%
Non-Outlier Range
Outliers
Extremes

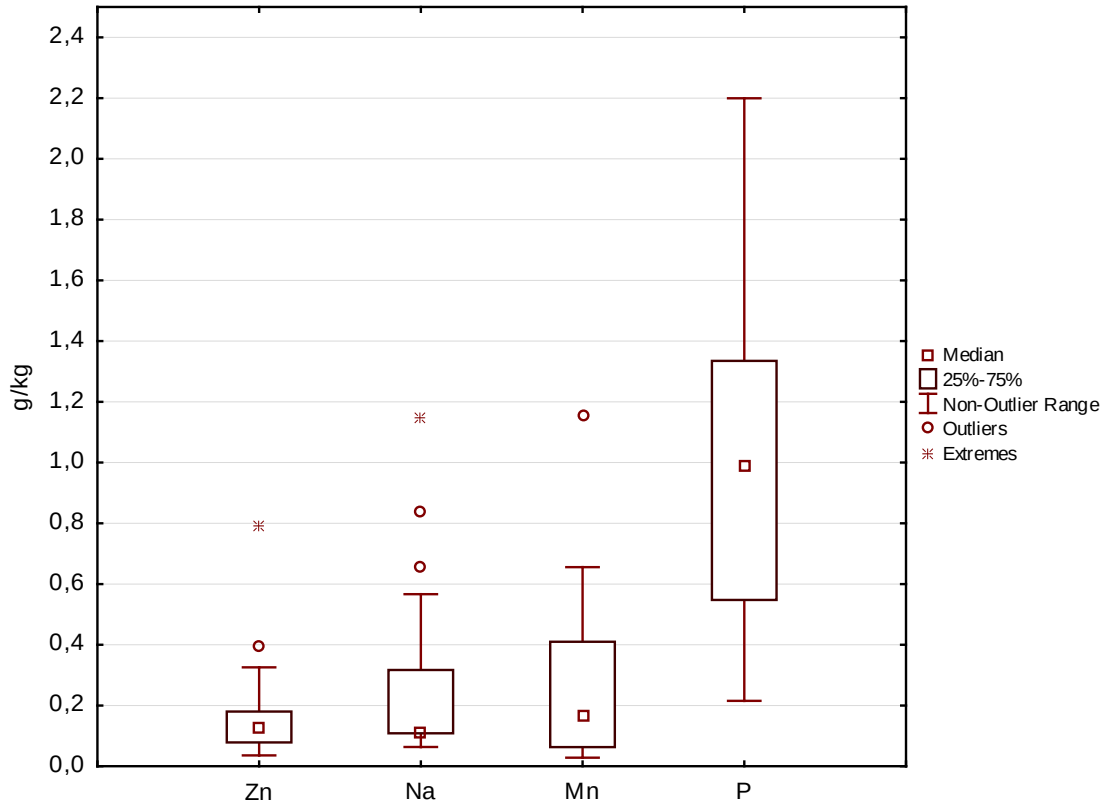



Figure 23: Ambient background concentration of elements in river sediment in Flanders, analysed with ICP-MS after aqua regia digestion according to CEN/TS 16171 (samples collected at 22 different locations in 2010-2011, see Figure 22)(data courtesy of VMM [92,93]).

| | River sediment monitoring 2010-2011 | River sediment monitoring 2006 | River sediment reference values | European river sediments |
|---|---|---|---|---|
| | $HNO_3$/HCl ICP-MS | $HNO_3$/HCl ICP-AES | | $HNO_3$/HCl |
| | *mg/kg* | *mg/kg* | mg/kg | *mg/kg* |
| **As** | 17 | 8 | 11 | 6 |
| **Cd** | 0.15 | 0.6 | 0.38 | 0.28 |
| **Cr** | 20 | 27 | 17 | 21 |
| **Cu** | 8.2 | 16 | 8 | 14 |
| **Hg** | 0.052[a] | 0.1 | 0.05 | 0.038 |
| **Mn** | 169 | | | 452 |
| **Ni** | 8.2 | 10 | 14 | 16 |
| **Pb** | 17 | 26 | 14 | 14 |
| **Se** | 1.0 | 1.5 | | |
| **Sn** | 1.3 | 1.4 | | 2.25 |
| **Zn** | 125 | 131 | 67 | 36 |

Table 5: Median ambient background concentration and reference values of trace elements in Flemish river sediment.

[a] thermal decomposition, amalgamation, and atomic absorption spectrophotometry was used for the determination of Hg according to EPA 7473.

River sediment monitoring 2010-2011: median elemental background concentrations in 22 Flemish river sediments following $HNO_3$/HCl digestion and analysis by ICP-MS [92,93].
River sediment monitoring 2006: median elemental concentrations in 105 river sediments, sampled and analysed in 2006 [89].
River sediment reference values: reference values for a standardized river sediment (*i.e.*, 11% clay, 5% organic matter)[91].
European river sediments: median values (*aqua regia*) in European stream sediments from The FOREGS Geochemical Baseline Mapping Programme [58].

For the elements Cd and Se, the superior sensitivity of ICP-SFMS, as compared to ICP-AES, is necessary to determine background concentrations. An advantage of ICP-MS is that in addition to trace elements at mg/kg level, also matrix elements at g/kg level can be determined in the same measurement run (panoramic analysis). The total Fe and Ca contents are relevant parameters to predict *heavy metal* concentrations in sediments, besides organic matter and clay content [89]. The results of these matrix elements at the 22 selected background locations are summarized below.

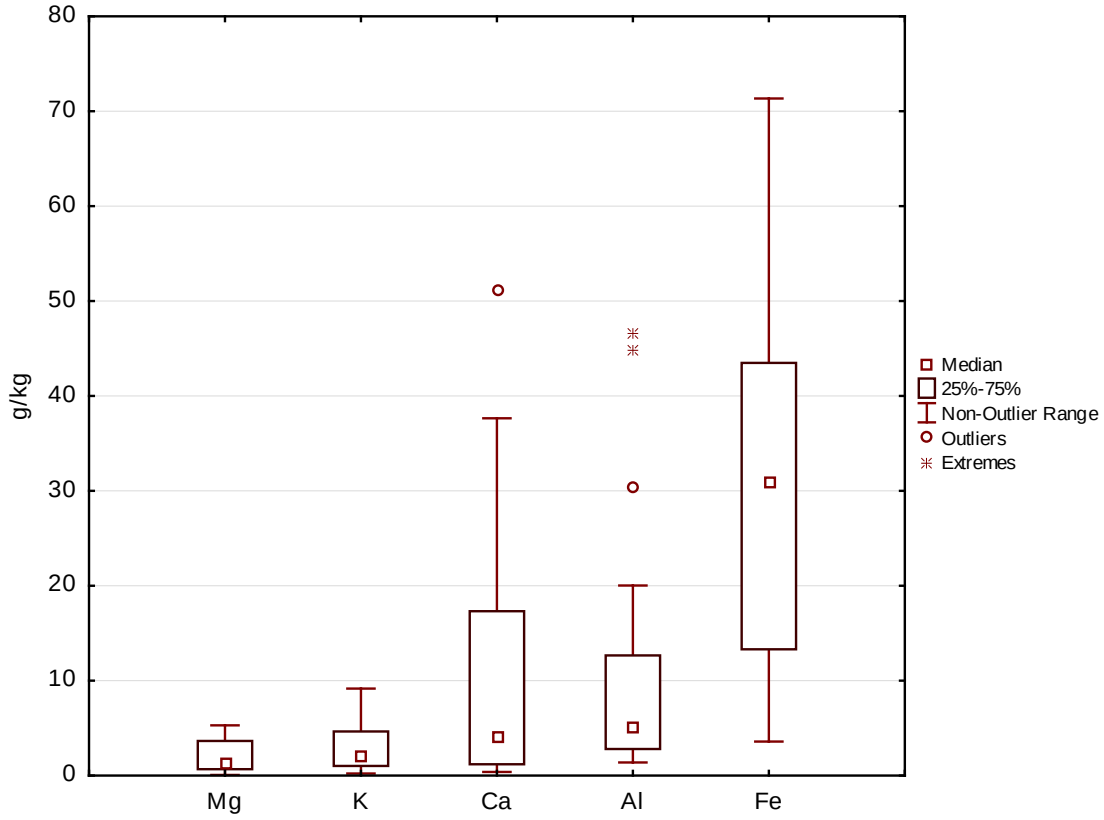



Figure 24: Ambient background concentration of matrix elements in river sediment in Flanders, determined after aqua regia digestion with ICP-MS according to CEN/TS 16171 (samples collected at 22 different locations in 2010-2011, see Figure 22) (data courtesy of VMM [92,93]).

## 2.5. AMBIENT BACKGROUND CONCENTRATION OF ELEMENTS IN SURFACE AND GROUND WATER IN FLANDERS

Water has been denoted as "*blue gold*" and this is also recognized in the preamble of the European Water Framework Directive where it is stated that: "*water is not a commercial product like any other, but rather a heritage, which must be protected, defended and treated as such*"[95].

The increasing demand for cleaner rivers and lakes, groundwater and coastal beaches has been evident for considerable time (since 1975, the need for water has doubled worldwide). This demand is one of the main reasons why the European Commission has made water protection one of the priorities of its work [96]. Since the adoption of the Water Framework Directive (WFD) in 2000, the European Water Policy has undergone a thorough restructuring process. As opposed to earlier water protection, which focused on single types of water, the area covered by this Directive extends to all aquatic systems, surface waters (rivers and lakes), groundwater and coastal waters.

Monitoring Programmes play a key role in the practical implementation process of the European Water Framework Directive. They form the basis for developing effective programmes of measure that aim at reaching the WFD quality aims. The WFD includes a plan of action for the implementation in the member states, setting out clear deadlines for each of the requirements, *e.g.*, monitoring programmes had to be implemented by the end of 2006.

The WFD identified the need to monitor water status throughout the Community on a systematic and comparable basis. Accordingly, there was a need for comparability between results obtained, not only by different laboratories, but also at different points in time or place. Under the 6$^{th}$ Framework Programme, the EU R&D project SWIFT-WFD (Screening methods for Water data InFormaTion in support of the implementation of the Water Framework Directive) was launched. The main objective of this project was to support the successful implementation of the WFD, which closely depends on the quality of monitoring data and its comparability form river basin to river basin. To do so, interlaboratory studies with classical laboratory-based analyses were organised for parameters regulated by the WFD for the assessment of laboratory performance in major component and trace element determination [97].

In commission of the Flemish Environment, Nature and Energy Department (LNE, see § 1.2), VITO participated in 3 environmental regulatory monitoring intercomparison exercises that were organised in the period 2004-2006 as one of the 94 laboratories from 21 European member states [98]. For trace element determination, the majority of participating laboratories used ICP-OES or ICP-MS; to a lesser extent AAS-based techniques were applied (Flame, graphite furnace or hydride generation). A general ranking of performances for all the analytes in all the exercises was made, individuating the more problematic analytes in terms of lack of comparability of results (expressed as average coefficient of variation (CV) %), lack of capacity to provide satisfactory or at least doubtful results (expressed as percentage of $|Z|$-scores > 3), and lack of sensitivity of analytical methods (expressed in terms of percentage of less than limit of detection results) (see Figure 25). The main problems were encountered for trace element determination that are on the top of the list (*i.e.*, highest difficulty ranking); Unexpectedly, analytes such as total P and nitrate were ranked as more difficult to determine then most pesticides. The determination of pH caused the least problems in terms of precision, accuracy and sensitivity.

The results of the European intercomparison exercises on environmental regulatory monitoring (2004-2006) suggested that the routinely applied methods for the determination of trace elements in water matrices should be improved to be able to fulfil WFD requirements. Furthermore, matrix effects need to be taken into account, and specific methods avoiding matrix interferences need to be implemented and routinely adopted (especially for As, Se and Cr). To date, dealing with matrix and

spectral interferences is still one of the main challenges in the routine adoption of ICP-MS as a monitoring method for surface water (see also § 1.4.1).

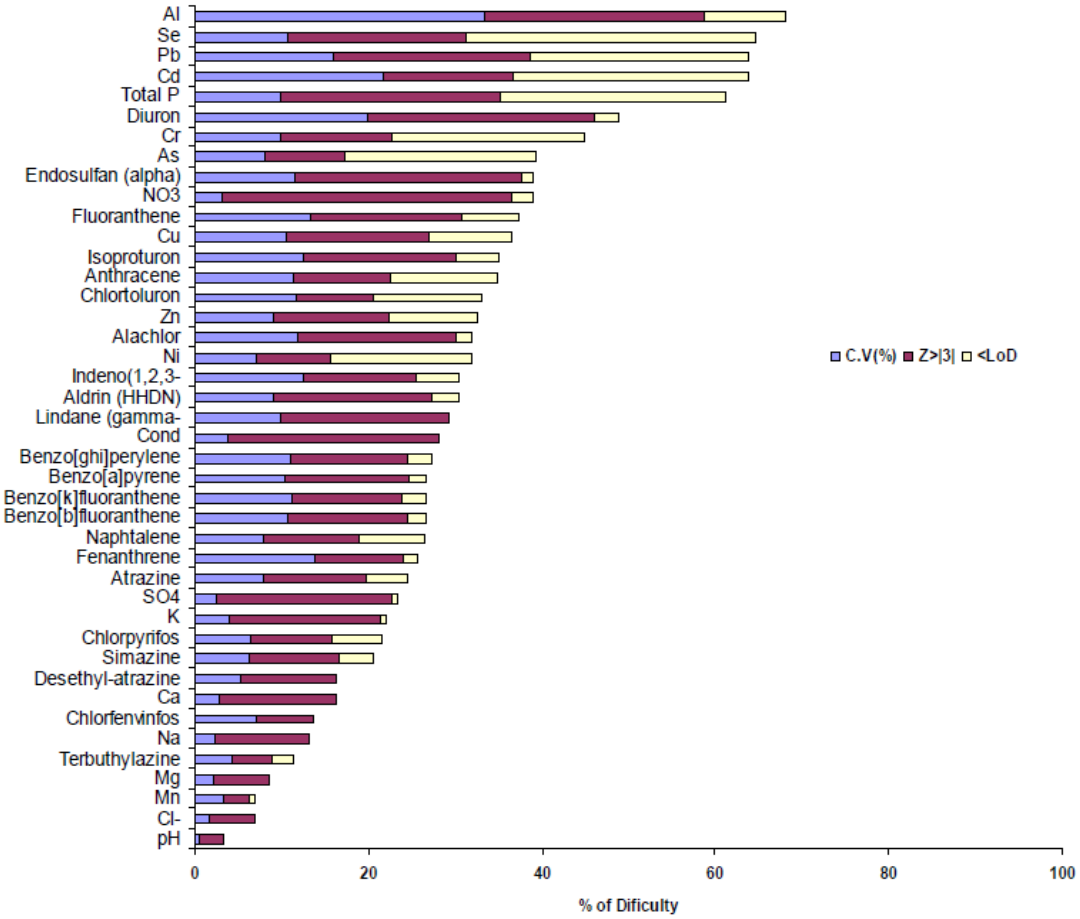



Figure 25: Cumulative difficulty ranking of performance for all analytes monitored (sum of precision (CV%, blue), accuracy (Z>|3|, purple) and sensitivity (< LoD, yellow) criteria)(figure courtesy of Final report on SWIFT-WFD PTs results [98]).

### 2.5.1. AMBIENT BACKGROUND CONCENTRATION OF ELEMENTS IN SURFACE WATER IN FLANDERS

When evaluating toxicity data to derive quality standards for metals, total metal concentrations are usually not directly related to ecotoxicological effects because many abiotic and biotic processes can modify the availability of metals, even rendering them unavailable for uptake. This means that the fraction available for uptake and toxicity may be a very small part of the total amount of metal present.

Due to several physicochemical processes, metals exist in different chemical forms which might differ in (bio)availability. Thus, the (bio)availability of metals in both laboratory tests and in the "real" environment may be affected by several physicochemical parameters such as the pH and hardness of water and the dissolved organic carbon (DOC) content.

The Water Framework Directive explicitly acknowledges the issues of (bio)availability and naturally occurring concentrations for metals [43]. Member states may, when assessing the monitoring results against the environmental quality standard (EQS), take into account:

(a) natural background concentrations for metals and their compounds, if they prevent compliance with the EQS value; and
(b) hardness, pH or other water quality parameters that affect the bioavailability of metals.

Ideally, the derivation of EQS for metals requires an explicit consideration of (bio)availability using speciation models or, failing that, to utilise dissolved concentrations instead of total concentrations.

On May 21st, 2010, the Flemish government approved a decree on new environmental quality standards for a wide range of dissolved elements (operationally defined as filtered through 0,45 µm membrane filter) in surface water. Today's distinction between dissolved and particulate phases in (geo)chemistry can be traced back to the application of 0.5 µm cellulose acetate membrane filters to ocean waters by Goldberg et al. (1952) [99]. Since then, different studies called for relinquishing the misleading delineation of particulate and dissolved phases at about 0.45 µm, but this operational definition has become firmly established by now [100,101]. The following paragraphs describe how ambient background concentrations of dissolved elements were derived in surface water for Flanders.

### → Background sampling locations

The Flemish Environment Agency started monitoring of dissolved elements in 2007 and systematically expanded the monitoring network to about 500 measuring points at present [106]. For the determination of median ambient background concentrations of dissolved trace elements in Flemish surface water, the same 22 background locations were chosen as for river sediment (ecotoxicological and biological class 1, see § 2.4 and Figure 22)[92,107].

### → European regulatory monitoring method

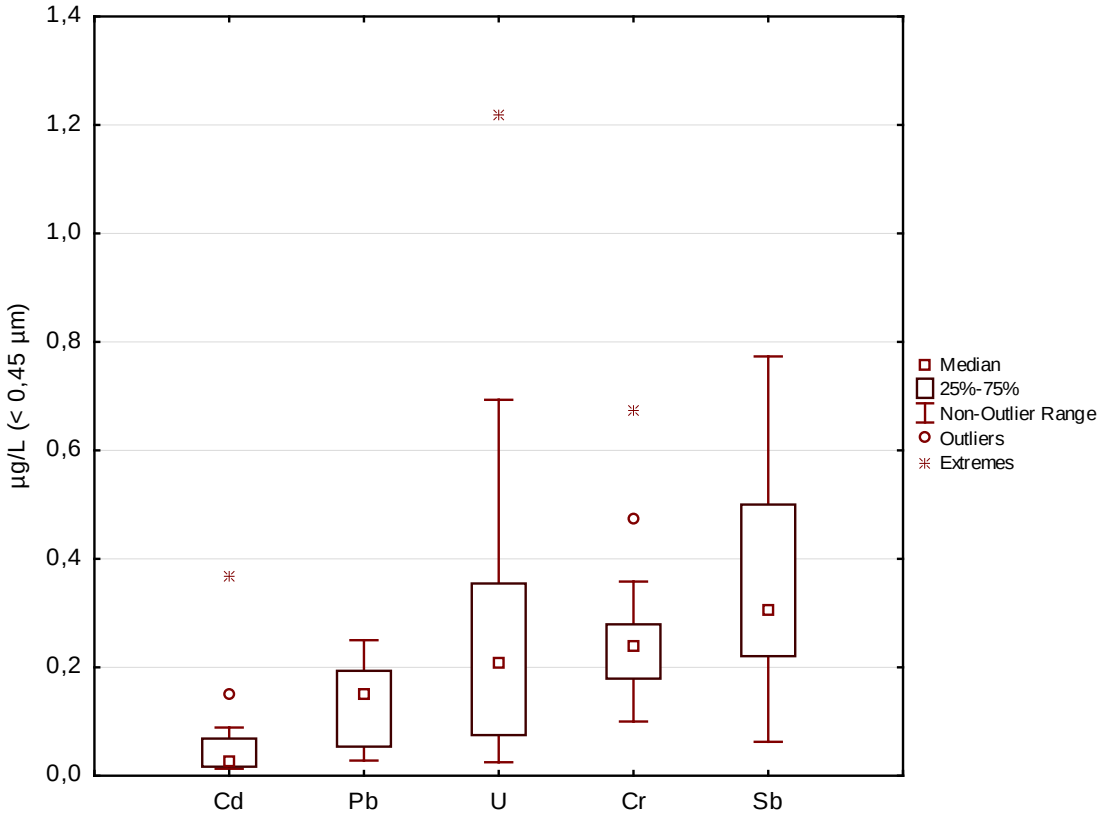
The methods used for the determination of dissolved elements in surface water were based on:

- EN 17294-1:2006 Water quality - Application of inductively coupled plasma-mass spectrometry (ICP-MS) - General guidelines
- EN 17294-2:2004 Water quality - Application of inductively coupled plasma-mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements
- EN 12846:2012 Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment

On average, the 22 selected background locations were sampled and measured more than 300 times over the period 2009 – 2012 by 3 different recognized laboratories [107]. For the elements Be, Cu, Hg, Mo, Se, Sn, Ti and Tl, more than 90 % of the reported values were lower than the quantification limit of the laboratory, therefore a (median) quantification limit is reported in Table 6. It should be noted that the quantification limits used by recognized laboratories in environmental regulatory monitoring are related to the legal requirements and, as such, they are not an indication of the sensitivity attainable by ICP-MS. For the other elements and on average, less than 40 % of the reported values were lower than the quantification limit of the laboratory. In order to calculate a mean concentration of each element for each of the locations, the approach as set by Directive 2009/90/CE (technical specifications for chemical analysis and monitoring of water status) was followed, *i.e.*, if the amount of an element in a given sample is below the limit of quantification, the measurement result shall be set to half of the value of the limit of quantification for the calculation of the mean value.

### → Background concentration of dissolved elements in surface water

Ambient background concentrations of dissolved elements in Flemish surface water, sampled on 22 locations with no acute impact on benthic biota and good biological quality are summarized in the figures below [92,107].



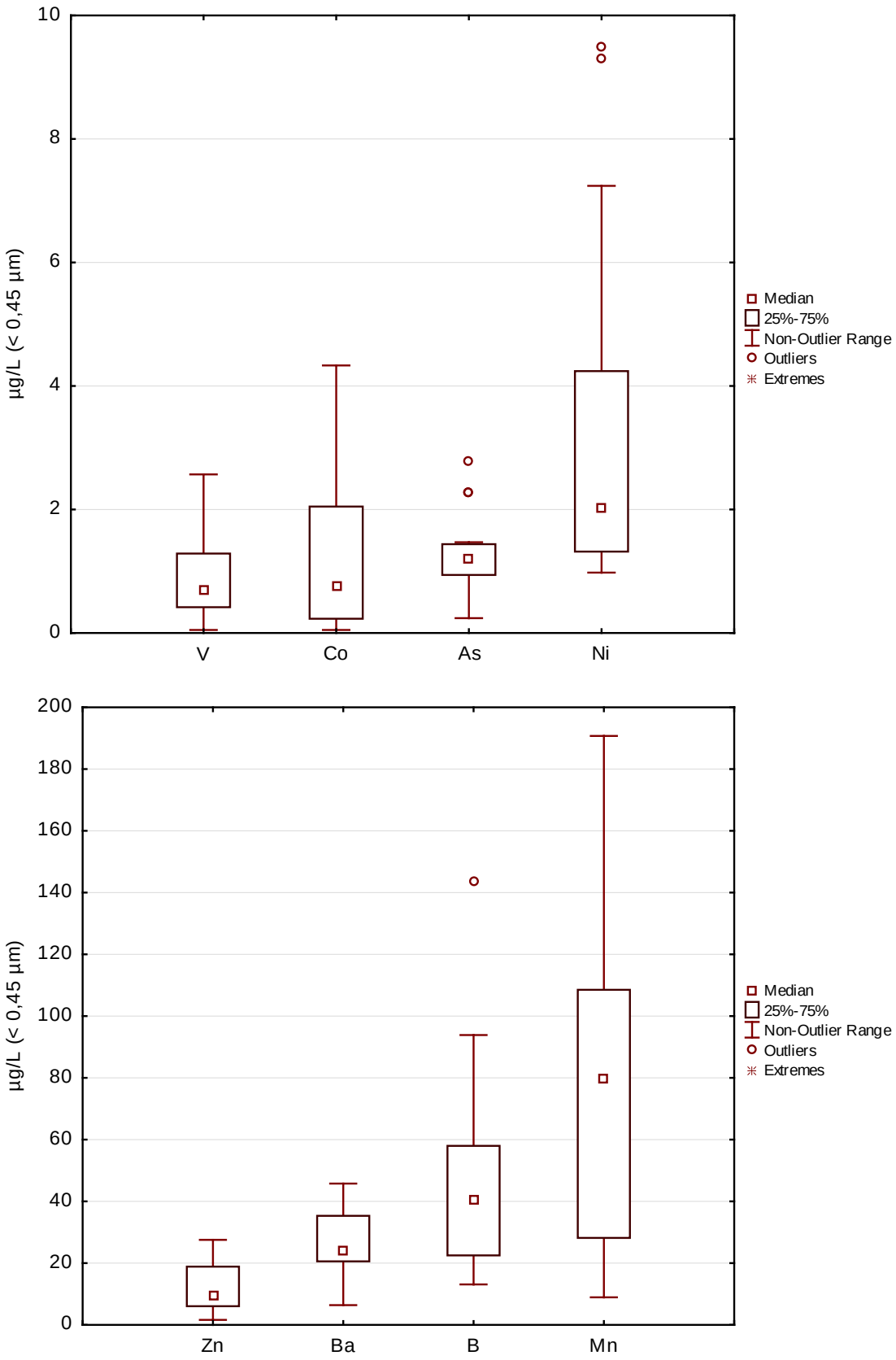



Figure 26: Ambient background concentrations of dissolved trace elements (<0,45 µm) in Flemish surface water as measured by ICP-QMS (average of 300 samples collected at 22 different locations in 2009-2012, see Figure 22) (data courtesy of VMM [92,107]).

The median ambient background concentrations of dissolved trace elements in Flemish surface waters of the monitoring campaign 2009-2012 are summarized in Table 6 [92,107]. For comparison, the median values for concentrations of dissolved elements in European stream water from the FOREGS Geochemical Baseline Mapping Programme and the environmental quality standard values as defined in VLAREM II Annex 2.3.1 are also represented [58].

| | Monitoring 2009-2012 | European stream water | EQS values VLAREM II |
|---|---|---|---|
| | *(< 0.45 µm)* | *(< 0.45 µm)* | *(< 0.45 µm)* |
| | µg/L | *µg/L* | *µg/L* |
| As | 1.2 | 0.63 | 3 |
| B | 40 | 16 | 700 |
| Ba | 24 | 25 | 60 |
| Be | < 0.25 | 0.009 | 0.08 |
| Cd | 0.027 | 0.01 | 0.08-0.25 |
| Co | 0.75 | 0.16 | 0.5 |
| Cr | 0.24 | 0.38 | 5 |
| Cu | <2 | 0.88 | 7 |
| Hg | <0.01[a] | | 0.05 |
| Mn | 80 | 16 | |
| Mo | < 2.5 | 0.22 | 340 |
| Ni | 2 | 1.9 | 20 |
| Pb | 0.15 | 0.093 | 7.2 |
| Sb | 0.31 | 0.07 | 100 |
| Se | < 2 | 0.34 | 2 |
| Sn | < 0.5 | | 3 |
| Ti | < 1 | 0.9 | 20 |
| Tl | < 0.05 | 0.005 | 0.2 |
| U | 0.21 | 0.32 | 1 |
| V | 0.71 | 0.46 | 4 |
| Zn | 9.6 | 2.7 | 20 |

Table 6: Median ambient background concentration and EQS values of dissolved trace elements in surface water.
[a] cold vapour-AFS was used for the determination of Hg according to EN 17852

All derived median concentrations of elements at the background locations are below the EQS values with an exception for Co. Although the question "*How low is low and how low do we need to go?*" can be adequately answered by ICP-MS in environmental regulatory monitoring of dissolved elements in surface water [44], more than 90 % of the values reported for the elements Be, Cu, Hg, Mo, Se, Sn, Ti and Tl during the monitoring campaign were lower than the quantification limit of the laboratory. Regulatory monitoring of trace-level metals commonly relies on infrequent grab sampling followed by instrumental analysis to determine filtered concentrations. However, limitations of these methods are often ignored. These primarily concern (i) potential contamination and changes in metal speciation during sample storage and transport, (ii) levels of suspended/dissolved organic matter or colloids, and (iii) sample volume, filtration equipment and size of the filter used [102]. As for most monitoring techniques, results obtained are operationally-defined (the protocol defines the answer),

and while this may facilitate comparability of results acquired across Europe, data generated may have little relevance to ambient dissolved or bioavailable metal concentrations where metals may be present in aquatic environments as free ions, complexed with organic and/or inorganic ligands or sorbed to suspended particles and colloids.

Until now, assessment of the sampling protocol, not commonly included in quality control schemes, has received little attention, and this may well become critical for implementation of legislation such as the WFD. Where contaminant levels fluctuate, optimisation of the sampling frequency is of utmost importance, and 12 equally spaced-sampling events per year may not provide representative information (*e.g.*, flood events). One possible solution is the use of passive sampling devices to provide time-weighted average (TWA) pollutant concentrations in water [102,103]. Passive samplers such as the diffusive gradient in thin film (DGT) device and Chemcatcher accumulate by diffusion a labile fraction of metals with minimal disturbance of the system and provide more toxicologically relevant and representative metal concentrations. It is now being recognised that passive samplers can play a valuable role in monitoring water quality within a legislative framework such as the European Union's Water Framework Directive [104,105]. The data from these devices can be used alongside the results obtained from conventional spot sampling to improve risk assessments and to provide information required to take decisions on undertaking potentially expensive remedial actions. It is expected that the aquatic monitoring sector will follow a transition similar to that which occurred in air monitoring, where data obtained from passive samplers or on-line measurement devices can be complementary used within a legal framework. But, as stated earlier, the introduction of harmonised and standardised analytical methods tend to delay the acceptance and use of new and innovative monitoring / screening methods.

Under the WFD, member states were required to report chemical status for fresh and coastal water bodies. The map below summarizes the chemical status for European surface waters at river basin district (RBD) scale in 2010 and describes the relative proportion of water bodies of good status, those at risk of failing to achieve good status and those of unknown status [85].

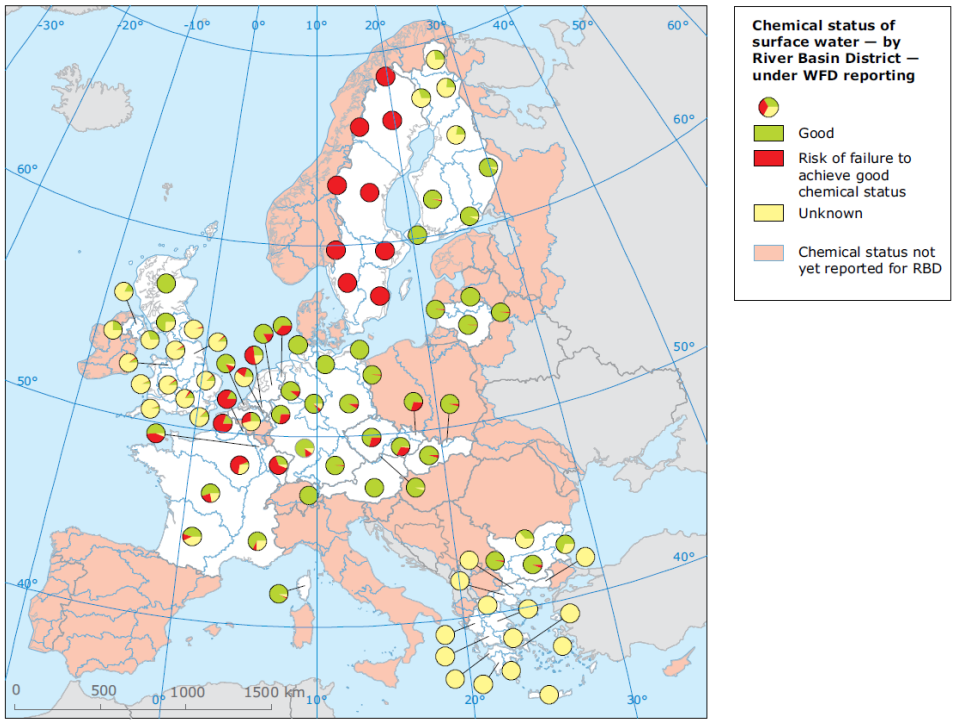



Figure 27: WFD chemical status of surface water as of December 2010 (figure courtesy of European Environment Agency [85]).

The information is based on data drawn from a variety of sources and reflects information as reported by December 2010. However, despite the improved knowledge base arising from this body of information reported by the different European member states, very often uncertainty remains as to whether the observed concentrations of a particular substance pose a risk to aquatic environments and human health. In this report, the European Environment Agency notes that the assessment is on-going, and that conclusions remain tentative. This can be illustrated by the example of the reported excessive levels of metals including cadmium and mercury, which challenge good chemical status in a number of RBDs. In Sweden, widespread excessive levels of mercury in aquatic biota mean that all RBDs currently fail to achieve good chemical status. In Sweden, unlike other countries, biota has been chosen as the matrix for monitoring, making detection more likely than in the water column, given the propensity of mercury to bioaccumulate. Such inconsistency in reporting chemical status between member states is of concern and interpretation or comparison of the chemical status should therefore be done carefully.

This example underlines that harmonization in communication and reporting of our chemical status is of concern besides the technical feasibility of analysis at these concentration levels and that no consistent map of the chemical status of European surface waters is yet available [45].

### 2.5.2. AMBIENT BACKGROUND CONCENTRATION OF ELEMENTS IN GROUND WATER IN FLANDERS

The European Groundwater Directive (2006/118/EC) establishes a regime which sets ground water quality standards and introduces measures to prevent or limit inputs of pollutants into groundwater. The directive establishes quality criteria that take account local characteristics and allow for further improvements to be made based on monitoring data and new scientific knowledge.

Aquifers from the same typology can have strongly different groundwater chemistry and natural background levels are rather a range of values than single values. Wendland *et al.* developed a European aquifer typology map as a tool for comparison of hydrochemical data sets across Europe and as a basis for referencing hydrogeochemical groundwater composition on a European scale [108]. Nine major aquifer rock types were distinguished and secondary criteria were used to further subdivide and refine the aquifer typology. M. Coetsiers *et al.* attempted to derive natural background levels for four aquifers in Flanders of the sand and gravel typology as $90^{th}$ and $97.7^{th}$ percentile of a carefully chosen dataset to approach the natural groundwater composition [108]. The range of natural background levels ($90^{th}$ percentile) in these four aquifers (fluvial Pleistocene and Tertiary marine) are summarised in Table 7.

In support of the implementation of the Water Framework Directive and the Groundwater Directive, new groundwater quality standards, threshold values and background levels were adopted in Flanders in 2010 (VLAREM II, Annex 2.4.1., background levels and threshold values were separately established per groundwater body). The following paragraphs describe how ambient background levels of dissolved elements were derived in ground water for Flanders.

#### → Background sampling locations

The Flanders Subsoil Database (Databank Ondergrond Vlaanderen) includes several groundwater monitoring networks with the intention of getting a representative picture of the groundwater quantity and quality of the aquifers in Flanders [86]. In the context of environmental monitoring, the phreatic groundwater monitoring network and the primary groundwater monitoring network are of importance.

The phreatic groundwater monitoring network was originally established as a monitoring tool in function of the European Nitrate Directive (91/676/EEC). Through this monitoring network, the presence of nitrate-vulnerable areas (the so-called hydrogeological homogeneous zones) was confirmed and analysed. Nevertheless, since 2007, the entire area of Flanders is nitrate-vulnerable area due to the widespread contamination problem. Now, the network measures the effects of the action programs (Manure Action Plans-MAP) taken in the scope of the Flemish Manure decree for a further improvement of the groundwater quality (see also § 4.3). The phreatic groundwater network is fully operational since 2004. In the meantime, the network has become multi-functional and forms part of the monitoring program in the scope of the Water Framework Directive (2000/60/EG) and the Groundwater Directive (2006/118/EG) as well. To meet the requirements, the network was further optimized and enlarged. On a half yearly basis, 2107 multi-level wells (with about 5100 filter screens) in agricultural area and approximately 80 multi-level wells (190 filter screens) in natural background area are sampled and analyzed.

Figure 28: Geographical distribution of the wells of the phreatic groundwater monitoring network across the different hydrogeological homogeneous regions (figure courtesy of Databank Ondergrond Vlaanderen [86]).

The primary monitoring network consists of about 435 wells with more than 800 screens, selected in order to provide representative data of important, mainly deeper, aquifers. The primary groundwater monitoring network aims primarily at establishing regional groundwater resources and at following the evolution of the quantity of the groundwater bodies in time. In support of the Water Framework Directive, the primary groundwater monitoring network is also increasingly used for groundwater quality research. In this context, it is mainly used to determine the physico-chemical background levels, but also for detecting anthropogenically induced changes in the quality of the deeper aquifers [87].

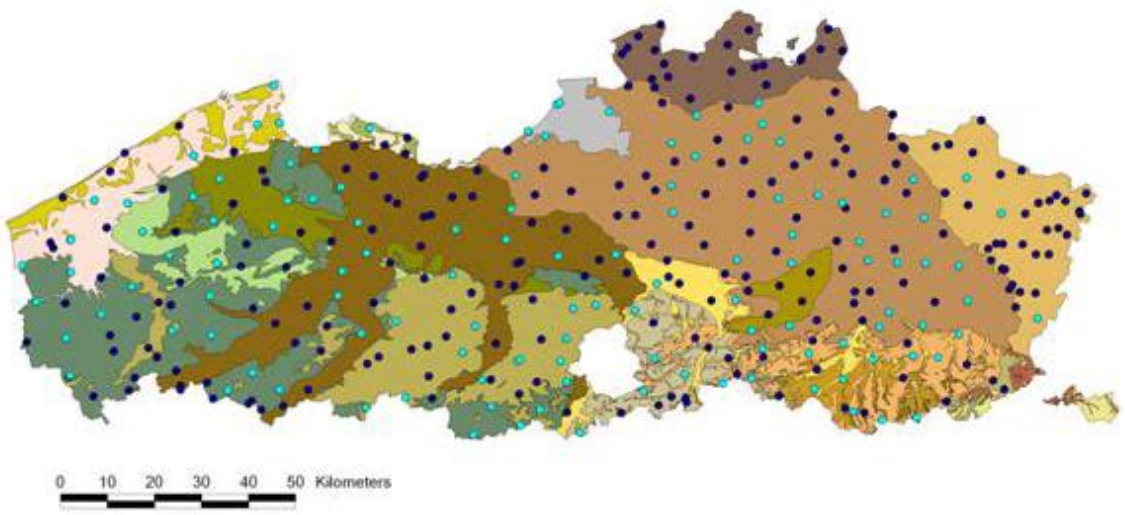



Figure 29: Geographical distribution of the wells of the primary groundwater monitoring network, with the phreatic groundwater bodies as background (figure courtesy of Databank Ondergrond Vlaanderen [86]).

For the determination of ambient background levels of dissolved elements in the 42 groundwater bodies defined in Flanders, data from the primary and the phreatic groundwater monitoring network of 2006 were used [88].

### → European regulatory monitoring method

The methods used for the determination of dissolved elements in ground water were based on:

- EN 17294-1:2006 Water quality - Application of inductively coupled plasma-mass spectrometry (ICP-MS) - General guidelines
- EN 17294-2:2004 Water quality - Application of inductively coupled plasma-mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements
- EN 11885:2009 Water quality - Determination of selected elements by inductively coupled plasma-optical emission spectrometry (ICP-OES)
- EN 15586:2003 Water quality - Determination of trace elements using atomic absorption spectrometry with graphite furnace
- EN 17852:2008 Water quality - Determination of mercury - Method using atomic fluorescence spectrometry
- EN 12846:2012 Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment

Different recognized laboratories were involved in the groundwater monitoring campaign of 2006 and for the determination of dissolved trace elements, different analytical techniques were used (ICP-AES, ICP-MS and GF-AAS)[88].

### → Background concentration of dissolved elements in ground water

The background levels were derived per groundwater body as the 90$^{th}$ percentile of the groundwater monitoring campaign of 2006. Most of the trace element concentrations determined in more than 2600 groundwater samples were reported as lower than the quantification limit of the laboratory (*inter alia* caused by the use of different analytical techniques)[88]. Based on this dataset, the expected median background concentrations for dissolved trace elements in groundwater are < 0.05 µg/L for Hg, < 0.1 µg/L for Cd, < 1 µg/L for Pb, Cr and Cu, < 10 µg/L for As and Ni and < 20 µg/L for Zn.

For the major elements, a wide range is observed in the background levels in the different groundwater bodies (*e.g.*, for Na a concentration range from 5 to 5000 mg/L).

The median ambient background concentrations of dissolved elements derived from regulatory monitoring in Flemish ground water are summarized in Table 7 (column ground water monitoring 2006)[88]. In addition, the range of natural background levels (90$^{th}$ percentile), derived by Coetsiers *et al.* in fluvial Pleistocene and Tertiary marine aquifers is given in Table 7 [108]. The range of the background levels defined for each of the 42 groundwater bodies (as defined in VLAREM II, Annex 2.4.1), is also represented in the table below (these regulatory values represent the 90$^{th}$ percentile of the measurements performed at background locations per groundwater body).

| | Fluvial Pleistocene / Tertiary marine aquifers | Ground water monitoring 2006 | Ground water Background levels (VLAREM II Annex 2.4.1) |
|---|---|---|---|
| | Range of 90$^{th}$ percentile | Median | Range of 90$^{th}$ percentile |
| | *(< 0.45 µm)* | *(< 0.45 µm)* | *(< 0.45 µm)* |
| | µg/L | µg/L | *µg/L* |
| **As** | 5.6 - 30 | < 10 | 1 - 60 |
| **B** | 0.3 - 1.2 | | |
| **Cd** | 0.12 - 0.5 | < 0.1 | 0.05 - 1 |
| **Cr** | 0.8 - 4 | < 1 | 1 - 37 |
| **Cu** | 5 - 10.2 | <1 | 0.5 - 7 |
| **Hg** | 0.05 - 0.25 | < 0.05 | 0.03 - 0.5 |
| **Ni** | 3.7 - 39 | < 10 | 5 - 60 |
| **Pb** | 0.5 - 5 | < 1 | 1 - 18 |
| **Sb** | 0.03 - 1 | | |
| **Zn** | 26 - 260 | < 20 | 16 - 250 |
| | mg/L | mg/L | *mg/L* |
| **Al** | 0.01 - 1.5 | < 0.1 | 0.01 - 0.8 |
| **Ca** | 73 - 200 | 79 | 4 - 700 |
| **Fe** | 5 - 44 | 2.3 | 0.12 - 50 |
| **K** | 10 - 36 | 3.5 | 3 - 200 |
| **Mg** | 12 - 39 | 10 | 2 - 800 |
| **Na** | 38 - 320 | 22 | 12 - 6000 |
| **Mn** | 0.3 - 1.3 | 0.26 | 0.02 - 2.2 |

Table 7: Range of 90$^{th}$ percentile concentrations in Fluvial Pleistocene and Tertiary marine aquifers, median ambient background concentrations derived from regulatory monitoring (2006) and range of regulatory background levels of dissolved elements in Flemish ground water (VLAREM II Annex 2.4.1).

The given ranges of ambient background concentrations in ground water point to ICP-MS as the method of choice, as the superior sensitivity combined with the wide linear dynamic range (determination of trace and major elements in the same run) favours the use of ICP-MS as compared to ICP-AES and GF-AAS.

## 2.6. SUMMARY OF AMBIENT BACKGROUND CONCENTRATIONS OF ELEMENTS IN FLANDERS

As a case study and for the first time, ranges of background concentration of *heavy metals* were summarised for all environmental compartments in Flanders based on European Standards on the one hand and on a selection of (non-polluted) background locations on the other. In a very short period of time, the majority of the human population has become urban, and it is estimated that by 2050 two out of every three people in the world will live in cities [110]. Urban areas are extremely important socially, economically, and culturally, but they also have a profound impact on the environment (*i.e.*, urban geochemistry). The background concentration estimates reported in Table 8, can be considered as an indicator of the current "natural" chemical status of our environment and can be used to assess future anthropogenic influences within an EU regulatory monitoring context.

| | soil | | | air | | | water | | |
|---|---|---|---|---|---|---|---|---|---|
| | EN 16174 CEN/TS 16171 | EN 16174 CEN/TS 16171 | EN 16174 CEN/TS 16171 | EN 14902 | EN 15841 | EN 15841 | EN 16174 CEN/TS 16171 | EN17294 | EN17294 |
| | 0-20 cm | 50-100 cm | tertiary | $PM_{10}$ | bulk deposition | wet deposition | river sediment | surface water | ground water |
| | mg/kg | mg/kg | mg/kg | ng/m³ | µg/m².day | µg/m².day | mg/kg | µg/L *(< 0.45 µm)* | µg/L (<0.45 µm) |
| **As** | 7.2 | 6.1 | 8.8 | 0.61 | 0.37 | 0.21 | 17 | 1.2 | < 10 |
| **Ba** | | | | 2.7 | | | | 24 | |
| **Cd** | 0.32 | 0.10 | 0.050 | 0.20 | 0.098 | 0.059 | 0.15 | 0.027 | < 0.1 |
| **Co** | 5.2 | 4.6 | 6.6 | | | | | 0.75 | |
| **Cr** | 25 | 24 | 62 | 2.0 | 0.94 | 0.40 | 20 | 0.24 | < 1 |
| **Cu** | 11 | 4.7 | 2.7 | 5.0 | 4.6 | 9.0 | 8.2 | <2 | < 1 |
| **Hg** | 0.062[a] | 0.027[a] | 0.01[a] | 0.7[b] | | 0.025[c] | 0.052[d] | < 0.01[e] | < 0.05 |
| **Mn** | | | | 4.3 | 23 | 8.1 | 169 | 80 | |
| **Mo** | 0.44 | 0.16 | 0.39 | 0.44 | | | | < 2.5 | |
| **Ni** | 7.4 | 6.3 | 12 | 1.8 | 1.0 | 0.67 | 8.2 | 2.0 | < 10 |
| **Pb** | 26 | 8.3 | 6.1 | 8.1 | 4.6 | 1.4 | 17 | 0.15 | |
| **Sb** | 0.5 | 0.14 | 0.32 | 1.1 | | | | 0.31 | |
| **Se** | 0.28 | 0.14 | 0.29 | | | | 1.0 | < 2 | |
| **Sn** | | | | | | | 1.3 | < 0.5 | |
| **Ti** | | | | 3.6 | | | | < 1 | |
| **V** | 40 | 26 | 62 | 2.2 | | | | 0.71 | |
| **Zn** | 57 | 26 | 29 | 22 | 21 | 12 | 125 | 9.6 | < 20 |

Table 8: Estimates of median ambient background concentrations of *heavy metals* present in the different environmental compartments in Flanders.

[a] CEN/TS 16175-2:2013 Sludge, treated biowaste and soil - Determination of mercury - Part 2: Cold vapour atomic fluorescence spectrometry (CV-AFS).
[b] EN 15852:2010, Ambient air quality - Standard method for the determination of total gaseous mercury.
[c] EN 15853:2010, Ambient air quality - Standard method for the determination of mercury deposition.
[d] EPA 7473:1998 Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry.
[e] EN 12846:2012 Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment.
EN 14902:2005 Ambient air quality - Standard method for the measurement of arsenic, cadmium, lead and nickel in the PM 10 fraction of suspended particulate matter.
EN 15841:2009, Ambient air quality - Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition.
CEN/TS 16171:2012 Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma-mass spectrometry (ICP-MS).
EN 16174:2012 Sludge, treated biowaste and soil - Digestion of *aqua regia* soluble fractions of elements.
EN 17294-1:2006 Water quality - Application of inductively coupled plasma-mass spectrometry (ICP-MS) - General guidelines.
EN 17294-2:2004 Water quality - Application of inductively coupled plasma-mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements.

The range of elemental background concentrations, derived from the different examples of Flemish regulatory monitoring, illustrate *a match made in heaven* with the sensitivity of ICP-MS instruments (see Table 8). This being said, it is also clear that the panoramic analysis capabilities of ICP-MS are not yet fully exploited in current environmental monitoring studies with respect to its linear dynamic range and multi-element capabilities [109].

For the determination of elements in soil and river sediment, the $HNO_3$/HCl/HF digestion which is currently prescribed in Flanders hampers the optimal use of ICP-MS. However, there is a trend in the European Committee for Standardization (CEN) to promote nitric acid and aqua regia as the sole acids to be used for environmental sample digestion. Additionally, with the incorporation of Hg in CEN/TS 16171 as one of the elements determinable by ICP-MS, the use of ICP-MS in future regulatory monitoring of solid matrices will certainly be favoured. The examples of environmental monitoring described in this chapter, show that the aqua regia digestion in combination with ICP-MS is a powerful tool for the determination of ambient background concentrations of major and trace elements. One must keep in mind that the choice of the acid digestion procedure will have implications on the measured concentration of some elements, as acid digestion procedures are prone to operational settings.

In support of the European Water Framework Directive, ICP-MS (EN 17294) became the only method of choice for chemical analysis and monitoring of dissolved elements in surface water. More monitoring studies using ICP-MS and with focus on low level determination of elements are needed to refine the derived estimates of ambient background concentrations (now often reported as < limit of quantification). However, dealing with matrix and spectral interferences is still one of the main challenges in the routine adoption of ICP-MS as a monitoring method. For the determination of concentrations in surface and ground water, it can be argued that the risk of sample contamination nowadays represents a far greater challenge than the instrumental limits of detection attainable with ICP-MS.

The same holds true for the determination of elements in fine particulates and atmospheric deposition: sampling and contamination free acid digestion are considered the most critical steps for accurate trace environmental monitoring. The European standard methods for the determination of elements in ambient air (EN 14902 and EN 15841) prescribes nitric acid digestion (in combination with $H_2O_2$ or traces HF), which also favours the use of ICP-MS as sensitive and multi-elemental determination method.

## 2.7. SUMMARY AND CONCLUSION

A clean, healthy and diverse environment is a prerequisite for prosperity and well-being for everyone and this can only be achieved through a common legal framework. This common framework is needed in order to assure that environmental pollution, no matter where it comes from, is assessed in the same way across national or even regional borders. At a European level, major legal acts include the Water Framework Directive, the Waste Framework Directive, the Air Quality Directive and the upcoming Soil Framework Directive and all of these include monitoring programs to report on the state of our environment.

European Standards (EN) related to the use of ICP-MS for the determination of elements in the different environmental compartments have been published starting from 2004 onwards and is still on-going. As a consequence, these European standard methods have been introduced as reference methods in the Flemish Environmental legislation and regulatory monitoring. Nowadays, European standard methods (EN) related to the use of ICP-MS are available for the determination of elements

in all environmental compartments (water, air, soil) and this is undoubtedly the most important advance in environmental regulatory monitoring of elements the last decade.

*Heavy metals* have unique characteristics that should be considered when assessing their environmental risks. Unlike most organic substances, *heavy metals* are neither created nor destroyed by biological or chemical processes. Rather, they are transformed from one chemical form into another. Moreover, in the context of risk assessment, one must keep in mind that *heavy metals* are naturally occurring constituents of our environment that vary in concentrations across geographic regions. In other words, as *heavy metals* are naturally present in our environment, knowledge of (regional) ambient background concentrations is needed to provide baseline data for pollution and risk assessment studies.

Because of the availability of ICP-MS instruments nowadays, it can be argued that the main hindrance to the implementation of the European monitoring requirements is not the technical feasibility of analysis at these concentration levels, but rather potential contamination during sampling, sample storage, sample handling and analysis. Two additional comments with respect to a harmonised implementation of the European monitoring requirements may be formulated at this point. First, as for most monitoring techniques, results obtained are operationally-defined. The protocol, *e.g.,* acid digestion, 0.45 µm filtration*, ...* defines the answer, and while this may facilitate comparability of results acquired across Europe, data generated may have little relevance to bioavailable metal concentration. Second, more harmonization in communication and reporting of our chemical environmental status between member states is needed to compare regulatory monitoring data on a European scale, *e.g.*, choice of sampling locations (*e.g.*, rural versus industrial) and type of sample (*e.g.*, biota versus water column).

As stated earlier, the panoramic analysis capabilities of ICP-MS are not yet fully exploited in environmental monitoring studies yet with respect to its linear dynamic range and multi-element capabilities. The determination of *heavy metals* in environmental monitoring has traditionally focused on a relative small number of elements (*e.g.*, As, Cd, Pb, Hg), but it is to be expected that future regulatory monitoring will include more elements (holistic approach) and that the panoramic analysis capabilities of ICP-MS will be further exploited. In this future context, high mass resolution ICP-MS instruments operated under clean room conditions will become the method of choice for regulatory environmental monitoring, as high mass resolution is a universal and powerful approach to overcome spectral interferences in routine applications. In addition, the labor-intensive steps of preparation of calibration standards, dilution of samples and the addition of internal standards can be automated by using an in-line auto-dilution/auto-calibration sample delivery system, which could make this approach well-suited for the demands of a high-throughput environmental laboratory. Furthermore, it significantly lowers the risk of contamination of the sample, standards or blanks, because all these functions are being carried out in-line, with no manual intervention by the analyst.

# CHAPTER 3 ELEMENTAL SPECIATION – DETERMINATION OF OXY-ANIONS IN WATER AND SOLID SAMPLES

## 3.1. PERSPECTIVE ON ELEMENTAL SPECIATION

During the second half of the 20$^{th}$ century, it became evident that trace elements play a major role whenever biological activities, environmental chemistry or material characteristics are discussed and the determination of trace elements has therefore gained outstanding importance in environmental and life sciences. Elements, even when present at very low concentrations in biological and environmental matrices, can exert fundamental influence on ecosystems and the vital functions of organisms (see also Table 1, p.27)[111].

In this context, analytical chemists increasingly realized that, in general, total concentrations of chemical elements cannot give information on mobility, bioavailability and the eventual impact of elements on ecological systems and biological organisms [112].

The chemical nature and quantity of the relevant element species in a matrix, its physical and chemical association, rather than the total element concentration, is highly responsible for the mobility, bioavailability and finally the ecotoxicological or toxicological impact of an element.

Elements usually interact as parts of macromolecules (complexes with humic substances, proteins, enzymes, hormones, *etc*.), low molecular weight metabolites (metal–peptide-complexes, metal-carrying metabolites) or according to their oxidation state. Therefore, only the knowledge on speciation provides sufficient information for adequately assessing whether an element is toxic, without (known) impact at a specific concentration or essential [112].

While the concept of ‘‘elemental fractionation’’ in the sense of distinguishing fractions of the total element concentration according to characterization, *e.g.*, as being ‘‘bioavailable’’, developed slowly around 1960, it was only during the late 1980s, that instrumental elemental analysis reached the detection power necessary to measure small fractions of trace elements - and only sometimes a single species - in environmental and biological samples (see also §1.4.2) [112].

In the past years, speciation analysis matured and many important technical and conceptual developments were published [113]. Separation and detection methods already established were combined in partly novel ways and modified according to the relevant speciation problems. Combination and hyphenation of separation techniques and element-selective or molecule-selective detection systems are now generally established as the basis for speciation analysis. Early approaches used off-line combinations of HPLC and AAS or even voltammetry. Further instrumental progress in speciation analysis was based on direct hyphenation of HPLC, GC or capillary electrophoresis (CE) to plasma-based detectors. Initially, this was realized by coupling to ICP-atomic emission spectrometry (ICP-AES), which in some cases was even completed with on-line hydride generation and UV digestion devices, but soon HPLC was coupled to ICP-mass spectrometry (ICP-MS).

Nowadays, the HPLC/ICP-MS coupling constitutes a widespread, sensitive and versatile speciation instrumentation, also providing multi-element/isotope ratio capabilities. Meanwhile, the use of such systems is well established, even for low species concentrations, *e.g.*, by the use of sector-field ICP-MS, or for oxy-anions like As and Se. Detection of the latter elements is critical when using ICP-MS, as their nuclide(s) suffer(s) from spectral interference. However, with the use of commercially available ICP-MS instruments using dynamic reaction cells (DRC) or collision cells, even this problem can be overcome (see also § 1.4.1). For addressing quantitative speciation approaches, species-unspecific

isotope dilution mass spectrometry (IDMS) was introduced successfully. With the availability of isotopically labelled species, *e.g.*, by in-house synthesis, even species-specific IDMS was becoming possible for reliable species quantification [114].

Together with the instrumental developments, however, the awareness grew that the terms and nomenclature used in the rapidly growing number of speciation papers was inconsistent and that the quality control with respect to accuracy and traceability of numerous published data was insufficient. The harmonization of terms related to speciation by giving clear definitions was elaborated by an expert group under the auspices of IUPAC (International Union of Pure and Applied Chemistry) as follows: *speciation analysis is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample; the chemical species are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure; the speciation of an element is the distribution of an element amongst defined chemical species in a system* [115,142]. Apart from clearly defining speciation terms, they also distinguished chemical speciation analysis from operationally defined procedures, which were not considered as real chemical speciation analysis, as predominantly the identification of the single species is missing.

Another conclusion from the IUPAC expert group was that quality control and quality assurance gained increasing importance in speciation analysis. Today, unequivocal identification of element species is a strong demand, although low species concentration, interfering matrix components, insufficient instrumental selectivity or sensitivity, *etc.* can still easily impede speciation attempts.

Very important for the development of interdisciplinary cooperation between scientists from different fields was a series of workshops organized within the framework of the EU-funded network "*Speciation 21*" during the years 1998-2000 [119]. The "*Speciation 21"* network linked scientists in analytical chemistry, working on the development of methods for the chemical speciation of trace elements, potential users from industry and representatives of legislative agencies, in the field of environment, food and occupational health and hygiene.

Since then and as a next logical step, elemental speciation is now also found under the keyword ''metallomics'' (speciation analysis employed to study metabolic pathways and their probable changes, *e.g.,* in Se metabolism [121]). Nowadays, *orthogonal speciation schemes (e.g.,* ESI-MS and HPLC/ICP-MS) and multi-disciplinary approaches are being used increasingly for (complex) species identification [111].

A multi-disciplinary approach including X-ray absorption near-edge spectroscopy (XANES) was used in this PhD dissertation for the validation of the determination of hexavalent chromium in ambient air (see § 3.3.3). XANES has proven to be well-suited for determining elemental speciation because it can directly and non-destructively analyse particulate matter samples at low concentration levels [136]. X-ray based techniques, such as XANES, are generally regarded as reference methods for solid state speciation since they enable the identification and quantification of chromium oxidation states while being non-destructive. The most employed techniques are (XANES), X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS)[129]. Whereas XPS and XANES will enable quantification of the redox status of , *e.g*., chromium, only the nature of the crystalline phases under which chromium is present can be revealed by XRD. In a XANES experiment, the absorption of X-ray photons by the sample is measured as a function of X-ray energy around and above an absorption edge of an element in the sample. Structural and electronic information can be extracted from the observed fine structure in the absorption spectrum. This fine structure is divided into X-ray Absorption Near Edge Structure (XANES, the fine structure around the absorption edge) and Extended X-ray Absorption Fine Structure (EXAFS, the fine structure above the edge: >50 eV). Analysis of variations in the X-ray absorption coefficient in the XANES and EXAFS spectral regions of the absorption spectrum provides structural information concerning the local environment of the element, in terms of oxidation state,

interatomic distances, and the type and number of coordinating ligands. The primary disadvantages of the XANES direct speciation analysis technique are that the structural information obtained represents a weighted average over the different chemical species of an element probed in the sample and the requirement of a synchrotron X-ray source [68].

In summary, speciation is a modern and current analytical discipline where many questions have to be answered, especially in environmental chemistry and the life sciences [143]. Many analytical techniques have therefore been developed and corresponding applications have been designed during the last 20 years, especially focusing on environmental and biological samples. These efforts often considered 'traditional' elemental species such as methyl mercury, hexavalent chromium, different selenium and arsenic species and also *heavy metals* bound by biomolecules. In the following paragraphs, the scientific papers related to the development of methods based on ICP-MS for the speciation of oxy-anions in an environmental context are introduced with emphasis on the connecting thread of the PhD dissertation, *i.e.,* the relation between the ICP-MS measurement, the environmental issue and the regulatory context. The scientific papers have been arranged chronologically in the following paragraphs (see timeline):

§ 3.2 Removal of selenate and selenite from waste water

K. Tirez, W. Brusten, S. Van Roy, N. De Brucker and L. Diels, Characterization of inorganic selenium species by ion chromatography with ICP-MS detection in microbial-treated industrial waste water, *J. Anal. At. Spectrom*., 2000, **15**, 1087-1092.

§ 3.3 The ban on hexavalent chromium

§ 3.3.1 The ban on hexavalent chromium in packaging material

K. Tirez, W. Brusten, A. Cluyts, J. Patyn and N. De Brucker, Determination of hexavalent chromium by species-specific isotope dilution mass spectrometry and ion chromatography – 1,5 – diphenylcarbazide spectrophotometry*, J. Anal. At. Spectrom*., 2003, **18**, 922-932.

§ 3.3.2 The ban on hexavalent chromium in electronic waste (RoHS and WEEE)

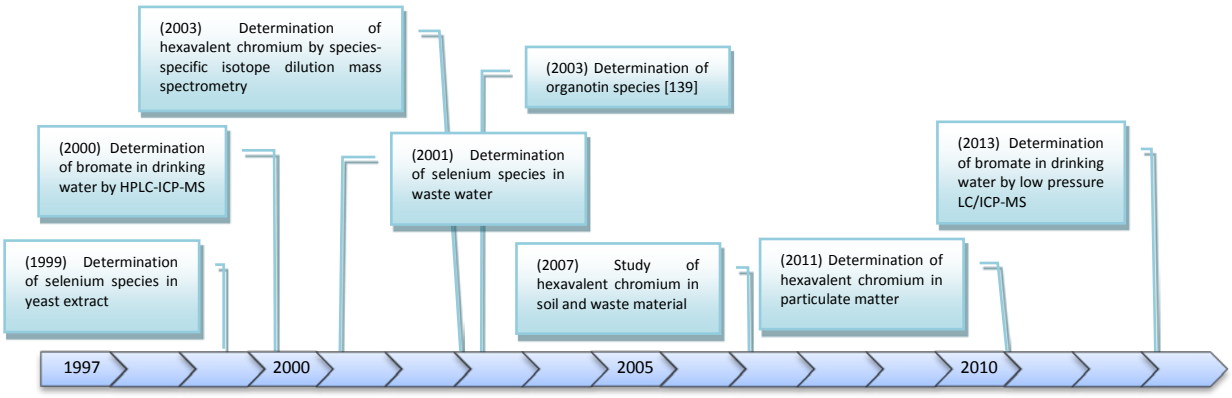
K. Tirez, H. Scharf, D. Calzolari, R. Cleven, M. Kisser, D. Lueck, Validation of a European Standard for the determination of hexavalent chromium in solid waste material, *J. Environ. Monit*., 2007, **9**, 749–759.

§ 3.3.3 Hexavalent chromium in ambient air

K. Tirez, G. Silversmit, N. Bleux, E. Adriaenssens, E. Roekens, K. Servaes, C. Vanhoof, L. Vincze, and P. Berghmans, Determination of hexavalent chromium in ambient air: a story of method-induced Cr(III) oxidation?, *Atmospheric Environment*, 2011, **45**, 5332-5341.

§ 3.4 Oxyhalide by-products in drinking water disinfection

K. Tirez, W. Brusten, M. Wevers, F. Beutels and F. Vanhaecke, Determination of bromate in drinking waters using low pressure liquid chromatography / ICP-MS, *J. Anal. At. Spectrom*., 2013, **28**, 1894 – 1902.




Timeline (1997 – 2013) showing the chronological order of the development of methods based on inductively coupled plasma-mass spectrometry (ICP-MS) for the speciation of metals and oxy-anions in an environmental context.

**Interesting links:**

- **European Virtual Institute for Speciation Analysis (EVISA),** is a service provider in the field of speciation analysis. EVISA's web portal is the primary source for all those seeking information on chemical species with respect to analysis, biological activity (toxicity, nutritional value, metabolism), legislation (laws, rules, standards) and research in related fields. http://www.speciation.net/

### 3.2. REMOVAL OF SELENATE AND SELENITE FROM WASTE WATER

It must be noted that two elements - selenium and arsenic - attracted (and still attract) special attention across all fields of speciation and the number of papers dealing with As- or Se speciation is still increasing rapidly. This is due to the discovery of new species and their structural elucidation, as well as to the detrimental health effects of several As species or the protective health effects of some Se-species.

Selenium plays a major nutritional and biological role in living systems, and speciation analysis of inorganic and organoselenium compounds to define exact biological roles is a major analytical challenge [120]. Selenium is an essential nutrient and has been known to be a necessary component of the human diet for many years (see Table 1, p.27). Selenium is also toxic at levels above the rather narrow optimum range in the human diet; daily consumption of less than 0.1 mg $kg^{-1}$ of body weight will result in selenium deficiency, while levels above 1 mg $kg^{-1}$ are considered toxic . Selenium is of interest as it may offer a protective effect against several degenerative diseases. The organic form of selenium provided by selenium yeast has been shown to differ in bioavailability and metabolism compared with inorganic (*e.g.*, selenate, selenite) forms of dietary selenium. Dietary supplementation with selenium yeast has been used to study the effects of selenium status on the risk of developing cancers or precancerous lesions. The potential beneficial effect of Se in terms of cancer prevention has led to widespread commercial interest in selenium-containing dietary supplements, sold in various chemical forms [120].

In 1999 and within the Speciation 21 Thematic network, an intercomparison exercise for selenium speciation in yeast and arsenic speciation in sea plant (IAEA-140 FUCUS sample) was organised [119]. The participants were encouraged to use different extraction and analytical methods. This was the starting point of the development of methods based on ICP-MS for the speciation of oxy-anions at VITO (Figure 30, selenium speciation in hot water yeast extract).

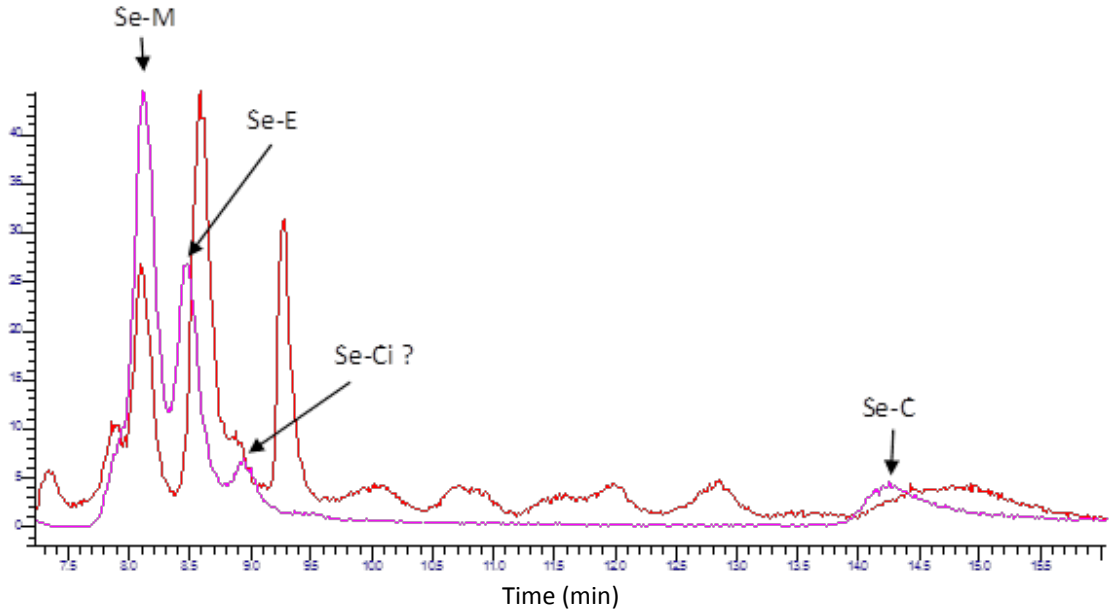



Figure 30: Overlay of a chromatogram of a standard solution (pink) of Se-ethionine (Se-E), Se-methionine (Se-M), selenocystine (Se-C) and selenocysteine (Se-Ci) with a chromatogram of a hot water extract of yeast (red). Samples analysed by quadrupole-based ICP-MS (Elan 6000) equipped with a micro-concentric nebuliser (MCN-100, Model M-2, CETAC; 10 µl sample loop; IC column: IONPAC AS10 microbore, 2 × 250 mm (Dionex); eluent: 100 mM NaOH + 1% EtOH at 200 µl $min^{-1}$.

Besides the beneficial properties of selenium species, selenium introduced to the environment can rapidly bioaccumulate via the food chain, and can be present at significant levels for higher animals. High selenium levels in wildlife exert known toxic effects, including general tissue damage and reproductive failure, as well as teratogenic effects [121]. In nature, selenium is most commonly observed as selenate (+VI), selenite (+IV), or selenide (-II). Though complexed selenium is of low toxicity, selenate and selenite are considered toxic. These two forms of selenium are generally found in water, and display bioaccumulation and bioavailability.

Selenium is often associated with sulphur-containing ores such as pyrite, sphalerite and chalcopyrite [122]. These sulfate/sulphite-containing ores are prevalent in the mining of metals such as copper, nickel, silver, lead and uranium. Consequently, selenium contamination has become an emerging issue in such mining processes. Selenium contamination typically occurs in the aqueous stream, and this stream must be treated prior to discharge.

Removal of oxy-anions such as selenite and selenate from wastewater has been achieved by filtration, chemical treatment and/or biomediated removal [122,123]. The removal of oxy-anions is much more difficult than that of the cations, because anions with a similar structure, such as nitrate, sulphate and phosphate, often co-exist at higher concentrations. Searching effective adsorbents, reagents and/or novel methods for the removal of the oxy-anions represents an important environmental remediation issue.

Recently, in a research project initiated by Essencia (Belgian Federation for Chemistry and Life Sciences industries) and VOKA (Flanders' Chamber of Commerce and Industry), the preventive or remedial actions that companies can take to ensure compliance with the environmental quality parameters for Flemish surface water in terms of the oxy-anions of antimony, boron, molybdenum and selenium were studied [123]. The results of laboratory tests confirmed that selenium is difficult to remove from industrial waste water by physico-chemical actions. Moreover, as the removal efficiency of Se (IV) was shown to be higher than that of Se (VI), knowledge of selenium speciation in waste water is essential to predict removal efficiency and consequently, the feasibility of water purification techniques to ensure compliance with the environmental quality parameters.

The paper presented hereafter describes the development of an HPLC/ICP-MS method for the characterisation of selenium species in support of the development of a biologically based technology for the removal of oxy-anions from heavily contaminated wastewaters (see paper: Characterization of inorganic selenium species by ion chromatography with ICP-MS detection in microbial-treated industrial waste water, J. *Anal. At. Spectrom.*, 2000). The efforts to set up an HPLC/ICP-MS system for the speciation of selenium at that time, were mainly devoted to the automation and a proper communication interface between the sample injection system, the HPLC pump and the ICP-MS instrument.

Nowadays, LC/ICP-MS can truly be considered widespread sensitive and versatile speciation instrumentation (see also § 3.4, where a low pressure LC system was used for the (routine) determination of bromate in drinking water). Recent approaches to determine Se species, specifically at ultratrace levels, have also focussed on a robust and work/time-efficient method by online coupling of a preconcentration (trap) column to an IC-ICP-MS system [124]. Other novel approaches used ICP tandem mass spectrometry (ICP-MS-MS) with $O_2$ reaction/collision gas to completely remove severe interferences with the Se speciation originating from the plasma source and the biological sample matrix [125].

# Characterization of inorganic selenium species by ion chromatography with ICP-MS detection in microbial-treated industrial waste water

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*Journal of Analytical Atomic Spectrometry*, 2000, **15**, 1087-1092.
(Reference list of this paper, see p. 84)

*Abstract*

*Microbial selenium reduction was investigated for application in the removal of selenium from industrial waste water. This paper presents the results of the development of a routine ICP-MS method for the determination of inorganic selenium species in microbial-treated industrial waste water. For the speciation of water soluble inorganic selenium species (selenate and selenite) two different anion exchange columns were compared. The column separation performance for the determination of selenium was investigated for both inorganic and some organic selenium species. The increase in sensitivity for selenium after the addition of carbon-containing solutions was investigated by the addition of increasing amounts of ethanol to the eluent. The optimum addition level of 2% v/v ethanol resulted in a sensitivity enhancement factor of 5 under the given instrumental settings of the ICP-MS. The ICP-MS instrument showed good long-term stability (3% over 40 h), as shown by the analysis of two independent control standards after every 10 samples with addition of arsenobetaine as the internal standard. The different selenium species showed the same signal sensitivity, resulting in a quantification limit of 1 µg/L per species. Over 600 microbial-treated waste water samples were characterized for selenate and selenite content. A selenium compound present in some of the samples could not be identified. No evidence of DL-selenocystine and DL-selenomethionine and DL-selenoethionine could be found. The microbial removal of selenium from industrial waste water was at first hampered by the presence of nitrate (denitrification) and the partial reduction of selenate was observed after the complete removal of selenite to the metallic form.*



## Introduction

Techniques for the removal of dissolved metals from waters are needed for a variety of applications, including mining and several environment-related issues. The requirements are driven by regulatory guidelines for the removal of site-specific pollutants with an overall goal of meeting national surface water standards. Laboratory tests have demonstrated that microbial reduction of metals is a promising technique for the removal of metal contaminants from mining process waters.[1] Various metals can be used as electron acceptors by microorganisms, and are subsequently reduced in the process. The reduced forms of some metals, such as arsenic, chromium and selenium, are less soluble and can be separated from the waste water. A cost-effective, off-the-shelf technology is not available for selenium removal from large-volumes of waste water. The microbial selenium reduction was investigated for application to selenium removal from industrial waste water. This paper concentrates on the development of a method for the determination of the inorganic selenium species in the microbially-treated industrial waste water.

Inorganic selenium is most commonly found in four oxidation states ($Se^{6+}$, $Se^{4+}$, $Se^{0}$ and $Se^{2-}$). Selenate ($SeO_4^{2-}$) and selenite ($SeO_3^{2-}$) are highly water soluble, but elemental selenium ($Se^{0}$) is much less soluble in water. The most reduced form, hydrogen selenide ($H_2Se$) occurs as a toxic gas, but is readily oxidized to elemental selenium in the presence of air. A typical selenium contaminated waste

water contains a mixture of selenate, selenite and elemental selenium. The relative proportions depend on the oxidation.

In the last few years, the development of analytical methods for selenium species determination has considerably increased (D'Ulivo *et al.*[2]). The determination of selenium species by ICP-MS is hampered by (i) the high ionization potential of selenium, the degree of ionization is only 30 % leading to poor sensitivity; and (ii) the several (poly-atomic) interferences on all selenium isotopes.[3] To overcome the poor sensitivity carbon containing solutions can be added. The enhancement effect is dependent on the ionization energy of the analyte and the most pronounced effect is seen on elements such as selenium and arsenic with ionization energies in the range of 9-11 eV.[4]

The use of an anion exchange column gives the opportunity to separate not only the selenium species but also possible interferences. Moreover the use of IC-ICP-MS for the quantitative determination of total selenium in industrial waste water can be a good alternative to circumvent the effect of large amounts of interfering anions as $Cl^-$, $Br^-$, $SO_4^{2-}$ and $PO_4^{3-}$ on the different selenium isotopes. The coupling of a micro-concentric nebuliser, operating at low flow rate, favors chromatographic microbore columns, which have the advantage of good resolving power and small sample amounts.[5] The superior chromatographic detection power of ICP-MS compared to flame atomic absorption spectrometry has also been demonstrated by Pedersen *et al.*[6] for the speciation of four selenium compounds.

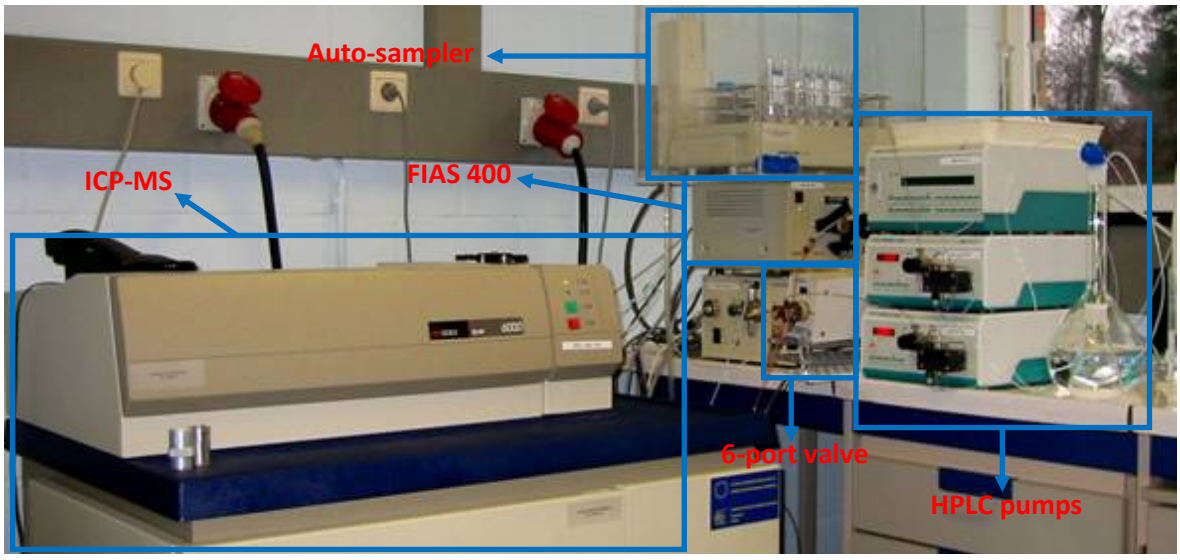
The aim of this study was to examine the speciation performance of two commercial available anion exchange columns, the influence of the addition of ethanol to enhance signal intensity and the effect of interferences on the different selenium isotopes. This should allow us to choose the most suitable isotope to obtain a reliable method for routine analysis.



## Experimental section

### Instrumentation

Samples were analysed on an Elan 6000 ICP-MS system (Perkin-Elmer, SCIEX, Thornhill, ON, Canada) equipped with an MCN-100 micro-concentric nebuliser (Cetac technologies, Omaha, NE, USA) fitted to a scott-type Ryton double-pass spray chamber.




Picture 1: HPLC system coupled to an Elan 6000 ICP-MS system.

During optimization of the instrument settings (Table 1), the MCN-100 was fed by means of a peristaltic pump. The speciation of the redox species was carried out by anion exchange chromatography with an ANX 3206 microbore column (Cetac) and an IONPAC AS 10 column (Dionex, Sunnyvale, CA, USA). Both columns were provided with a guard column to remove dissolved and particulate contaminants from the sample and eluent before they reached the column. The eluent was pushed through the column via a series 10 HPLC pump (Perkin-Elmer). A FIAS 400 (Perkin-Elmer) peristaltic pump provided the filling of a PEEK sample loop. The sample loop was connected to an automated 6-port valve (LabPRO 6, Rheodyne, California, USA). The measurement system, including sample uptake, filling of the loop, injection on the column and ICP-MS measurement is computerized. The integration of the chromatograms was performed with Turbochrom (Perkin-Elmer). Before analysis the instrument was preconditioned by aspirating the eluent for at least 1 hour.

| parameter | Value |
|---|---|
| **instrument settings** | |
| **nebuliser gas flow** | 0.9 ± 0.05 l/min |
| **RF power** | 1200 V |
| **analog stage voltage** | -1950 V |
| **pulse stage voltage** | 1500 V |
| **lens voltage** | 5 ± 1 V |
| **measured peak width** | 0.7 amu |
| **dead time detector** | 40 ns |
| | |
| **measurement settings** | |
| **scan mode** | peak hopping |
| **dwell time** | 30 ms |
| **sweeps / reading** | 5 |
| **readings / replicate** | 1 |
| **replicates** | 1000 |
| | |
| **Isotopes monitored** | $^{76}Se$, $^{77}Se$, $^{78}Se$, $^{82}Se$, $^{35}Cl$, $^{79}Br$, $^{75}As$ |

Table 1: Optimised instrumental measurement settings ICP-MS, Elan 6000.

**Standard solutions and reagents**

For the preparation of all solutions ultra-pure water with a resistivity of 18 MΩ $cm^{-1}$ obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA) was used. Stock standard solutions of 2 µg $ml^{-1}$ were prepared from 100 µg $ml^{-1}$ selenate and selenite standards (Inorganic Ventures, Lakewood, NJ, USA). Calibration standards were diluted from these stock solutions. The concentration level of the standards was 50, 150 and 250 ng $ml^{-1}$ Se(IV) and 50, 250 and 500 ng $ml^{-1}$ Se(VI). The standards were prepared in 100 mM NaOH (*pro analysi*, Merck, Darmstadt, Germany) for the use of the AS-10 column. A 5 mM ammonium malonate (Inorganic Ventures) solution was used as eluent for the separation of selenium species on the ANX 3206 column. DL-Selenocystine, DL-Selenomethionine and DL-Selenoethionine were purchased from Sigma (Bornem, Belgium). Stock standard solutions of 100 µg $ml^{-1}$ of each compound in ultra-pure water were stored in the dark at 4°C. A quality control standard solution of 25 ng $ml^{-1}$ Se(IV) was diluted from a multi-element standard solution of 100 µg $ml^{-1}$ Se (10580 ICP Multi Element Standard VI, Merck). This quality control standard was analysed after every 10 samples. A commercial available 1031 µg $kg^{-1}$ arsenobetaine reference material solution (European Commission, CRM 626) was used as internal standard.[7] The signal enhancement studies were performed with ethanol (*pro analysi*, Merck).

### Sample treatment

The study for the microbial removal of selenium from industrial effluents was performed with four selected bacteria. Two belonged to the genus of Pseudomonads and were isolated from a contaminated industrial site in the UK. Two belonged to the Spinghomonads and were isolated from a soil of the mining region in Likasi in the Republic of Congo. *Pseudomonas fluorescens* J3/73b and J1/15a and *Spinghomonas sp.* AS44 and AS99 were used. Sand columns (10 cm height and 2.5 cm diameter) were inoculated with the mentioned bacteria. After growth of the bacteria in the columns, waste water was circulated through the fixed sand bed. A carbon source, glucose or acetate, was added to the waste water in a final concentration of 0.1%. Samples were taken as a function of time for the determination and characterization of the removed selenium species. The samples were filtered through a 0.45 µm membrane filter (Schleicher&Schuell, Dassel, Germany) to remove suspended solids and micro organisms and then stored in the dark at 4 °C. Prior to measurement the samples were diluted 5-fold and a concentrated solution of the eluent was added to match the appropriate separation conditions.

## Results and discussions

### Interferences

The selenium isotope masses 76, 77, 78 and 82 were chosen for the study, as the abundance of $^{74}Se$ is too small to achieve the required sensitivity (Table 2).[8] Although all monitored selenium isotopes suffer from polyatomic argon interference, only $^{80}Se$ is unmeasurable because of the large $^{40}Ar_2^+$ interference (Table 2). The isobaric interference of krypton (present as trace element in the argon supply) and the argon polyatomic interferences result in an increase of the ICP-MS background signal. This increase depends on the relative abundances of the interfering constituents. The resulting height of the baseline in the chromatograms depends on the given instrumental settings: $^{77}Se$ (70 cps: $^{40}Ar^{36}ArH^+$) < $^{82}Se$ (1500 cps: $^{82}Kr^+$ and $^{40}ArH_2^+$) << $^{78}Se$ (13500 cps: $^{78}Kr^+$ and $^{40}Ar^{38}Ar^+$) < $^{76}Se$ (65500 cps: $^{40}Ar^{36}Ar^+$). Although the baseline levels are stable during measurement, they generate, to a certain extent, a higher noise, resulting in less accurate results for $^{78}Se$ and $^{76}Se$ for low selenium concentrations.

From the point of view of sensitivity, selenium isotope 82 is preferred to isotope 77, because the relative abundance is higher (Table 2), resulting in a 13% gain in signal. When choosing a suitable analytical mass, the possibility of matrix interferences must be considered. In this case however, when performing ion chromatography, these interferences can be circumvented. The chloride ions, which interfere as $^{40}Ar^{37}Cl$ on $^{77}Se$, have a different retention time and do not interfere on the measurement of $^{77}Se$. Considering the background level and the abundance, the selenium isotope 82 was selected for quantitative measurement and the $^{76}Se$, $^{77}Se$ and $^{78}Se$ isotopes for qualitative purposes.

| isotope | natural abundance (ref. 8) (%) | isobaric interference | poly-atomic interference |
|---|---|---|---|
| $^{74}Se$ | 0.89 | $^{74}Ge^+$ | $^{40}Ar^{34}S^+$ |
| $^{76}Se$ | 9.37 | $^{76}Ge^+$ | $^{36}Ar^{40}Ar^+$, $^{38}Ar^{38}Ar^+$, $^{31}P_2{}^{14}N^+$ |
| $^{77}Se$ | 7.63 | - | $^{40}Ar^{37}Cl^+$, $^{40}Ar^{36}ArH^+$ |
| $^{78}Se$ | 23.77 | $^{78}Kr^+$ | $^{38}Ar^{40}Ar^+$, $^{31}P_2{}^{16}O^+$ |
| $^{80}Se$ | 49.61 | $^{80}Kr^+$ | $^{40}Ar_2^+$ |
| $^{82}Se$ | 8.73 | $^{82}Kr^+$ | $^{40}Ar_2H_2^+$, $^{81}BrH^+$, $^{34}S^{16}O_3^+$ |

Table 2: Relative natural abundances and some interferences on selenium isotopes.

**AS-10 column versus ANX 3206 column**

Initially the ANX 3206 column was used for the determination of the inorganic selenium species. The specifications for the eluent concentrations provided by the manufacturers for optimal separation of selenate and selenite were applied. The optimisation study included different flow rates (100, 200, 300 ml $min^{-1}$) and sample loop volumes (10, 25, 50 ml). The analysis of the actual industrial waste water led to the following observations: the samples contained large amounts of chloride and bromide ions; and, in some treated waste waters, an unknown selenium peak appeared in front of the selenite (Fig. 1).

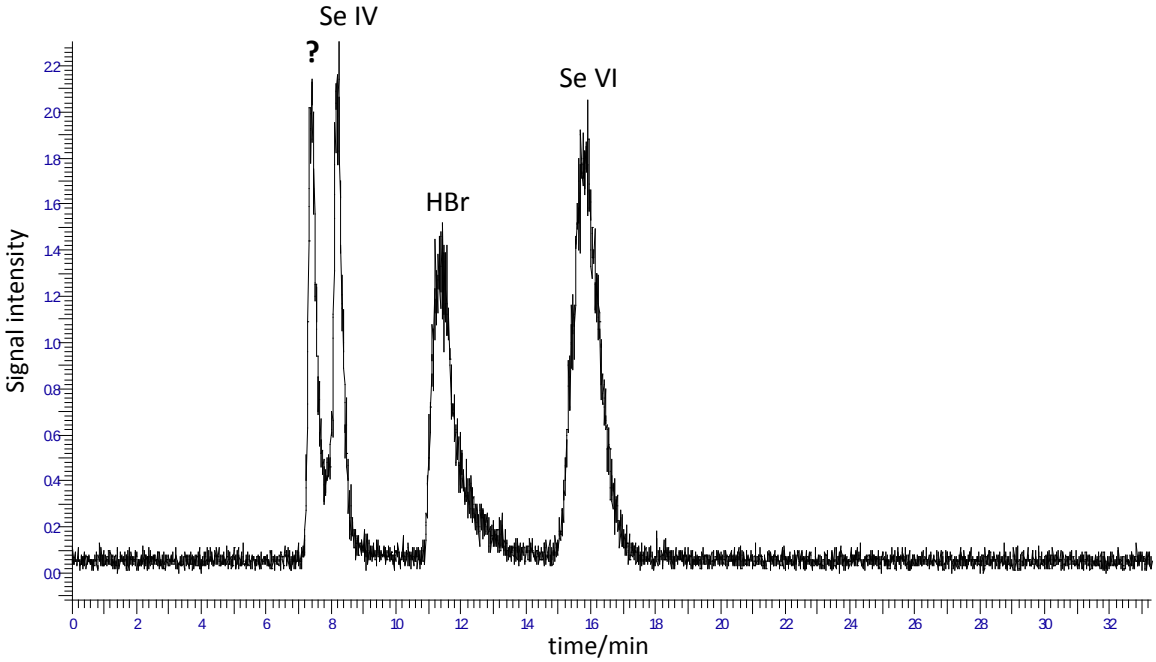



Fig.1 Microbial treated industrial waste water analysed with ANX 3206 column, eluent 5 mM ammonium malonate, flow rate of 200 µl $min^{-1}$, monitored isotope $^{82}Se$.

A sample loop volume of 10 ml combined with a flow rate of 200 ml $min^{-1}$ gave optimal separation of the selenium species and interfering chlorides and bromides. The long term stability of the ICP-MS measurement on the quality control standard of 25 ng $ml^{-1}$ Se(IV) in 5 mM ammonium malonate was 2% (12 h, n=5). The unknown peak could be identified as selenium after comparison of the signal of the four different selenium isotopes.

In an attempt to identify this unknown selenium species, standard solutions of DL-selenocystine, DL-selenomethionine and DL-selenoethionine were analysed. Due to a minor resolution of the organic selenium components, the comparison of retention times of these organic selenium components with the unknown selenium species in the chromatogram were ambiguous. In order to identify the unknown peak, the AS-10 column was tested. The same optimization criteria were examined (flow rate of 200 ml $min^{-1}$; 10 ml loop), leading to a better resolution of the selenium species (Fig. 2).

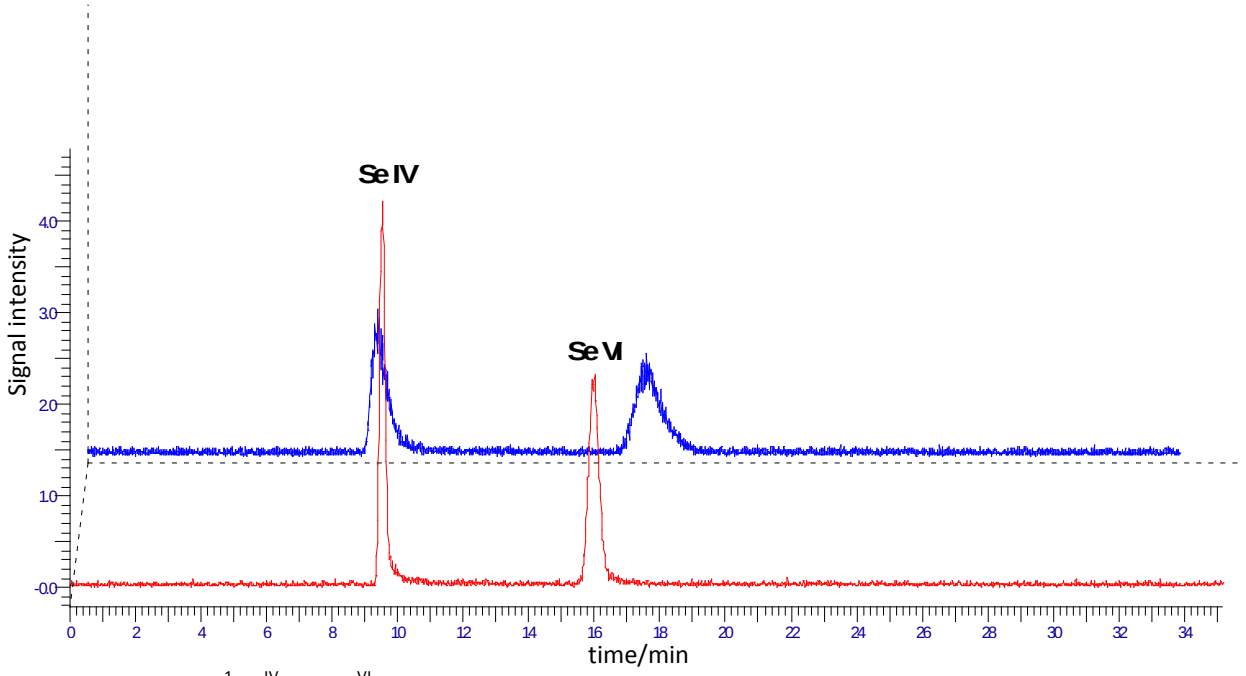



Fig. 2: 50 ng ml$^{-1}$ $Se^{IV}$ and $Se^{VI}$ measured on ANX 3206 (upper), eluent 5 mM ammonium malonate, flow rate 200 µl min$^{-1}$; measured on AS-10 (lower), eluent 100 mM NaOH + 1 % EtOH, flow rate 200 µl min$^{-1}$.



Successive spiking of the industrial waste water with DL-selenocystine, DL-selenomethionine and DL-selenoethionine did not help to positively identify the unknown selenium species. No evidence of DL-selenoethionine was expected, since it does not occur naturally. Most frequently, reduced selenium is bound to amino acids and released when the cell dies.[9,10] Also methylation reactions were mentioned by Altringer *et al.*[11] In a study on the aquatic chemistry of selenium by Cooke *et al.*[12] in surface waters, six dissolved selenium species were identified: selenate and selenite, non-volatile organic selenides (selenoamino acids and dimethylselenonium ion) and the volatile methylated forms dimethyl selenide and dimethyl diselenide. As equal sensitivity was observed for the organic and inorganic selenium species, the concentration of the unidentified selenium species could be determined and amounted to a maximum of 20% of the total selenium content. On the basis of the better performance characteristics, the AS-10 column was used for further investigations.

**Signal enhancement**

Several studies have demonstrated the signal enhancing effect of the addition of carbon to the solution to be analysed, or in the analysis of carbon containing solutions such as wine and port.[3,4,13] The addition of organic compounds modifies the ionisation equilibrium in the plasma. Different mechanisms for this signal enhancement have been proposed.[3] The most pronounced effect is seen, as stated earlier, on elements such as selenium and arsenic with ionization energies in the range of 9±11 eV.

An overview and study of different carbon-containing solutions is presented by Gammelgaard *et al.*[4] In our study ethanol was used as the enhancement solution. It has been shown that optimum RF power and nebuliser gas flow depend on the content of ethanol in the solution. Initially the ICP-MS instrument settings were optimised with a 200 ng ml$^{-1}$ Se (100 mM NaOH, 2% v/v ethanol) solution and were kept constant during the experiments. Several samples of 200 ng ml$^{-1}$ Se solutions in 100 mM NaOH with increasing amounts of ethanol (0.5±5% v/v) were analysed and the net results (corrected for background contribution) are shown in Fig. 3 for three different isotope masses. In order to stabilize the signal, the measurement was performed after aspiration of the solution for approximately 10 min. A continuous decrease (20%) of the signal of the 5% v/v ethanol solution

during the aspiration period was observed. To eliminate memory effects of the ethanol addition, rinsing of the system for 60 min was needed to reach the basic level. As can be seen in Fig. 3 an enhancement factor of 5 was achieved in 2% v/v ethanol, which is in agreement with literature data.[3]

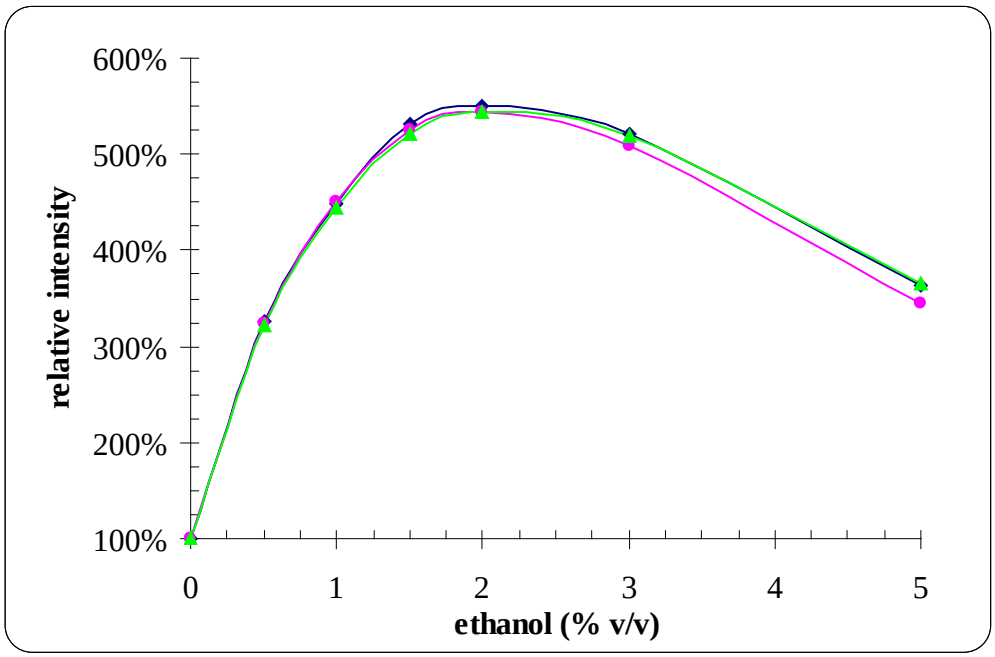



Fig. 3: Net relative intensities of 200 ng ml$^{-1}$ Se 100 mM NaOH solutions in increasing amounts of ethanol (lines represent $^{78}$Se, $^{77}$Se and $^{82}$Se).

**Analytical characteristics**

Internal standardisation is used to correct for signal drift, instrument instability, signal suppression or signal enhancement caused by the matrix. In previous studies the similarity in mass of the internal standard and the element of interest was a major point of concern for a good correction. The use of an enhancement reagent assumes an internal standard with a first ionization energy close to that of selenium. Because speciation studies are performed, one can choose a stable selenium compound not present in the sample under investigation, *e.g.*, DL-selenomethionine, to act as an internal standard for the other selenium compounds. A possible cause of error is that the component can degrade to a selenium compound of interest during the measurement run. To counteract the possible degradation of the internal standard and the consequent formation of selenium compounds of interest, the use of a stable organic arsenic compound, *e.g.*, arsenobetaine, can be considered. No evidence of arsenobetaine (nor DL-selenomethionine) is expected in the treated industrial waste water. Arsenic is close to selenium regarding its mass and ionization energy and may therefore be used as an internal standard. Arsenic is mono-isotopic resulting in high sensitivity and it has been demonstrated that arsenobetaine is a stable compound.[7] Therefore 100 ng ml$^{-1}$ arsenobetaine (CRM 626) was added to every analysed sample to correct for signal instability. After filtration of the microbial-treated waste water to remove microorganisms, the sample was diluted in 100 mM NaOH just before measurement and the internal standard was added. For a typical routine measurement run, including calibration standards, quality control solutions and waste water, the integrated peak areas of the internal standard in each sample are shown in Fig. 4.

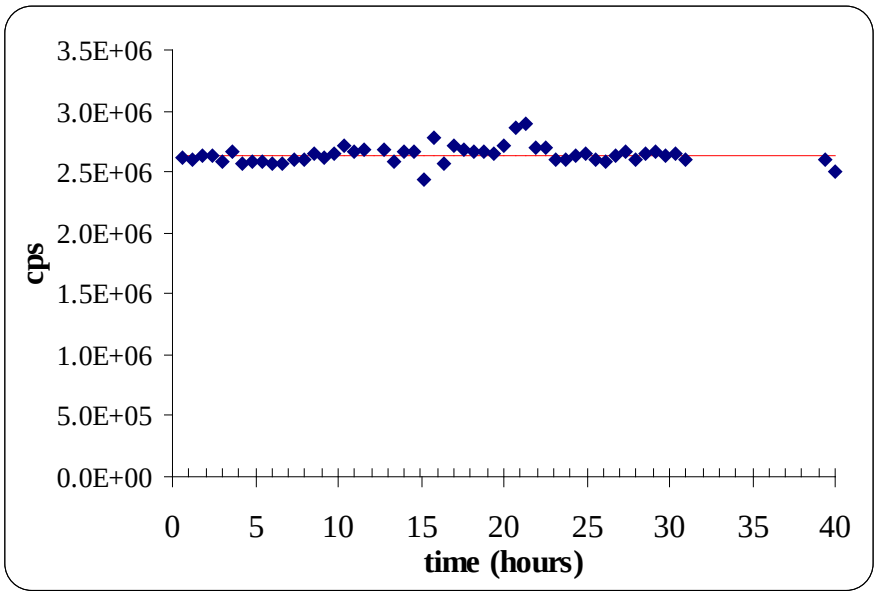



Fig. 4: Integrated peak areas of the arsenobetaine internal standard (100 ng ml$^{-1}$ CRM 626) on 54 consecutive IC-ICP-MS determinations measured over a period of 40 hours (relative standard deviation 2.8 %).



The IC-ICP-MS results showed good long term stability; a relative standard deviation of 2.8% is calculated for 54 consecutive measurements over a period of 40 h. The repeatability of the quality control standards over the same period, after internal standard correction, amounted to 25.2 ± 0.4 ng ml$^{-1}$ Se(IV) (n=6) and 506.8 ± 6.8 ng ml$^{-1}$ Se(VI) (n=6). An overview of the simultaneous monitored isotopes is given in Fig. 5.

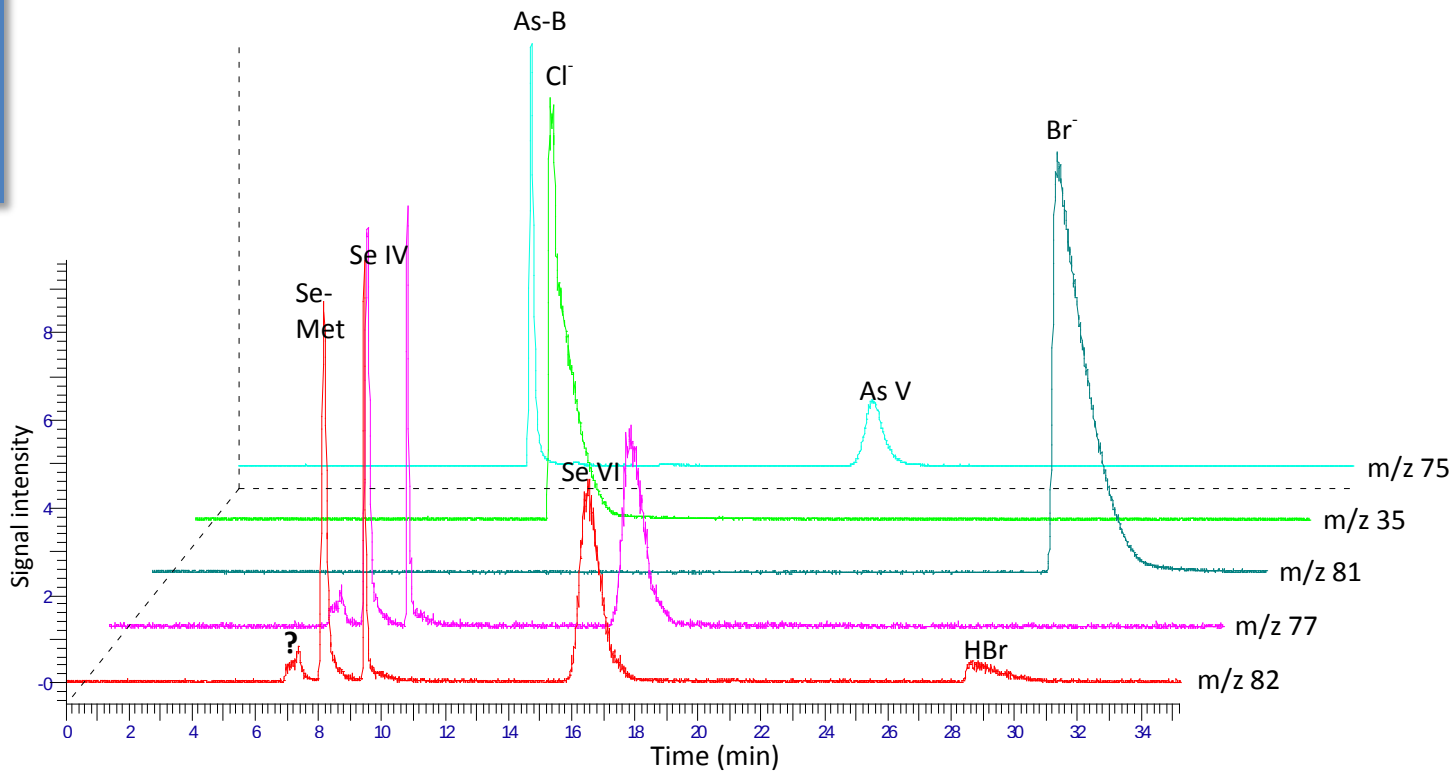



Fig. 5: Industrial treated waste water spiked with 100 ng ml$^{-1}$ Se DL-Selenomethionine (Se-Met) and 100 ng ml$^{-1}$ arsenobetaine (As-B) analysed with AS-10 column, eluent 100 mM NaOH + 2% v/v EtOH, flow rate 200 µl min$^{-1}$, 10 µl sample loop. The unidentified selenium species is marked with a (?).

It can be seen that the interfering chlorides and bromides are well separated from the analytical species of interest. A limit of quantification (10σ) of 1 ng $ml^{-1}$ Se was calculated based on the standard deviation of 5 replicates of a 2 ng $ml^{-1}$ Se(IV) solution. In the same run a limit of quantification (10σ) of 0.3 ng $ml^{-1}$ As was calculated based on the standard deviation of 5 replicates of a 2 ng $ml^{-1}$ As(V) solution. The detection limits for the selenium species are in agreement with the HPLC-ICP-MS results reported by Pedersen *et al*.[6] using 3% methanol as enhancement reagent.

**Stability**

For accurate determination of selenium species, major concerns are the sampling, storage and sample pretreatment. At all these stages, volatilization, adsorption, desorption, contamination and interconversion of species, *etc*. may occur. Extensive stability studies of selenium species in a variety of matrices have been reviewed.[1,14] In pure aqueous solution at -20°C without acidification, no variation of selenate and selenite was observed over 12 months. At room temperature the maximum time of sample storage was found to be between 2 and 9 months depending on the material of the container. It was also noticed that chlorides tend to stabilise both species. A seawater reference material certified for selenite was stable over 5 years if stored in a cool place. A ground water containing selenium was stable for up to 13 months stored at 4 °C in a polyethylene container and the stability of selenium compounds in purified samples followed the order selenate>selenomethionine>selenite.[1] In other studies, however, losses of selenium and a conversion of selenite to selenate after four weeks was observed in groundwater samples stored in polyethylene at 4 °C.[14] Long-term stability studies of organic selenium species in aqueous solutions by Olivas *et al.*[15] showed that the best results were obtained with Pyrex containers stored at 4 °C in the dark. No significant losses of selenocystine and selenomethionine were observed over one year. Rapid losses of trimethylselenonium, however, were observed under any conditions.

In this study the industrial waste waters were filtered through a 0.45 µm membrane filter to remove suspended solids and micro organisms, and stored in Pyrex containers in the dark at 4 °C. Prior to measurement the samples and calibration solutions were diluted 5-fold in 100 mM NaOH. No conversion of selenite, DL-selenomethionine and DL-selenoethionine was observed over a period of 12 months. The selenate stock solution showed a 2% conversion to selenite after a period of 6 months. In the chromatogram of freshly prepared DL-selenocystine in 100 mM NaOH two peaks were observed.

The smallest peak was expected to be selenocysteine, the reduced form of selenocystine. Similar observation in stock standard solutions of selenocystine has been reported by Emteborg *et al.*[16] Since the retention time did not overlap with the unidentified selenium species in the industrial waste water no further investigations were performed (*e.g.*, reduction of DL-selenocystine with mercaptoethanol as described by Burnell *et al.*[17]).

**Microbial selenium removal**

As this paper concentrated mainly on the development of a routine IC-ICP-MS method, the results of microbial selenium removal are briefly summarised. For an extensive review of the over 600 analysed waste water samples we refer to the synthesis report of the coordinating Brite-Euram project.[18] It was observed that selenate and selenite are in competition with nitrate (denitrification) as the electron acceptor. The industrial waste water contained nitrate at nitrogen concentrations between 10 and 50 mg $ml^{-1}$, hampering the selenium reduction. The bacteria could reduce the effluent selenium concentration to concentrations below 1 mg $ml^{-1}$. The reduction of selenate is observed after complete removal of selenite. The reduction of selenate to the metallic form was the most time-consuming step in the removal of selenium from industrial waste water but was never complete. The selenium removal by *Pseudomonas fluorescens* J3/73b from a non-ferrous waste

water is shown in Fig. 6. The selenium concentration was reduced from 2.6 mg $ml^{-1}$ to 0.5 mg $ml^{-1}$. Selenite is completely reduced in contrast to selenate. Experiments showed optimal reduction of selenium under anoxic conditions with glucose as the carbon source.

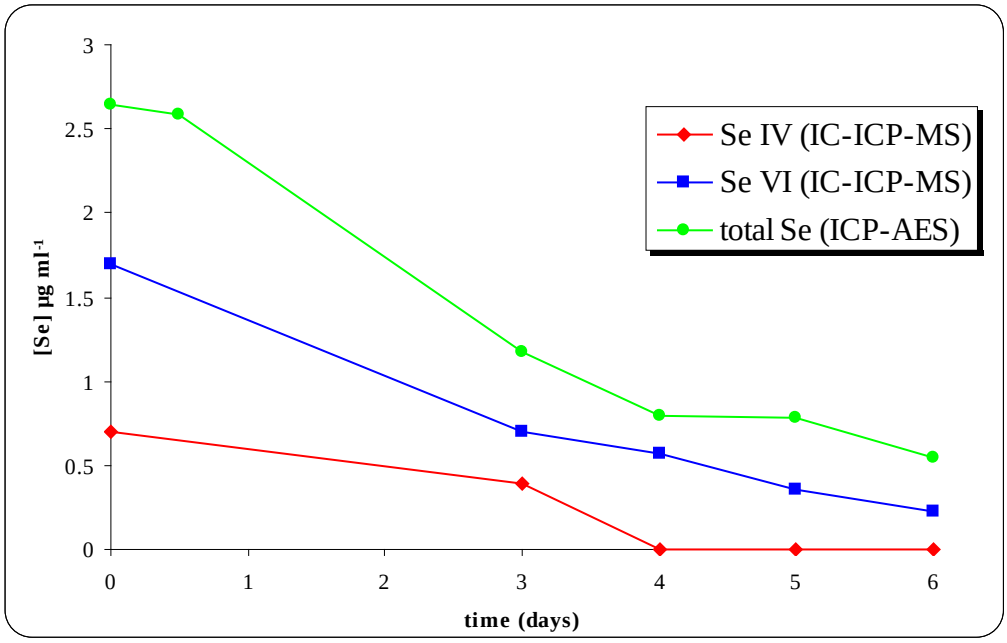



Fig. 6: Microbial selenium removal by *Pseudomonas fluorescens* J3/73b in a non-ferrous industrial waste water.

## Conclusion

A robust routine IC-ICP-MS method for the determination of selenate and selenite and some organic selenium species is presented. To correct for signal drift, instrument instability and signal enhancement caused by the addition of 2% v/v ethanol to the eluent, an arsenobetaine solution is used successfully as the internal standard for the analysis of industrial waste water. The addition of ethanol results in a selenium signal enhancement factor of 5 and a quantification limit of 1 ng $ml^{-1}$ Se. The reduction of selenate to the metallic form is the most time-consuming step in the removal of selenium from industrial waste water. The microbial removal of selenite is, in contrast to selenate, complete.

**Acknowledgements**
We wish to thank Magnus Johansson (IRMM, Geel, Belgium) for aid in the instrumental setup and discussions on the subject, Valère Corthouts (VITO) for the development of an uncloggable MCN and Jos Broeckx (VITO) for total selenium determinations using ICP-AES. Furthermore we would like to thank Dirk Mestach (Nijlen Correct Translating Agency) for a critical review.
This work was supported by the Brite-Euram programme of the European Commission in the project (BE96-3584) ``Development and assessment of biotechnological methods for the removal of metal anions from waste water (BIROX)''.

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### 3.3. THE BAN ON HEXAVALENT CHROMIUM

Chromium has been used extensively in the chemical industry in applications such as metal plating, leather tanning, pigment or anti-corrosion coatings [126]. Chromium production processes, as well as its different uses, are responsible for the release of chromium compounds into the environment (soil, surface and ground waters).

Chromium can exist in numerous chemical forms with oxidation states ranging from 0 to VI, the trivalent and hexavalent forms being more likely to occur in the environment due to their higher stability. An Eh-pH diagram of the Cr-O-H system, depicting the dominant aqueous species and stable solid phases, is represented in Figure 31 [127]. When assessing the potential toxicity of chromium, the concept of speciation must be emphasized: Cr(III) is considered as an essential micronutrient in the human diet and is used as a nutritional supplement for humans and animals (see also Table 1, p.27). In contrast, Cr(VI) is highly toxic in case of both acute and chronic exposure and its compounds are regulated through the Dangerous Substances Directive and classified as human carcinogens by the United States Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC).

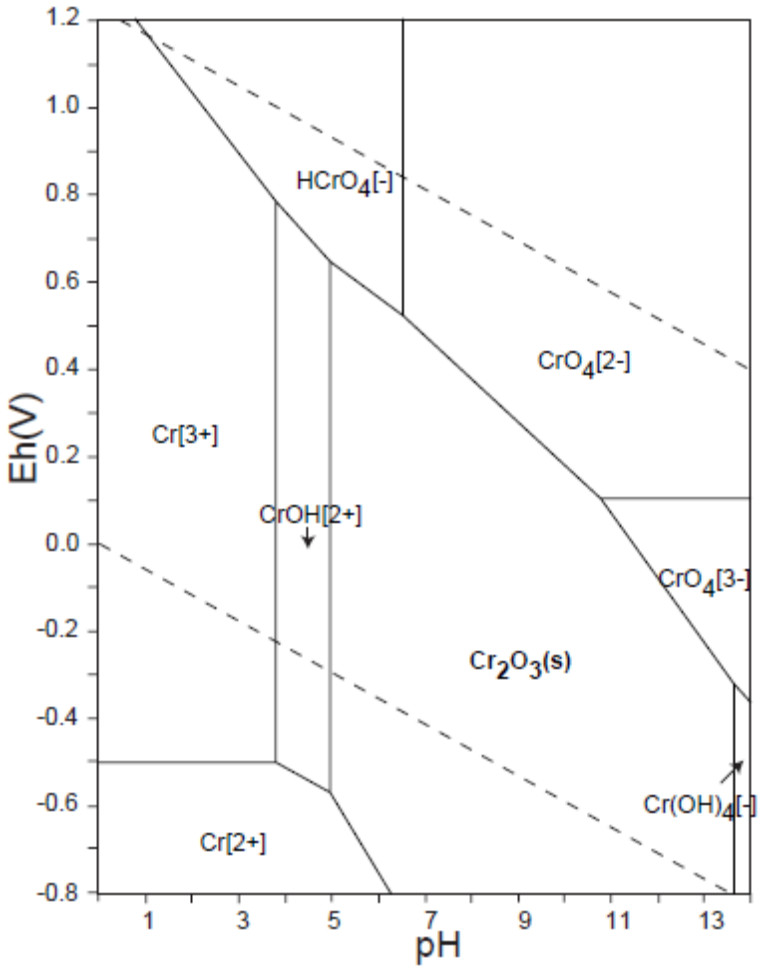


Figure 31: $E_h$-pH diagram of the system Cr-O-H ($\Sigma$ [Cr] = $10^{-10}$, 298.15 K, $10^5$ Pa)(figure courtesy of [127]).

The difference in toxicological properties between Cr(III) and Cr(VI) compounds is closely related to the chemical characteristics of the species, which also influence the stability, mobility, and bioavailability of these species in the environment. Several recent regulations have incorporated the

speciation of elements in restrictions imposed on environmental quality (workplace air) and on products (cement, packaging, toys and anti-corrosion coatings).

Analytical techniques that allow the distinction between and quantification of Cr(III) and Cr(VI) species are necessary for successful implementation of such regulations. The major challenge encountered by these techniques is to avoid any change of chromium speciation during the analysis. When wet-chemistry analytical methods are to be used on solid samples (*e.g.*, soils, waste, etc.), an extraction step has to be performed. This step can lead to difficulties with regards to the yield of extraction, meaning the result would be underestimated in case of incomplete extraction. In the following paragraphs, studies related to the determination of Cr(VI) on solid samples are summarised in chronological order.

### 3.3.1. THE BAN ON HEXAVALENT CHROMIUM IN PACKAGING MATERIAL

In 2001, VITO was commissioned by the Belgian Federal Public Service of Health, Food chain safety and Environment to review the most critical types of packaging on the Belgian market with respect to the concentration levels of lead, cadmium, mercury and hexavalent chromium. According to EU directive 94/62/EC on Packaging and Packaging waste, member states shall ensure that the sum of these four elements shall not exceed 100 mg $kg^{-1}$.

In the qualitative and quantitative market analysis performed by VITO, some 200 packaging materials were screened with X-ray fluorescence for total metal content [132]. A selection of 40 critical packaging materials (total chromium content higher than 100 mg $kg^{-1}$) were further analysed for Cr(VI) content. The materials analysed were, among others, glass packaging, plastic packaging, wrapping papers and metal packaging.

Different extracting solutions have been used for the extraction of Cr(VI) form solid materials. The method yielding the best results relied on a combination of $Na_2CO_3$ and NaOH with continuous swirling and heating at 95°C. This approach was promoted in 1996 by the US EPA with the reference US EPA Method 3060A and was adopted as basis of the European standard EN 15192:2006 as well (see further, §3.3.2).

Once the Cr(VI) is extracted, different quantification methods are available. For the purpose of screening critical types of packaging on the Belgian market, two different methods for the determination of Cr(VI) were implemented at VITO. The first method consisted of an ion chromatography-1,5-diphenylcarbazide spectrophotometry method, in which Cr(VI) in solution oxidizes 1,5-diphenylcarbazide to give a red/violet complex with chromium, which can be quantified photometrically at 540 nm. The second and most accurate one is performed using high-performance liquid chromatography coupled to inductively coupled plasma-mass spectrometry (HPLC/ICP-MS) and involves isotopic spiking of the sample to enable the correction of species interconversion taking place during preparation and analysis steps [141] (see paper: Determination of hexavalent chromium by species-specific isotope dilution mass spectrometry and ion chromatography-1,5-diphenylcarbazide spectrophotometry, *J. Anal. At. Spectrom.,* 2003).

# Determination of hexavalent chromium by species-specific isotope dilution mass spectrometry and ion chromatography-1,5-diphenylcarbazide spectrophotometry

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*Journal of Analytical Atomic Spectrometry*, 2003, **18**, 922-932.
(Reference list of this paper, see p. 106)

*Abstract*

*The accuracy of the determination of hexavalent chromium ($Cr^{6+}$) in solid matrices remains a challenging field of effort and improvement. An alkaline digestion (0.5 M NaOH / 0.28 M $Na_2CO_3$) followed by ion chromatography and spectrophotometrical determination by post column derivatisation with 1,5-diphenylcarbazide (DPC) provides accurate and reproducible results. To gain a better insight into the species interconversion during the digestion the concept of species-specific isotope dilution mass spectrometry by adding enriched chromium isotopes that have been chemically converted into trivalent ($Cr^{3+}$) and hexavalent chromium was used. For the analysis of the digestion solutions ion chromatography coupled to inductively coupled plasma – mass spectrometry (IC-ICP-MS) was peformed. The limit of detection in the digestion solution by the latest technique amounted 0.8 ng $ml^{-1}$ $Cr^{6+}$ .The accuracy of an alkaline digestion on solid waste materials was compared with a water extraction (leaching test industrial waste), indicating that the alkaline digestion is accurate from point of view of minimal species interconversion on the one hand and maximum amount $Cr^{6+}$ extracted on the other, while significant oxidation and reduction reactions were observed during leaching tests with water. In the frame of European Directive 94/62/EC on Packaging and Packaging waste, the developed analytical method has been successfully used to compare the concentrations of $Cr^{6+}$ on 40 packaging materials against the regulatory limit value of 100 mg/kg by weight (sum of concentration levels of lead, cadmium, mercury and hexavalent chromium).*



## Introduction

An accurate and precise method for extracting and analyzing hexavalent chromium ($Cr^{6+}$) in soils, sediments, waste materials and airborne particulates is needed because of human, ecological and legal concerns related to $Cr^{6+}$ in the environment [1]. $Cr^{6+}$ compounds are known to be toxic and carcinogenic agents for a variety of organisms. They are mobile in soil/water systems, much more than trivalent chromium ($Cr^{3+}$) compounds, because $Cr^{6+}$ compounds are strong oxidizers and highly soluble as anionic forms, while $Cr^{3+}$ compounds tend to form relatively inert precipitates near neutral pH [2].

The distribution of $Cr^{6+}$ and $Cr^{3+}$ strongly depends on pH and potential. According to the $E_h$-pH phase diagram, $Cr^{6+}$ is thermodynamically stable at relatively higher pH and $E_h$, while $Cr^{3+}$ is stable at relatively low pH and $E_h$ [3]. Kinetics also play an important role in the interconversion between $Cr^{6+}$ and $Cr^{3+}$ [4].

From the literature published in the last years it can be concluded that there is a good number of procedures including different analytical techniques for the speciation of $Cr^{6+}$ and $Cr^{3+}$ in solution [5-12]. When it comes to chromium speciation in solid matrices, accuracy of the methods remains a

field of additional effort and improvement. A review on analytical methodologies for chromium speciation in solid matrices by *Marques et al*. emphasis the lack of reported recovery by most authors [2]. Possible analytical biases in the analysis of $Cr^{6+}$ in soil samples using an alkaline digestion solution (US EPA 3060A) have been described [1,4,13]. The results indicated that the digestion (US EPA 3060A) combined with a spectrophotometric detection method (US EPA 7196A) provided satisfactory performance in quantifying the amount of total $Cr^{6+}$ [14]. The authors stressed the necessity however to characterise ancillary parameters, such as oxidation reduction potential (ORP), pH, TOC, $Fe^{2+}$ and $S^{2-}$ to make an affirmative determination regarding the capacity of the sample to contain $Cr^{6+}$. Reducing conditions, as defined by the Cr $E_h$-pH phase diagram, the presence of TOC, $S^{2-}$ or $Fe^{2+}$, or acidic conditions, singularly or in combination, indicate the potential for a sample to (i) reduce a laboratory $Cr^{6+}$ spike or (ii) not sustain the existence of $Cr^{6+}$ in the sample's native environment [15,16]. The results also showed that both water soluble ($K_2CrO_4$) and insoluble ($BaCrO_4$, $PbCrO_4$) forms of $Cr^{6+}$ can be used to obtain satisfactory matrix spike recovery results. Furthermore method-induced oxidation only occurs with freshly precipitated $Cr(OH)_3$, which is not likely to be present in environmental samples. Aged $Cr(OH)_3$ as well as $Cr_2O_3$ do not oxidize when subjected to method US EPA 3060A [1]. This viewpoint of analytical biases in the analysis of $Cr^{6+}$ in soil samples is subscribed by *Huo et al*. as well [4]. The author compared speciated isotope dilution mass spectrometry (SIDMS) with a diphenylcarbazide spectrophotometric method for the determination of $Cr^{6+}$ in soil and indicated possible biases during digestion and the possibility to mathematically correct for species transformation. The principle of SIDMS has been demonstrated in the patent and literature [10,17].

SIDMS uses the concept of spiking the sample with known amounts of enriched isotopes that have been chemically converted into the same forms of the species to be analysed. The isotopic spike for each species has a unique isotope enrichment. In the case of chromium, two isotopic spikes, $^{53}Cr^{6+}$ enriched in $^{53}Cr$ and $^{50}Cr^{3+}$ enriched in $^{50}Cr$, are prepared for the simultaneous determination of $Cr^{3+}$ and $Cr^{6+}$. Environmental samples containing Cr species are spiked with both $^{53}Cr^{6+}$ and $^{50}Cr^{3+}$. The species are separated at the end of the manipulation by means of chromatography and different isotope ratios are measured. In contrast to "classic" chromatography, which is a snapshot in time recording the state of affairs at the end of the manipulation, any interconversions that occur after spiking are traceable by SIDMS and can be quantitatively corrected by monitoring isotopes in each species. The determination of chromium by inductively coupled plasma-mass spectrometry (ICP-MS) in environmental samples is hampered by polyatomic interferences [12,18]. The combination of elements that can give rise to interference at the analytical masses of Cr (*i.e.*, 50, 52, 53, 54) are Ar, C, Ca, Cl, K, O and S, in other words, those normally present in environmental matrices as well as the plasma gas and in the reagents used for digestion. The use of ion chromatography when coupled to an ICP-MS results, besides the speciation of the chromium species, in an opportunity to separate possible interferences from the isotopes of interest.

However for so far, and as stressed by the authors of the SIDMS method, the monitoring and correction for the oxidation of $Cr^{3+}$ during the preparatory alkaline digestion was under investigation. In contrast to solutions where the $Cr^{3+}$ and $Cr^{6+}$ content and consequently the interconversion of species can be determined via SIDMS, the preliminary alkaline digestion of the solid sample followed by filtration makes a reproducible recovery of the $Cr^{3+}$ spike almost impossible. The alkaline digestion at pH 12, used to stabilize the original $Cr^{6+}$ in the sample, makes the $Cr^{3+}$ spike to precipitate. Although acidifying the filtrate afterwards would thermodynamically resolve the added $Cr^{3+}$ spike, this is due to the slow kinetic properties of $Cr^{3+}$ on the one hand and the instability of $Cr^{6+}$, the element of concern, under these conditions a tricky task [19]. This statement was confirmed in preliminary experiments performed in our lab, where the enriched spike solutions $^{50}Cr^{3+}$ was added to the digestion mixture (pH 12) and could not be recovered as soluble chromium species even after acidification and gentle heating. Coedo *et al.* reported however a speciation of chromium in steelmaking solid wastes, where after the alkaline digestion soluble $Cr^{3+}$ compounds present as the

negatively charged $Cr(OH)_4^-$ could be determined [20]. The authors present a method to differentiate $Cr^{6+}$, soluble $Cr^{3+}$ as the negatively charged $Cr(OH)_4^-$ complex and insoluble $Cr^{3+}$ (coming from $Cr_2O_3$ and Cr metal). For the determination of the latter a fusion was performed. In none of the analysed samples however soluble $Cr^{3+}$ as the negatively charged $Cr(OH)_4^-$ complex was found.

The interconversion of species can not be determined via SIDMS in soils as the $Cr^{3+}$ present may be chemically different from the added spike. As mentioned previously, $Cr_2O_3$ and aged $Cr(OH)_3$ precipitate are resistant to oxidation, free $Cr^{3+}$ and freshly precipitated $Cr(OH)_3$ are relatively easy to oxidize. Although the fresh $Cr(OH)_3$ precipitate is not a representative form of $Cr^{3+}$ in environmental samples, the possibility of biases caused by oxidised $Cr^{3+}$ can not be excluded [4].

A review of different digestion methods from soil is given by James *et al.* [21]. There is at this time a consensus on the use of an alkaline digestion solution to achieve minimal species interconversion and maximum extraction efficiency of hexavalent chromium on solid materials (see also §3.3.2).
Due to the impossibility to measure $Cr^{3+}$ in the alkaline digestion solution the existing calculations for speciated isotope dilution mass spectrometry on liquid solutions had to be modified in a way that maximum information can still be obtained from the spiking of both chromium species. A method of calculation is presented in this paper indicating if conversion from $Cr^{6+}$ to $Cr^{3+}$ or $Cr^{3+}$ to $Cr^{6+}$ was likely to occure during the digestion.

The determination of hexavalent chromium is required in legislation of some member states of the European Union concerning acceptance criteria for industrial waste on landfill and regulatory values in packaging material. In this paper results are shown of the application of this analytical method of species-specific isotope dilution mass spectrometry is these two European legislation related topics.



## Method of calculation

Due to the impossibility to measure $Cr^{3+}$ in an alkaline solution, the existing calculations for speciated isotope dilution mass spectrometry as presented in the US EPA 6800 method and U.S patent 5,414,259 [17,22] had to be modified in a way that maximum information can still be obtained from the spiking of both chromium species. In these two references is demonstrated that the concentration of the different species as well as the interconversion can be deconvoluted from the following equations:

$$R^{III}_{50/52} = \frac{\left({}^{50}A_x C_x^{III} W_x + {}^{50}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}$$

$$R^{III}_{53/52} = \frac{\left({}^{53}A_x C_x^{III} W_x + {}^{53}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}$$

$$R^{VI}_{50/52} = \frac{\left({}^{50}A_x C_x^{III} W_x + {}^{50}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s^{VI} C_s^{VI} W_s^{VI}\right)(1-\beta)}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)(1-\beta)}$$

$$R^{VI}_{53/52} = \frac{\left({}^{53}A_x C_x^{III} W_x + {}^{53}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s^{VI} C_s^{VI} W_s^{VI}\right)(1-\beta)}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)(1-\beta)}$$

where,

$R^{III}_{50/52}$ is the mass bias corrected measured isotope ratio of $^{50}Cr$ to $^{52}Cr$ of $Cr^{3+}$ in the spiked sample

$^{50}A_x$ is the atomic fraction of $^{50}Cr$ in the sample

$C^{III}_x$ is the concentration of $Cr^{3+}$ in the sample (µmole/g, unknown)

$^{50}A^{III}_s$ is the atomic fraction of $^{50}Cr$ in the $^{50}Cr^{3+}$ spike

$C^{III}_s$ is the concentration of $Cr^{3+}$ in the $^{50}Cr^{3+}$ spike (µmole/g)

$C^{VI}_s$ is the concentration of $Cr^{6+}$ in the $^{53}Cr^{6+}$ spike (µmole/g)

$W^{III}_s$ is the weight of the $^{50}Cr^{3+}$ spike (g)

$C^{VI}_x$ is the concentration of $Cr^{6+}$ in the sample (µmole/g, unknown)

$\alpha$ is the percentage of $Cr^{3+}$ oxidized to $Cr^{6+}$ after spiking (unknown)

$\beta$ is the percentage of $Cr^{6+}$ reduced to $Cr^{3+}$ after spiking (unknown)

These formulas are based on a chemical pure isotope enriched spike of both components. In other words the chromium isotope enriched material contains only one redox species of chromium. To confirm this assumption both solutions of isotope enriched material were analysed in order to control their chemical purity. While no detectable $^{50}Cr^{6+}$ was present in the $^{50}Cr^{3+}$ isotope enriched spike solution, 2 % of the isotope enriched $^{53}Cr^{6+}$ spike was present as $^{53}Cr^{3+}$. For this reason the above mentioned formulas had to be changed in order to correct for this impurity of $^{53}Cr^{3+}$ in the isotope enriched $^{53}Cr^{6+}$ spike. This was done by introducing a chemical purity factor (P) in these equations. This purity factor stands for the fraction $Cr^{6+}$ in the $^{53}Cr$ isotope enriched material.

$$R^{III}_{53/52} = \frac{\left({}^{53}A_x C^{III}_x W_x + {}^{53}A^{III}_s C^{III}_s W^{III}_s + (1-P)\cdot {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1-\alpha) + \left({}^{53}A_x C^{VI}_x W_x + P\cdot {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s\right)\beta}{\left({}^{52}A_x C^{III}_x W_x + {}^{52}A^{III}_s C^{III}_s W^{III}_s + (1-P)\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1-\alpha) + \left({}^{52}A_x C^{VI}_x W_x + P\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)\beta}$$

$$R^{III}_{50/52} = \frac{\left({}^{50}A_x C^{III}_x W_x + {}^{50}A^{III}_s C^{III}_s W^{III}_s + (1-P)\cdot {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1-\alpha) + \left({}^{50}A_x C^{VI}_x W_x + P\cdot {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s\right)\beta}{\left({}^{52}A_x C^{III}_x W_x + {}^{52}A^{III}_s C^{III}_s W^{III}_s + (1-P)\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1-\alpha) + \left({}^{52}A_x C^{VI}_x W_x + P\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)\beta}$$

$$R^{VI}_{53/52} = \frac{\left({}^{53}A_x C^{III}_x W_x + {}^{53}A^{III}_s C^{III}_s W^{III}_s + (1-P)\cdot {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s\right)\alpha + \left({}^{53}A_x C^{VI}_x W_x + P\cdot {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1-\beta)}{\left({}^{52}A_x C^{III}_x W_x + {}^{52}A^{III}_s C^{III}_s W^{III}_s + (1-P)\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)\alpha + \left({}^{52}A_x C^{VI}_x W_x + P\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1-\beta)}$$

$$R^{VI}_{50/52} = \frac{\left({}^{50}A_x C^{III}_x W_x + {}^{50}A^{III}_s C^{III}_s W^{III}_s + (1-P)\cdot {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s\right)\alpha + \left({}^{50}A_x C^{VI}_x W_x + P\cdot {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1-\beta)}{\left({}^{52}A_x C^{III}_x W_x + {}^{52}A^{III}_s C^{III}_s W^{III}_s + (1-P)\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)\alpha + \left({}^{52}A_x C^{VI}_x W_x + P\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1-\beta)}$$

The concentration of $Cr^{3+}$ and $Cr^{6+}$ in the sample as well as possible interconversions can be derived from these equations. However, as mentioned above, due to the alkaline digestion no $Cr^{3+}$ spike is recovered and consequently the $R^{III}_{50/52}$ and $R^{III}_{53/52}$ can not be measured. Therefore a new model was conceived based on the ratios $R^{VI}_{50/52}$ and $R^{VI}_{53/52}$,

$$R^{VI}_{50/52} = \frac{P\cdot {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s + {}^{50}A_x C^{VI}_x W^{VI}_x + {}^{50}A^{III}_s C^{III}_{s\,convert} W^{III}_s}{P\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s + {}^{52}A_x C^{VI}_x W^{VI}_x + {}^{52}A^{III}_s C^{III}_{s\,convert} W}$$

$$R^{VI}_{53/52} = \frac{P\cdot {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s + {}^{53}A_x C^{VI}_x W^{VI}_x + {}^{53}A^{III}_s C^{III}_{s\,convert} W^{III}_s}{P\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s + {}^{52}A_x C^{VI}_x W^{VI}_x + {}^{52}A^{III}_s C^{III}_{s\,convert} W}$$

where,

P chemical purity factor, fraction $Cr^{6+}$ in the $^{53}Cr$ enriched material.

$C^{III}_{s\,convert}$ the concentration of $Cr^{3+}$ in the $^{50}Cr^{3+}$ spike converted to $Cr^{6+}$

These equations take into account the possible conversion of the added isotope enriched $Cr^{3+}$ spike to $Cr^{6+}$ during the digestion and subsequent handling. When $Cr^{3+}$ oxidation occures, the $Cr^{3+}$ present as chemical impurity in the isotope enriched $Cr^{6+}$ spike will also be (partially) converted and has to be included into the equation,

$$R^{VI}_{50/52} = \frac{P\cdot {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s + {}^{50}A_x C^{VI}_x W^{VI}_x + {}^{50}A^{III}_s C^{III}_{s\,convert} W^{III}_s + \frac{C^{III}_{s\,convert}}{C^{III}_s}\cdot(1-P)\cdot {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s}{P\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s + {}^{52}A_x C^{VI}_x W^{VI}_x + {}^{52}A^{III}_s C^{III}_{s\,convert} W^{III}_s + \frac{C^{III}_{s\,convert}}{C^{III}_s}\cdot(1-P)\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s}$$

$$R^{VI}_{53/52} = \frac{P\cdot {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s + {}^{53}A_x C^{VI}_x W^{VI}_x + {}^{53}A^{III}_s C^{III}_{s\,convert} W^{III}_s + \frac{C^{III}_{s\,convert}}{C^{III}_s}\cdot(1-P)\cdot {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s}{P\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s + {}^{52}A_x C^{VI}_x W^{VI}_x + {}^{52}A^{III}_s C^{III}_{s\,convert} W^{III}_s + \frac{C^{III}_{s\,convert}}{C^{III}_s}\cdot(1-P)\cdot {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s}$$

From these equations the following relative fractions of $Cr^{6+}$ present in the alkaline digestion can be derived,

$F^{VI}_{spike} = \frac{C^{VI}_s}{C^{VI}_s + C^{III}_{sconvert} + C^{VI}_x}$ : the fraction $Cr^{6+}$ of the enriched $^{53}Cr^{6+}$ spike

$F^{VI}_{natural} = \frac{C^{VI}_x}{C^{VI}_s + C^{III}_{sconvert} + C^{VI}_x}$ : the fraction natural $Cr^{6+}$ extracted from the sample

$F^{III}_{spike} = \frac{C^{III}_{sconvert}}{C^{VI}_s + C^{III}_{sconvert} + C^{VI}_x}$ : the fraction converted $Cr^{3+}$ from the enriched $^{50}Cr^{3+}$ spike

When the total amount of $Cr^{6+}$ present in the sample, $Cr^{VI}_{total}$, is calculated by means of linear regression based on natural $Cr^{6+}$ standard solutions and summation of the integrated peak areas on all chromium isotopes, the concentration of the different fractions $Cr^{6+}$ in the alkaline digest can be derived,

$\left[Cr^{VI}_{spike}\right] = F^{VI}_{spike}\cdot\left[Cr^{VI}_{total}\right]$ : the concentration of $^{53}Cr^{6+}$ spike

$\left[Cr^{VI}_{natural}\right] = F^{VI}_{natural}\cdot\left[Cr^{VI}_{total}\right]$ : the concentration of natural $Cr^{6+}$

$\left[Cr^{III}_{spike}\right] = F^{III}_{spike}\cdot\left[Cr^{VI}_{total}\right]$ : the concentration of converted $^{50}Cr^{3+}$ spike

In contrast to SIDMS the calculated $Cr^{6+}$ concentration extracted from the sample is not corrected for possible reduction reactions encountered during the alkaline digestion. However the actual concentration of the $^{53}Cr^{6+}$ spike in the digest is a measure of the recovery and gives an indication of conversion from $Cr^{6+}$ to $Cr^{3+}$ was likely to occure during the digestion. The actual concentration of the converted $^{50}Cr^{3+}$ spike in the digest gives an indication of the fact that conversion (oxidation) from

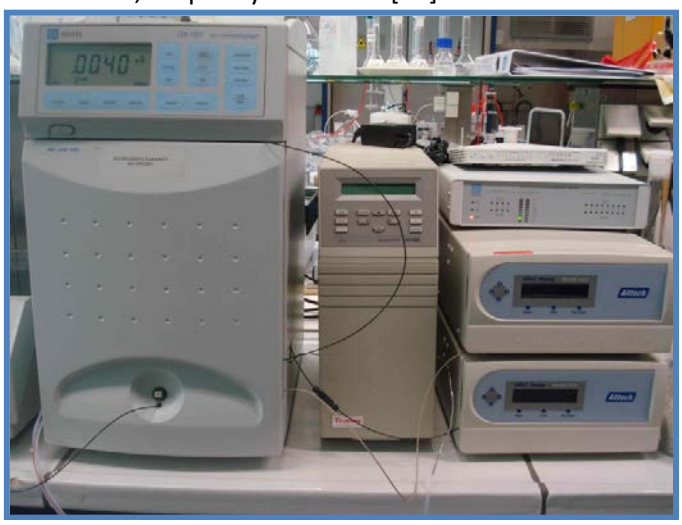
$Cr^{3+}$ to $Cr^{6+}$ was likely to occure during the digestion. One could correct for these possible reactions by first determing the amount of $Cr^{3+}$ in the sample by substracting the total amount of chromium (after acid digestion) by the amount of $Cr^{6+}$ in the sample and secondly take into account the percentage of $Cr^{3+}$ converted to $Cr^{6+}$. Because of the different properties of the chemical forms of $Cr^{3+}$ regarding this digestion and the slow kinetic properties of $Cr^{3+}$ it is however questionable to compare the behaviour of the native $Cr^{3+}$ with the added $^{50}Cr^{3+}$ spike.

## Experimental

### Instrumentation

Samples were analysed on an Elan 6000 ICP-MS system (Perkin-Elmer, SCIEX, Thornhill, ON, Canada) equipped with a MCN-100 micro-concentric nebuliser (Cetac technologies, Omaha, NE, USA) fitted to a Scott-type double pass spray chamber (Perkin-Elmer, see also Picture 1). The speciation of the redox species was carried out by anion exchange chromatography on an IONPAC AS 11 microbore column (2 mm i.d.) and an IONPAC AS 10 microbore column (Dionex, Sunnyvale, CA, USA). Both columns were provided with a guard column to remove dissolved and particulate contaminants from the sample and eluent before reaching the column. The eluent was pushed through the column via a HPLC pump model 2250 (BISCHOFF, Leonberg, Germany), all fittings as well as the pump head were made in PEEK . A FIAS 400 (Perkin-Elmer) peristaltic pump provided the filling of a 25 µl PEEK sample loop. The sample loop was connected to an automated 6-port valve (LabPRO 6, Rheodyne, California, USA). The measurement system, including sample uptake, filling of the loop, injection on the column and ICP-MS measurement is computerized. The integration of the chromatograms was performed with Turbochrom (Perkin-Elmer). Before analysis the instrument was preconditioned by aspirating the eluent for at least 1 hour.

Hexavalent chromium was also spectrophotometrically determined after ion chromatography by post column derivatisation with 1,5-diphenylcarbazide [23].



Picture 2: Ion chromatography instrument equipped with post-column derivatisation.

Although direct spectrophotometric analysis, without ion chromatography, is often applied in water analysis, several problems have been documented when this method is applied to some types of samples with complex matrices [4]. Analysis of bulk samples using this methodology suffers from potential interferences by other coloured species or species forming coloured reaction products with DPC, such as V, Mo and Hg. Low results and poor recoveries were observed when samples contained substances that reduce $Cr^{6+}$ in acidic solution [24]. To avoid the aforementioned interferences the speciation of the redox species was carried out by anion exchange chromatography on an IONPAC AS

7 column (Dionex, Sunnyvale, CA, USA). The column was provided with a guard column to remove dissolved and particulate contaminants from the sample and eluent before reaching the column. The eluent was pushed through the column via an isocratic pump P1000 (Spectro-Physics analytical, San Jose, California). The post column reagent was added via an isocratic pump P1500 (Spectro-Physics analytical, San Jose, California). The 20 µl PEEK sample loop was manually filled. Post column derivatisation of the $Cr^{6+}$ with diphenylcarbazide was followed by detection of the coloured complex at 540 nm with a UV-150 detector spectrophotometer (Spectro-Physics analytical).

Some of the alkaline digestions were performed with ultrasound-assisted leaching. The ultrasonic radiation was applied by means of a Branson 5210 (47 kHz, 185 W, Soest, the Netherlands).

**Standard solutions and reagents**

For the preparation of all solutions ultra-pure water with a resistivity of 18 MΩ $cm^{-1}$ obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA) was used. A stock solution of 1000 mg $l^{-1}$ $Cr^{6+}$ was prepared by dissolving 2.828 g potassium dichromate (*pro analysi*, Merck, Darmstadt, Germany) in 1 l. A Stock solution of 1000 mg $l^{-1}$ $Cr^{3+}$ was purchased (Merck). A quality control stock solution of 1000 mg $l^{-1}$ $CrO_4^-$ was purchased (Merck).

For the determination of the chemical purity of the enriched chromium isotope solutions on the AS 11 column, 0.14 M $NH_4NO_3$ (Merck) was used as eluent (flow rate 0.4 ml $min^{-1}$). This eluent solution was acidified to pH 3 with concentrated subboiled nitric acid (Merck). For the determination of $Cr^{6+}$ in the extracted solid samples on the AS 11 column, 250 mM NaOH (Merck) was used as eluent (flow rate 0.35 ml $min^{-1}$). To control the stability of the ICP-MS the eluent was spiked with an internal standard of 10 ng $ml^{-1}$ Cesium. This signal, measured on $^{133}Cs$, was continuously monitored during the measurement of the chromatogram. For the determination of $Cr^{6+}$ in the extracted solid samples on the AS 7 column, 250 mM $(NH_4)_2SO_4$ - 49 mM $NH_4OH$ (Merck) was used as eluent (flow rate 1 ml $min^{-1}$).

Calibration standards were diluted from the stock solutions. The concentration level of the standards was 50, 150 and 250 ng $ml^{-1}$ $Cr^{3+}$ and $Cr^{6+}$. The standards were prepared in the appropriate eluent concentration. For the determination of the dead time of the detector a 200 ng $ml^{-1}$ $Cr^{6+}$ solution prepared in 0.14 M $NH_4NO_3$ was measured. For the determination of the mass bias a 50 ng $ml^{-1}$ $Cr^{6+}$ solution prepared in the appropriate eluent was used.

*Preparation of $^{53}Cr^{6+}$ isotope enriched solution*

Approximately 5 mg of a $^{53}Cr$ isotope enriched $Cr_2O_3$ solid material (supplied by the Institute for Reference Materials and Measurements (IRMM), Geel, Belgium) was weighed in a beaker. 5 ml of $HClO_4$ (Merck) was added and the solution was heated during 3 hours until complete digestion. After cooling to room temperature the solution was diluted to 500 ml with Milli-Q water in a volumetric flask. The concentration of the stock solution amounted approximately 10 mg $l^{-1}$. The relative abundances of the chromium isotopes in the enriched material are summarised in table 1.

| isotope | natural Cr | $^{53}Cr^{6+}$ spike | $^{50}Cr^{3+}$ spike |
|---|---|---|---|
| $^{50}Cr$ | 4.345 | 0.04 | 93.725 |
| $^{52}Cr$ | 83.789 | 2.63 | 6224 |
| $^{53}Cr$ | 9.501 | 97.21 | 0.042 |
| $^{54}Cr$ | 2.365 | 0.12 | 0.010 |

Table 1. Relative abundances (%) of isotopes of natural chromium [35], $^{53}Cr^{6+}$ enriched spike and $^{50}Cr^{3+}$ enriched spike.

*Preparation of $^{50}Cr^{3+}$ isotope enriched solution*

Approximately 5 mg of a $^{50}Cr$ isotope enriched $Cr_2O_3$ solid material (supplied by the Institute for Reference Materials and Measurements (IRMM), Geel, Belgium) was weighed in a beaker. 5 ml of $HClO_4$ (Merck) was added and the solution was heated during 3 hours until complete digestion. After cooling to room temperature, 2 ml $H_2O_2$ was added and the solution was heated again for a 30 minutes. The solution was cooled again and diluted to 500 ml with Milli-Q water in a volumetric flask. The concentration of the stock solution amounted approximately 10 mg $l^{-1}$. The relative abundances of the chromium isotopes in the enriched material are summarised in table 1.

Preliminary alkaline digestions showed significant oxidation of the added $Cr^{3+}$ spike. This could be related to the presence of traces of $H_2O_2$ in the spike solution. Although in acid medium $Cr^{6+}$ is converted to $Cr^{3+}$ in the presence of $H_2O_2$, in alkaline medium oxidation takes place of $Cr^{3+}$ in the presence of this chemical [25]. To decompose the traces of $H_2O_2$ in the spike solution without altering the redox species of chromium, the solution was treated in a UV digestion apparatus for 8 hours (UV digester 705, Metrohm, Herisau, Switzerland).

**Alkaline digestion for hexavalent chromium (US EPA method 3060A)[13]**

Only a brief summary is given of US EPA method 3060A in order to visualise all components that may interfere in the latter ICP-MS determination. Approximately 2.5 g of a sample is placed into a 250 ml digestion glass vessel and spiked with an aliquot of enriched isotope $^{50}Cr^{3+}$ and enriched isotope $^{53}Cr^{6+}$, finally 50 ml of the digestion solution is added. The digestion solution consists of a 0.5 M NaOH and a 0.28 M $Na_2CO_3$ solution. Also approximately 61 mg $Mg(NO_3)_2$ is added as well as 0.5 ml of a 1.0 M $K_2HPO_4$ / $KH_2PO_4$ buffer (pH 7). The addition of $Mg^{2+}$ in a phosphate buffer to the alkaline digestion solution has been showed to suppress the oxidation of $Cr^{3+}$. In US EPA method 3060A an addition of 400 mg $MgCl_2$ is prescribed, but due to the ClO interference on chromium isotopes and the matrix effects observed in the ICP-MS analysis due to the high amount of salts, the added amount has been changed to 60 mg $Mg(NO_3)_2$.

The sample is covered witch watch glass and heated at 363-368 K for at least 60 minutes with continuous stirring. The contents is quantitatively transferred, after gradually cooling to room temperature, to the filtration apparatus (polytetrafluoroethylene filter). Special attention must be paid to the filter media. Reduction of $Cr^{6+}$ to $Cr^{3+}$ has been reported on sampling filter media such as mixed cellulose ester filters. Polyvinyl chloride (PVC), polyvinyl fluoride (PVF) or polytetrafluoroethylene (PTFE) filter media may be used and it is recommended to treat filters with base prior to filtration [26]. The filtrate and rinses of the digestion vessel are collected in a 100 ml volumetric flask and diluted with Milli-Q water. The filtrate was injected on the AS 10 column without further treatment for the ICP-MS analysis. For the spectrophotometric analysis, an appropriate amount of the eluent ($(NH_4)_2SO_4$ , $NH_4OH$) was added to the filtrate.

The digestion can also be performed with ultrasound-assisted leaching. Ultrasonic radiation has shown to be a powerful aid in the acceleration of extracting a number of analytes of solid samples. The ultrasound-assisted digestion of hexavalent chromium has been successfully applied to soils and industrial hygiene samples [27-29].

A 30 day holding time for $Cr^{6+}$ digestion from solid materials and a 7 day holding time for $Cr^{6+}$ analysis once solubilised in the alkaline digestate has been scientifically designated as appropriate for $Cr^{6+}$ analysis according to this procedure [30].

$Cr^{6+}$ is easier to reduce in a pH 7 solution than in a pH 12 solution. Although the alkaline digestate can be stored for future analysis, it is recommended to neutralise the solution prompt before measurement, as $Cr^{6+}$ has been observed to reduce during neutralisation. This reduction may be kinetically slow, but extended storage time could cause significant loss of $Cr^{6+}$ [4].

**Water extraction for hexavalent chromium**

For the water extraction, approximately 2.5 g of a sample was placed into a 250 ml digestion vessel and 50 ml water was added. The sample was covered witch watch glass and heated at 363 -368 K for at least 60 minutes with continuous stirring. The contents was quantitatively transferred, after gradually cooling to room temperature, to the filtration apparatus (0.45 µm membrane filter). The filtrate and rinses of the digestion vessel were collected in a 100 ml volumetric flask and diluted with water. In case of spiking, the aliquots of enriched material were added on the sample before addition of the extraction medium.

**Calculations**

The equations mentioned in the method of calculation paragraph have been solved with the standard tools of the MATLAB software (version 5.2, Mathworks Inc., Natick, MA). Although the regression analysis can easily be done by the standard tools of MATLAB, the statistical toolbox has been used, in order to perform also some t-tests on the intercept.



## *Results and Discussion*

***Chemical purity of the enriched isotope material (Dionex AS 11)***

*The SIDMS equations assume chemical pure isotope enriched spikes of both redox species. A Dionex AS 11 chromatographic* column coupled to a guard column was optimised for the determination of $Cr^{3+}$ and $Cr^{6+}$. The optimisation also included the separation of both chromium species from the major interferences of concern (table 2).

| *isotope* | *Isobaric* | *Ar interference* | *matrix interference* | *double charged* |
|---|---|---|---|---|
| $^{50}Cr$ | **$^{50}Ti$** (5.4)<br>**$^{50}V$** (0.25) | $^{36}Ar^{14}N$ (0.34)<br>$^{38}Ar^{12}C$ (0.06) | **$^{34}S^{16}O$** (4.20)<br>$^{35}Cl^{15}N$ (0.28)<br>$^{37}Cl^{13}C$ (0.27) | $^{100}Mo^{2+}$ (9.63) |
| $^{52}Cr$ | - | **$^{40}Ar^{12}C$** (98.5)<br>$^{36}Ar^{16}O$ (0.34)<br>$^{38}Ar^{14}N$ (0.06) | **$^{35}Cl^{16}OH$** (75.6)<br>$^{35}Cl^{17}O$ (0.03)<br>$^{36}S^{16}O$ (0.02) | $^{104}Pd^{2+}$ (9.3)<br>$^{104}Ru^{2+}$ (18.3) |
| $^{53}Cr$ | - | **$^{40}Ar^{13}C$** (1.1) | **$^{37}Cl^{16}O$** (24.2)<br>$^{35}Cl^{18}O$ (0.15)<br>$^{36}S^{16}OH$ (0.02) | $^{106}Cd^{2+}$ (1.2)<br>$^{106}Pd^{2+}$ (27.1) |
| $^{54}Cr$ | **$^{54}Fe$** (5.80) | **$^{40}Ar^{14}N$ (99.24)**<br>$^{38}Ar^{16}O$ (0.06) | **$^{37}Cl^{16}OH$** (24.2) | $^{108}Pd^{2+}$ (26.7) |

Table 2. Major interferences on the chromium isotopes measured by ICP-MS (relative abundance).

In figure 1 a chromatogram of the possible interferences and both chromium species is shown. It can be seen that $Cr^{3+}$ is retained on the anion exchange column. $Cr^{3+}$ has a strong tendency to form hexacoordinated octahedral complexes with ligands such as water, ammonia, halides, sulfates and

organic acids [31]. A possible explanation for the retention of $Cr^{3+}$ on this column is related to the presence of the functional groups of the Dionex AG11 column, as proposed by Charles *et al*. [32]. They are alkanol quaternary ammonium and can interact with the water molecules of the $Cr(H_2O)_6^{3+}$ complex leading to increased retention.

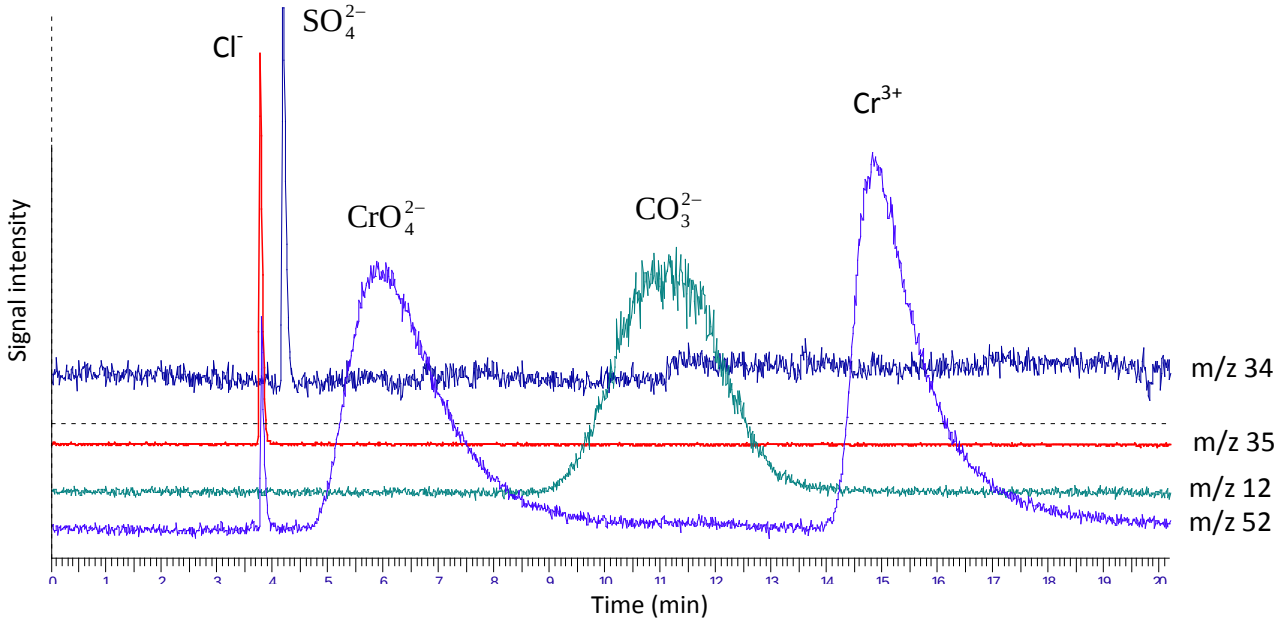



Figure 1: Retention times of the different alkaline digestion reagents after optimisation of Dionex AS 11 column (eluent: 0.14 M $NH_4NO_3$ (pH 3); flow rate: 0.4 ml $min^{-1}$; sample loop 25 µl). Chromatograms of a mixture containing 20 mg $l^{-1}$ $SO_4^{2-}$ (m/z 34), 10 mg $l^{-1}$ $Cl^-$ (m/z 35), 50 mg $l^{-1}$ $CO_3^{2-}$ (m/z 12), 100 µg $l^{-1}$ $Cr^{3+}$ and 100 µg $l^{-1}$ $Cr^{6+}$.

To confirm the assumption of chemical pure spikes, both solutions of isotope enriched material were analysed. The solutions were diluted in 0.14 M $NH_4NO_3$ and injected on the column (figure 2).

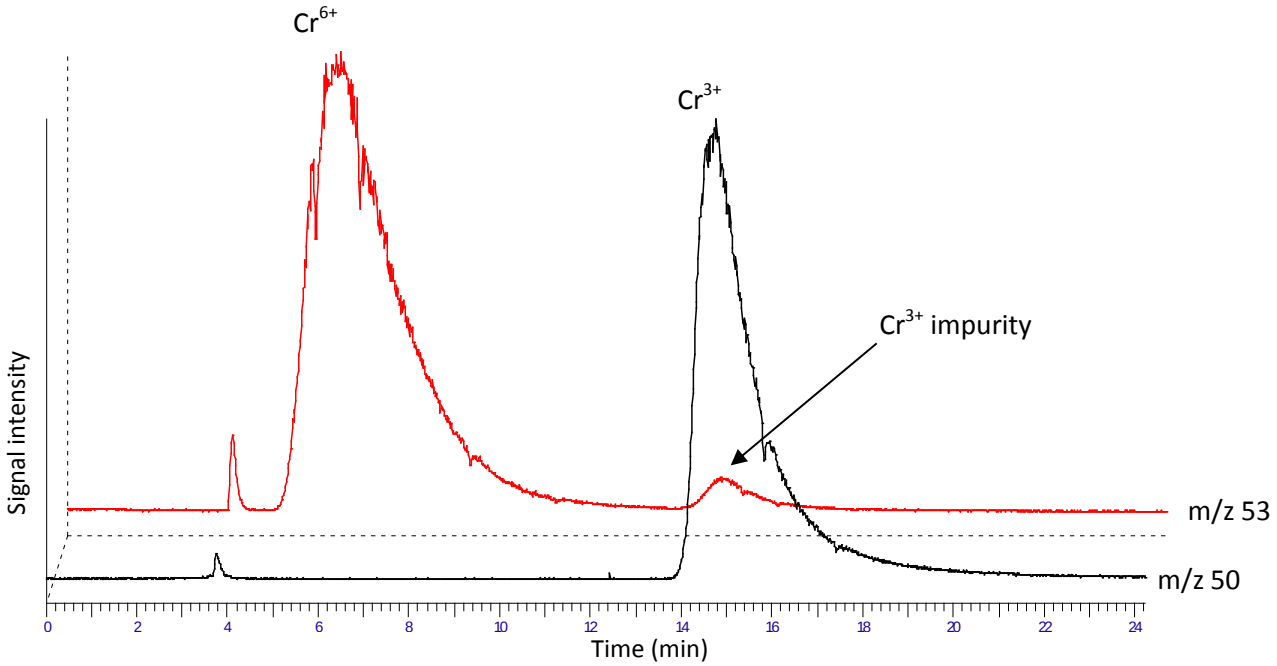



Figure 2: Chemical purity of isotope enriched materials analysed on Dionex AS 11 column. Upper chromatogram $^{53}Cr^{6+}$ spike, lower chromatogram $^{50}Cr^{3+}$ spike; eluent: 0.14 M $NH_4NO_3$ (pH 3); flow rate: 0.4 ml $min^{-1}$; sample loop 25 µl.

While no detectable $^{50}Cr^{6+}$ was present in the $^{50}Cr^{3+}$ isotope enriched spike solution, 2 % of the isotope enriched $^{53}Cr^{6+}$ spike was present as $^{53}Cr^{3+}$. In order to correct for this impurity of $^{53}Cr^{3+}$ in the isotope enriched $^{53}Cr^{6+}$ spike the equations were adjusted. This was done by introducing a chemical purity factor (P) in the equations as already mentioned in the calculation paragraph. This purity factor stands for the fraction $Cr^{6+}$ in the $^{53}Cr$ isotope enriched material.

**Determination of hexavalent chromium in alkaline digestion (Dionex AS 10)**

To improve the calculations for the determination of hexavalent chromium in the alkaline digestion based on IC-ICP-MS measurements, the relative standard deviation on the mass bias was optimised and the influence of spectral interferences investigated.

**Determination of mass bias**

The observed isotope ratios deviates from the standard values as a function of the difference in mass between the two isotopes [33]. The true ratio of isotopes A and B , $(A/B)_t$, can be related to the measured ratio, $(A/B)_m$, by:

$$\left(\frac{A}{B}\right)_m = \left(\frac{A}{B}\right)_t \cdot (1 + a \cdot n)$$

where *a* is the bias per mass unit, and n is the mass difference between isotopes A and B. Also, determination of the dead time is critical when ratios of isotopes with different relative abundances are calculated. The relation between the measurement time parameters, dwell time and number of sweeps, of the ICP-MS on the standard deviation of the measured ratios was studied (figures 3 and 4).

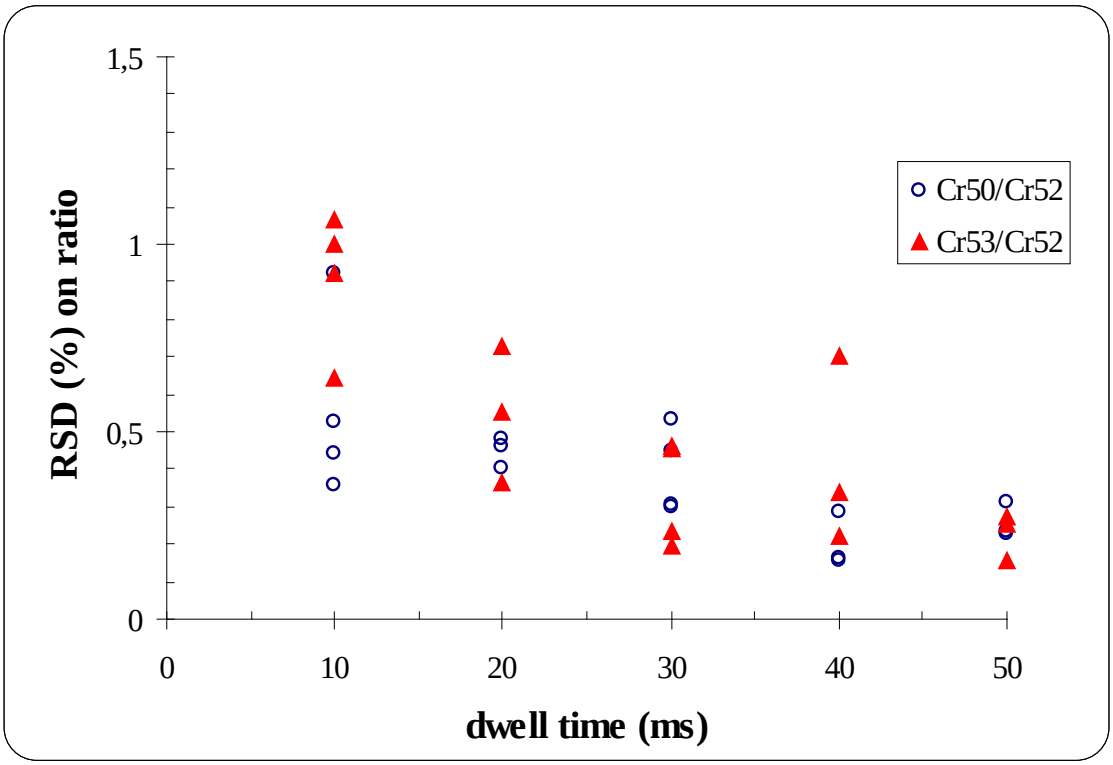



Figure 3: Relative standard deviation on the ratios $^{50}Cr/^{52}Cr$ and $^{53}Cr/^{52}Cr$ in function of the dwell time (number of sweeps 300) measured on a 50 ng $ml^{-1}$ Cr solution.

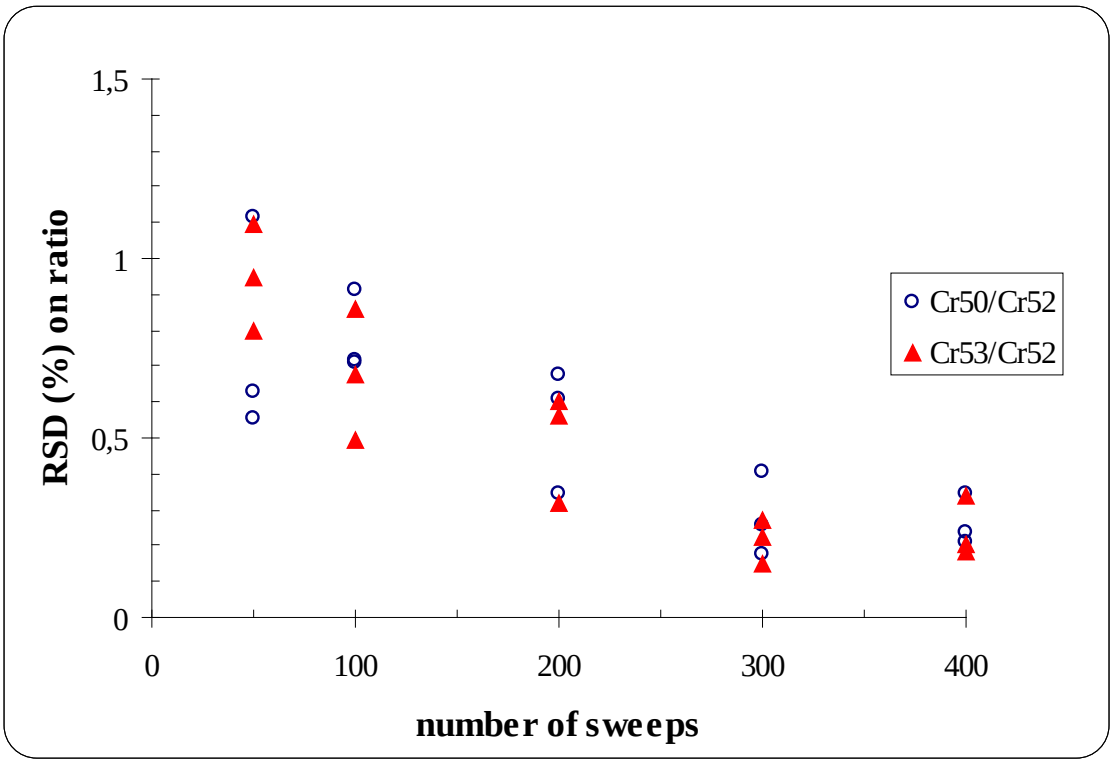



Figure 4: Relative standard deviation on the ratios $^{50}Cr/^{52}Cr$ and $^{53}Cr/^{52}Cr$ in function of the number of sweeps (dwell time 30 ms) measured on a 50 ng $ml^{-1}$ Cr solution.

Under the given conditions a dwell time of 30 ms per element and 300 number of sweeps resulted in a satisfactory compromise between total analysis time and standard deviation on the ratios. Under the given optimised time conditions the mass bias was calculated before every measurement run on a 0.25 M NaOH solution containing 50 µg $l^{-1}$ $Cr^{6+}$. Over a period of two months an average bias per mass unit, a, of 0.036 ± 0.004 (n = 14) was calculated, *i.e.*, $\left(^{50}Cr/^{52}Cr\right)_m = \left(^{50}Cr/^{52}Cr\right)_t \cdot \left(1 + 0.036 \cdot (-2)\right)$ and $\left(^{53}Cr/^{52}Cr\right)_m = \left(^{53}Cr/^{52}Cr\right)_t \cdot \left(1 + 0.036 \cdot (1)\right)$. The optimised instrumental measurement settings of the IC-ICP-MS are summarised in table 3.

| parameter | value |
|---|---|
| instrument settings | |
| nebuliser gas flow | 0.9 ± 0.05 l/min |
| RF power | 1200 W |
| analog stage voltage | -1950 V |
| pulse stage voltage | 1500 V |
| lens voltage | 5 ± 1 V |
| measured peak width | 0.7 amu |
| dead time detector | 40 ns |
| | |
| measurement settings | |
| scan mode | peak hopping |
| dwell time | 30 ms |
| sweeps / reading | 5 |
| total measurement time | 15 minutes |
| | |
| Isotopes monitored | $^{12}C$, $^{31}P$, $^{34}S$, $^{35}Cl$, $^{50}Cr$, $^{52}Cr$, $^{53}Cr$, $^{54}Cr$ and $^{133}Cs$ |

Table 3. Optimised instrumental measurement settings ICP-MS.

**Analytical characteristics**

As the concentration of NaOH in the alkaline digestion amounted 0.25 M, the optimisation of the $Cr^{6+}$ speciation on the AS 10 chromatographic column was performed with 0.25 M NaOH as eluent. Neutralising the alkaline digestion before measurement has been shown to give precipitation of lead chromate at high concentrations. Moreover during neutralisation to a pH of 7.5, reduction of $Cr^{6+}$ and detection of small amounts of $Cr^{3+}$ have been observed on soil extracts spiked with $Cr^{6+}$ solutions [4]. The flow rate was optimised in order to separate the major interferences from the analyte of concern. Special attention was paid to the interfernce arising from $CO_3^{2-}$, essential in the digestion for dissolution of $BaCrO_4$ [4]. A chromatogram recorded under optimised conditions can be seen in figure 5.

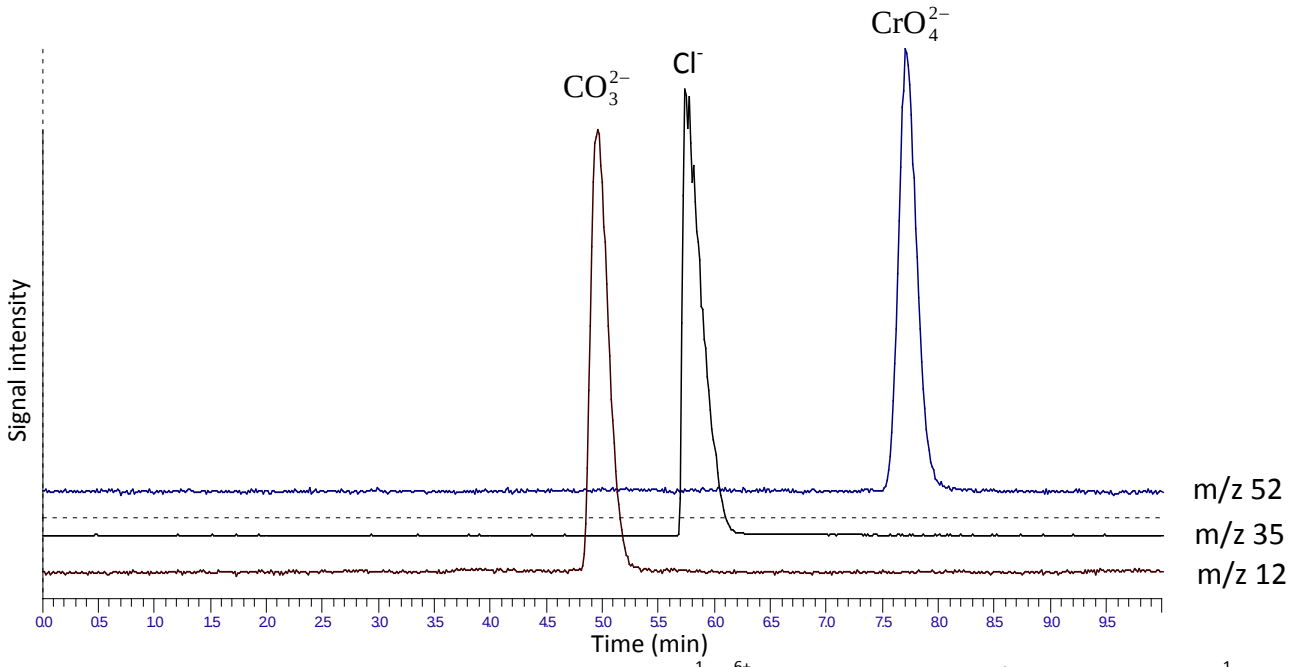



Figure 5: Alkaline digestion solution spiked with 100 ng $ml^{-1}$ $Cr^{6+}$, eluent 0.25 M NaOH, flow rate 350 µl $min^{-1}$, sample loop 25 µl.

The stability of the IC-ICP-MS system operating under these conditions (NaOH) has been demonstrated in a previous paper [34]. A relative standard deviation of 2.8 % was calculated for 54 consecutive measurements of the internal standard over a period of 40 h. To correct for the instability of the ICP-MS in this study, the eluent was spiked with an internal standard of 10 ng $ml^{-1}$ Cesium. The signal of the internal standard, measured on $^{133}Cs$, was continuously monitored during the measurement of the chromatogram. The integrated peak areas of the analytes of concern were corrected for the measured value of the internal standard. The detection limit, calculated as three times the standard deviation on 10 determinations of a 5 ng $ml^{-1}$ $Cr^{6+}$ standard solution, amounted 0.8 ng $ml^{-1}$ $Cr^{6+}$.

**Alkaline digestion versus water extraction**

In the legislation of some of the member states of the European Union the determination of hexavalent chromium among others is required in leaching tests in order to meet regulatory criteria for acceptance on landfill. In these leaching tests a waste samples is leached with water in a specific liquid to solid ratio. In order to study the influence of the extraction medium, 3 waste samples were extracted in duplo in water and alkaline medium. The samples can be characterised as filter cake, chromium dust and low carbon pitslag. In each medium the samples were extracted as such and spiked with an aliquot of enriched isotope $^{50}Cr^{3+}$ and enriched isotope $^{53}Cr^{6+}$. The digestion solutions

were analysed with ion chromatography diphenylcarbazide (IC-DPC) and ion chromatography inductively coupled plasma-mass spectrometry (IC-ICP-MS).

As can be seen from the differences in the duplo analysis (results reported in table 4 and 5), the alkaline digestion is – as expected - more reproducible than the water extraction. Moreover the extraction efficiency for $Cr^{6+}$ is higher in the alkaline digestion in comparison with the water extraction.

The added $Cr^{6+}$ spike is stable during the alkaline digestion (recovery in all samples > 90%). The recovery of the $Cr^{6+}$ spike in the water extraction however varied between 46 to 90 % and also oxidation of the added $Cr^{3+}$ spike was observed, indicating species interconversion during the water extraction. Calculation of the recovery of $Cr^{6+}$ in case of measurement with IC-DPC is sometimes misleading as the value is calculated on the difference of two measurements performed on two different extractions. While in the case of measurement with species-specific isotope dilution mass spectrometry the calculation is performed on the same extraction. The oxidation of the added $Cr^{3+}$ spike is negligible during the alkaline digestion (the observed oxidation may be due to traces of $H_2O_2$ present in the spike solution).

| | IC-DPC | | | IC-ICP-MS | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| identification | $[Cr^{VI}_{total}]$ | R | $[Cr^{VI}]$ | $[Cr^{VI}_{total}]$ | $[Cr^{VI}_{natural}]$ | $[Cr^{VI}_{spike}]$ | R | $[Cr^{III}_{spike}]$ | Ox. | $[Cr^{VI}]$ |
| | ng ml$^{-1}$ | % | mg kg$^{-1}$ | ng ml$^{-1}$ | ng ml$^{-1}$ | ng ml$^{-1}$ | % | ng ml$^{-1}$ | % | mg kg$^{-1}$ |
| sample1 | 259 | | 74 | 260 | | | | | | 74 |
| sample1 +spike[a] | 541 | 176 | 110 | 561 | 416 | 138 | 86 | 6.1 | 3.8 | 120 |
| sample1 | 281 | | 79 | 269 | | | | | | 76 |
| sample1 +spike[a] | 372 | 57 | 60 | 378 | 246 | 127 | 79 | 4.6 | 2.9 | 69 |
| sample2 | 2155 | | 433 | 1838 | | | | | | 369 |
| sample2+ spike[b] | 3856 | 532 | 701 | 3238 | 2985 | 246 | 77 | 7 | 2.2 | 592 |
| sample2 | 1984 | | 390 | 2218 | | | | | | 436 |
| sample2+ spike[b] | 3915 | 603 | 706 | 3560 | 3290 | 266 | 83 | 4 | 1.3 | 646 |
| sample3 | 240 | | 48 | 230 | | | | | | 46 |
| sample3+ spike[a] | 379 | 87 | 43 | 365 | 266 | 74 | 46 | 25.2 | 15.8 | 52 |
| sample3 | 240 | | 47 | 212 | | | | | | 42 |
| sample3+ spike[a] | 391 | 94 | 45 | 384 | 237 | 144 | 90 | 2.6 | 1.6 | 46 |

Table 4. Water extraction of three different waste samples (sample 1 (filter cake), sample 2 (chromium dust) and sample 3 (low carbon pitslag).
[a] added amount of spike 160 ng ml$^{-1}$ $^{50}Cr^{3+}$ + 160 ng ml$^{-1}$ $^{53}Cr^{6+}$;
[b] added amount of spike 320 ng ml$^{-1}$ $^{50}Cr^{3+}$ + 320 ng ml$^{-1}$ $^{53}Cr^{6+}$.

| | IC-DPC | | | IC-ICP-MS | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| identification | $[Cr^{VI}_{total}]$ | R | $[Cr^{VI}]$ | $[Cr^{VI}_{total}]$ | $[Cr^{VI}_{natural}]$ | $[Cr^{VI}_{spike}]$ | R | $[Cr^{III}_{spike}]$ | Ox. | $[Cr^{VI}]$ |
| | ng ml$^{-1}$ | % | mg kg$^{-1}$ | ng ml$^{-1}$ | ng ml$^{-1}$ | ng ml$^{-1}$ | % | ng ml$^{-1}$ | % | mg kg$^{-1}$ |
| sample1 | 2334 | | 659 | 1964 | | | | | | 554 |
| sample1 +spike[a] | 2469 | 84 | 649 | 2241 | 2078 | 157 | 98 | 3 | 1.9 | 584 |
| sample1 | 2242 | | 626 | 2023 | | | | | | 565 |
| sample1 +spike[a] | 2100 | -89 | 542 | 2070 | 1919 | 151 | 94 | 2.5 | 1.6 | 536 |
| sample2 | 5056 | | 1024 | | | | | | | |
| sample2+ spike[b] | 5530 | 148 | 1019 | | | | | | | |
| sample2 | 5007 | | 993 | 4745 | | | | | | 941 |
| sample2+ spike[b] | 5288 | 88 | 973 | 4876 | 4570 | 298 | 93 | 8 | 2.5 | 895 |
| sample3 | 421 | | 82 | 394 | | | | | | 77 |
| sample3+ spike[a] | 603 | 114 | 85 | 621 | 450 | 168 | 105 | 3 | 1.9 | 87 |
| sample3 | 411 | | 81 | 370 | | | | | | 72 |
| sample3+ spike[a] | 586 | 109 | 83 | 543 | 384 | 157 | 98 | 2.5 | 1.6 | 75 |

Table 5. Alkaline extraction of three different waste samples (sample 1 (filter cake), sample 2 (chromium dust) and sample 3 (low carbon pitslag).
[a] added amount of spike 160 ng ml$^{-1}$ $^{50}Cr^{3+}$+ 160 ng ml$^{-1}$ $^{53}Cr^{6+}$;
[b] added amount of spike 320 ng ml$^{-1}$ $^{50}Cr^{3+}$+ 320 ng ml$^{-1}$ $^{53}Cr^{6+}$.

Key to the used symbols in table 4 and 5:

IC-DPC

- $[Cr^{VI}_{total}]$ : the amount of $Cr^{6+}$ present in the extraction solution, ng ml$^{-1}$
- R, recovery : the theoretical recovery assuming that added spike (*e.g.* 160 ng ml$^{-1}$ $Cr^{6+}$) is completely recovered. The recovery is calculated as the difference between the total amount of $Cr^{6+}$ present in the spiked and unspiked (as such) extraction solution
- $[Cr^{VI}]$: the amount of $Cr^{6+}$ extracted from the sample, mg kg$^{-1}$

IC-ICP-MS

- $[Cr^{VI}_{total}]$ : the amount of $Cr^{6+}$ present in the extraction solution, ng ml$^{-1}$
- $[Cr^{VI}_{natural}]$ : the amount of extracted natural $Cr^{6+}$ present in the extraction solution, ng ml$^{-1}$
- $[Cr^{VI}_{spike}]$ : the amount of enriched $Cr^{6+}$spike present in the extraction solution, ng ml$^{-1}$
- R, recovery : The recovery is calculated as the difference between the amount of $Cr^{6+}$ spike present in the extraction solution $[Cr^{VI}_{spike}]$ and the theoretical added amount of spike (*e.g.* 160 ng ml$^{-1}$)
- $[Cr^{III}_{spike}]$ : the amount of enriched $Cr^{3+}$ spike converted to $Cr^{6+}$, ng ml$^{-1}$
- Ox., oxidation : The oxidation is calculated as the difference between the amount of converted $Cr^{3+}$ spike ($[Cr^{III}_{spike}]$) and the theoretical added amount of spike (*e.g.*, 160 ng ml$^{-1}$);
- $[Cr^{VI}]$: the amount of $Cr^{6+}$ extracted from the sample, mg kg$^{-1}$

**Alkaline digestion on packaging materials**

In December 1994 the EEC Council of Ministers passed a directive on Packaging and Packaging waste 94/62/EC. In Article 11 of this directive concentration levels of *heavy metals* in packaging have been assigned. Member states shall ensure that the sum of the concentration levels of lead, cadmium, mercury and hexavalent chromium present in packaging or packaging components shall not exceed 100 mg/kg by weight. In order to overview the most critical types of packaging on the Belgian market, a qualitative and quantitative market analysis was performed by our institute. In the frame of this study, some 200 packaging materials were screened with X-Ray Fluorescence for total metal content. A selection of 40 critical packaging materials (total chromium content higher than 100 mg/kg) were further analysed for $Cr^{6+}$ content. The materials analysed were glass packaging, plastic packaging, wrapping papers and metal packaging.


Picture 3: Examples of household packaging: glass packaging, (beer) crates, steel packaging, pieces of plastic bags and homogenized plastic nets.

For the determination of $Cr^{6+}$ an alkaline digestion, described as above, was performed. $Cr^{6+}$ was analysed in the digestion solutions with IC-DPC and IC-ICP-MS. $Cr^{6+}$ can be found in chromate-based paints. Chromate-based paints primers are applied, as a first-coat primer, for corrosion inhibition. These paint primers generally consist of a paint matrix containing a sparingly soluble chromate salt such as strontium chromate. The chromate based paints contain an epoxy polymer, a chromate salt, a combination of organic solvents, dispersion agents and other fillers. To improve extraction efficiency from paint samples, the use of 1,4 dioxane in a second successive alkaline digestion was reported. Empirical observation indicated that 1,4-dioxane broke up the paint samples into strands and filaments. This increased the surface area of the paint available to the digestion solution and enhanced the extraction of Cr from the paint matrix. However only a slight improvement using 1,4-

dioxane was reported [26]. For this reason no modifications were applied in this study to the alkaline digestion method.

A good correspondence was found between the total $Cr^{6+}$ content analysed with IC-DPC and IC-ICP-MS. The duplo analysis performed on each sample (spiked and unspiked) were in good agreement, indicating that the alkaline digestion was a reproducible method for extracting $Cr^{6+}$ from packaging material. It has to be stressed that this method determines the alkaline soluble $Cr^{6+}$, which is based on literature the most complete but may differ from the total $Cr^{6+}$ content. However it is the author's opinion that at this moment this digestion is state of the art from point of view of minimal species interconversion on the one hand and maximum amount $Cr^{6+}$ extracted on the other. Some results of this study are shown in table 6.

| | IC-DPC | | | IC-ICP-MS | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Identif. | $[Cr^{VI}_{total}]$ | R | $[Cr^{VI}]$ | $[Cr^{VI}_{total}]$ | $[Cr^{VI}_{natural}]$ | $[Cr^{VI}_{spike}]$ | R | $[Cr^{III}_{spike}]$ | Ox. | $[Cr^{VI}]$ |
| | ng ml$^{-1}$ | % | mg kg$^{-1}$ | ng ml$^{-1}$ | ng ml$^{-1}$ | ng ml$^{-1}$ | % | ng ml$^{-1}$ | % | mg kg$^{-1}$ |
| Orange net | 1723 | | 71 | 1579 | | | | | | 65 |
| Orange net + spike[a] | 1739 | 16 | | 1699 | 1600 | 94 | 94 | 4.5 | 4.5 | 63 |
| Orange net | 71 | | 2.9 | 62 | | | | | | 2.6 |
| Orange net + spike[a] | 160 | 89 | | 169 | 66 | 101 | 101 | 2.0 | 2.0 | 2.7 |
| Yellow net | 190 | | 8.5 | 201 | | | | | | 9.0 |
| Yellow net + spike[a] | 318 | 128 | | 321 | 216 | 102 | 102 | 1.8 | 1.8 | 9.0 |
| Yellow shopping bag | 541 | | 22 | 495 | | | | | | 20 |
| Yellow shopping bag + spike[a] | 662 | 121 | | 666 | 552 | 108 | 108 | 5.2 | 5.2 | 22 |
| Yellow shopping bag | 321 | | 13 | 342 | | | | | | 14 |
| Yellow shopping bag + spike[a] | 438 | 117 | | 405 | 308 | 93 | 93 | 4.6 | 4.6 | 12 |
| Yellow drum | 16660 | | 660 | 16400 | | | | | | 650 |
| Yellow drum + spike[a] | 15520 | 1134 | | 16400 | 16240 | 116 [b] | 116 | 3.1 | 3.1 | 640 |
| Yellow drum | 8 | | 0.31 | 6.6 | | | | | | 0.3 |
| Yellow drum + spike[a] | 100 | 92 | | 104 | 4 | 99 | 99 | <1 | <1 | 0.2 |
| Red drum | 99 | | 3.8 | 102 | | | | | | 3.9 |
| Red drum + spike[a] | 202 | 103 | | 212 | 110 | 101 | 101 | 1.3 | 1.3 | 4.2 |

Table 6. Alkaline extraction on some packaging materials (the key to the used symbols is given in table 4-5).[a] added amount of spike 100 ng ml$^{-1}$ $^{50}Cr^{3+}$ + 100 ng ml$^{-1}$ $^{53}Cr^{6+}$. [b] this sample was, due to the high concentration of natural $Cr^{6+}$, analysed in 100 fold diluted. The actual measured enriched spike $Cr^{6+}$ in this solution amounted 1.16 ng ml$^{-1}$. The recovery of 116 % is based on this measurement but has to be seen as an indicative value as the detection limit is around 1 ng ml$^{-1}$.

Of all analysed samples two packaging materials contained concentrations higher than 100 mg /kg. A yellow metal drum used for industrial packaging contained 650 mg/kg $Cr^{6+}$ and a gold coloured wrapping paper contained 210 mg/kg $Cr^{6+}$. The recovery of the enriched spike $Cr^{6+}$ measured with IC-ICP-MS varied between 90 and 110% indicating that during the digestion all $Cr^{6+}$ compounds were stable. Except for some analysed steel cans (containing fruit, vegetables, sardine) the enriched spike $Cr^{6+}$ was not recovered. The oxidation of the added enriched spike $Cr^{3+}$ was negligible in all digestions. The approximately 2 % oxidation occurred as well in the blank solution were enriched $Cr^{3+}$ was added indicating that this problem was likely to originate from traces of $H_2O_2$ present in the enriched $Cr^{3+}$ spike solution.

From this study it could be concluded that critical packaging are predominantly coloured materials. Presence of *heavy metals* in the sample was not attributed to the bulk sample but in most cases to the applied colouring agents and pigments (red and yellow pigments, *e.g.*, lead chromate). In table 7 and 8, for each type of respectively household and industrial packaging a summary is made of the total flow on the Belgian market, the flow of the critical packaging and the *heavy metal(s*) causing an exceeding of the limits.

| type of packaging | packaging flow | critical packaging | critical packaging flow (% of total packaging flow) | 100 mg/kg limit exceeded due to: |
|---|---|---|---|---|
| glass | 44.40% | **decorated glass** | appr. 0.05% | Cd, Pb, possibly Cr (VI) |
| | | transparent glass | appr. 20% | Pb |
| | | brown glass | 24.4% | Pb |
| | | green glass | | Pb |
| | | blue glass | | Pb |
| paper/cardboard | 18.60% | / | / | / |
| steel | 10.90% | / | / | / |
| aluminium | 1.60% | / | / | / |
| plastic bottles | 8.30% | / | / | / |
| plastic | 10.80% | **shopping bags** | small | Pb, Cr (VI) |
| | | **nets** | small | Pb, Cr (VI) |
| | | crates | appr. 1.2% | Pb, Cd |
| wood | Small | / | / | / |
| beverage carton | 2.70% | / | / | / |
| others: | | | | |
| **wrapping foil** | Small | | | Cr (VI), Pb |
| others | 2.80 % | / | / | / |

Table 7: Flows and problem areas per type of household packaging on the Belgian market.

| type of packaging | packaging flow (min-max) | critical packaging | critical packaging flow (min-max %) | 100 mg/kg limit exceeded due to: |
|---|---|---|---|---|
| paper/cardboard | 24-49 % | / | / | / |
| metal | 8-10 % | **drums** | almost all metal packaging are drums | Pb, Cr (VI) |
| plastic | 13-21 % | pallets | unknown | possibly Pb |
| wood | 28-43 % | / | / | / |
| others | 2-2.4 % | brown glass | unknown | Pb |

Table 8: Flows and problem areas per type of industrial packaging on the Belgian market.

## Conclusions

This study has proven that, regarding some of the legal concerns related to $Cr^{6+}$ in the environment, the alkaline digestion according to US EPA 3060A followed by ion chromatography - 1,5-diphenylcarbazide spectrophotometry is suited for routine analysis of hexavalent chromium in solid matrices. The ability of the species-specific isotope dilution mass spectrometry to calculate the recovery of the enriched hexavalent chromium spike on the one hand and the oxidation of the Cr III

spike on the other in the digestion solution was a helpful tool to assess the species interconversion and consequently the validity of the digestion.

This method determines the alkaline soluble $Cr^{6+}$, It can be stated however that based on literature this method is one of the most rigorous digestions but still can differ from the total $Cr^{6+}$ content. The accuracy of the determination of hexavalent chromium in solid matrices remains a challenging field of effort and improvement from point of view of minimal species interconversion on the one hand and maximum amount of $Cr^{6+}$ extracted on the other.

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### 3.3.2. THE BAN ON HEXAVALENT CHROMIUM IN ELECTRONIC WASTE (ROHS AND WEEE)


Waste of electrical and electronic equipment (WEEE or e-waste) and the Restriction of Hazardous Substances (RoHS Compliance) has become an intensely debated global issue [128]. Electronic and electrical products, such as refrigerators, washing machines, mobile phones, personal computers, printers, and television sets, are ubiquitous in the modern society. At the same time, continuing technological innovation has resulted in early obsolescence of many electronic/electrical products. The average lifespan (2 yr) of a new computer, *e.g.*, was in 2005 less than half of that (4.5 yr) in 2000, and has been continually declining. A combination of increasing ownership and shortened lifespan has led to rapid growth in the amounts of unwanted and obsolete electronics (commonly known as e-waste). It was estimated that the global rate of e-waste generation globally is approximately 40 million tons $yr^{-1}$.

Numerous studies have revealed that abundant toxic compounds, including, but not limited to, *heavy metals* (Cr(VI), Hg, Cd, Pb), polychlororinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) could be leached into the ambient environment during e-waste disposal according to primitive methods, posing serious risks to environmental and human health. Well-managed sanitary landfills have been demonstrated to be the most efficient option for preventing these toxic compounds from leaching. The relatively high cost for e-waste disposal in developed countries has driven recycling operations to developing countries such as China, India, and Pakistan (Figure 32 , left). It is estimated that nearly 80% of all e-waste generated in developed countries is exported elsewhere.


Figure 32: Map (left) of the main routes of transboundary transport of e-waste and (right) e-waste processing regions in China (e = e-waste recycling site, courtesy of [128]).

Presently, approximately 70% of e-waste generated worldwide is processed in China every year. The Guangdong Province of South China and the Zhejiang Province of East China (Figure 32, right) are the two regions with the most intensive e-waste recycling activity, mainly due to their convenient locations for import. Primitive recycling operations can release large amounts of toxic compounds, subjecting local workers to health hazards. Significantly higher levels of chromium, of 1160 ng $m^{-3}$ in

airborne particles, of 137−477 µg $g^{-1}$in soil from an e-waste recycling site and of 307 µg $g^{-1}$ in surface sediment from the Nanguan River, draining through an e-waste recycling area of Taizhou, were found (for comparison, see also ambient concentrations in Table 8, p.66)[128].

Human health is seriously threatened by e-waste recycling via direct exposure routes such as inhalation and dust ingestion. Concern about the high toxicity of Cr(VI) resulted in legislative demands by the European Union to restrict its usage and to reduce the environmental impact of disposed (e)-wastes [129].

Since July 2006, electrical and electronic equipment (EEE) brought onto the European Market, has to be RoHS (Restriction of Hazardous Substances) compliant. This compliancy implies the restriction of six hazardous substances, *i.e.,* lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE) in EEE.

To support the Belgian Inspectorate with the enforcement of this legislation, an inspection campaign was developed by VITO as an exercise to gain experience in the different aspects of RoHS inspection [133]. A total of 88 electrical and electronic devices were (non-destructively) screened on-site by VITO and Federal inspectors in different electronic shops with EDXRF. In total 27 products were purchased at 5 different locations and dismantled in the laboratory for further testing. For detecting the presence of Cr(VI) in chromate coatings (on screws), a spot-test screening procedure using cotton sticks impregnated with diphenylcarbazide was used. Based on independent visual ratings, a lower limit of detection of 20-50 ng Cr (VI) by point sampling of the screening method was estimated. The spot test represented a good and specific method for screening the presence of Cr(VI) in chromate coatings.


Picture 4: RoHS inspection campaign, electrical and electronic devices were (non-destructively) screened on-site in different electronic shops with EDXRF; 27 products were purchased and dismantled for further testing.

From the year 2000 onwards, VITO was commissioned by OVAM to participate in the European Committee for Standardization - technical committee 292 - Characterization of waste (CEN TC 292, see also § 1.3) in support of the implementation of the EU landfill Directive. Within this workgroup, a European document describing the state-of-the-art extraction and determination methods for the total content of hexavalent chromium in raw waste and other solid materials was prepared (CEN/TR 14589:2003). Thereafter, and in accordance with the recommendations of this technical report, VITO in coordination with the Federal Institute for Materials Research and Testing (BAM, Germany) organised an inter-laboratory comparison in 2005-2006 for the validation of a European standard (EN 15192) for the determination of hexavalent chromium in solid material.

Despite the good analytical performance of the wet-chemistry analytical methods, their use for determination of Cr(VI) in solid materials always requires an extraction step, which may induce modification of the speciation. Even if the precision of the quantification step is an important

parameter, a complete or quantitative extraction step still is the main challenge to obtain accurate results.

Different extracting solutions have been used for the extraction of Cr(VI) from solid materials. Based on a review study of digestion methods from soil published in 1995, the method yielding the best results relied on a combination of $Na_2CO_3$ and NaOH with continuous swirling and heating at 95°C [134]. This approach was promoted in 1996 by the US EPA with the reference US EPA Method 3060A and was adopted in 2006 as the basis of the European standard EN 15192:2006 as well (see paper: Validation of an European standard for the determination of hexavalent chromium in solid material, *J. Environ. Monit*., 2007). There is at this time a consensus on the use of an alkaline digestion solution to achieve minimal species interconversion and maximum extraction efficiency of hexavalent chromium from solid materials. However and despite the availability of these standard methods, it remains difficult to determine whether observed differences between extraction methods are due to interconversion of chromium species in the extracts or to a low extraction yield or to both.

Recently and using X-ray Absorption Near Edge Structure (XANES), it was reported that a combination of $Na_2CO_3$ and NaOH does not completely solubilize all forms of hexavalent chromium, depending on the matrix of the soil samples [135]. On the same soil sample that was used in the inter-laboratory comparison for the validation of the European standard EN 15192 (see Table 1a, soil 2, p. 115), only 57% of the total Cr(VI) content measured by XANES was extracted. This work also showed that the use of spiked soils for extraction studies is not an ideal approach for studying alkaline extraction methods as this does not necessarily reflect the complexities of real soils. It is conceivable that XANES spectroscopy can serve as a benchmark for improvements or modifications to alkaline extraction methods, which might consist of sequential extraction approaches or different extraction conditions, tailored to the type of matrix being studied. This future work would be of particular importance in the case of environmental studies dealing with the toxicity of Cr(VI), which may concern easily extractible Cr(VI) but also more insoluble phases.

The conclusion of the European validation study: "*The accuracy of the determination of Cr(VI) in solid matrices remains a challenging field in terms of maximum extraction efficiency and minimum species interconversion*" was confirmed but the problem was not resolved.

# Validation of an European standard for the determination of hexavalent chromium in solid material

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(Reference list of this paper, see p. 127)

*Abstract*

*A European standard for the determination of Cr(VI) in solid material has been elaborated in the framework of an international co-operation and finally validated in the course of an interlaboratory comparison. The procedure is based on the alkaline digestion prescribed by US EPA method 3060A followed by ion chromatography and determines an operationally defined content of Cr(VI), including water-soluble and insoluble chromates. A preliminary robustness study was carried out in order to compare different extraction methodologies and to study the equivalency of different analytical methods for the determination of Cr(VI) in alkaline extracts of soil and waste materials. During an interlaboratory validation trial with 19 European laboratories a set of 4 samples (2 soil and 2 waste samples) was analysed to determine performance characteristics for different combinations of digestion and detection methods. With the procedures prescribed by the new European standard (EN 15192) acceptable results were obtained for both soil samples and one of the waste samples (sludge). However, for the second waste sample (fly ash) a large deviation in analytical results was observed. This indicates that particularly for waste materials a possible occurrence of strong matrix effects has to be considered and supplementary quality control data are needed in order to assess the validity of analytical results. The accuracy of the determination of Cr(VI) in solid matrices remains a challenging field in terms of maximum extraction efficiency and minimum species interconversion.*



## Introduction

The two oxidation states of chromium present in the environment, *i.e.,* Cr(III) and Cr(VI), are different in physico-chemical properties. Cr(III) is considered to be a trace element species essential for the proper functioning of living organisms. Hexavalent chromium (Cr(VI)) compounds are known to be toxic and carcinogenic agents for a variety of organisms. Toxicity, mobility and bioavailability of chromium strongly depend on its chemical form. Most Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to sparingly soluble Cr(III) species. Because of the ecological relevance of chromium species in the environment, a number of reviews of analytical methods for the determination of Cr(VI) have been published.[1-5]

To limit the release of Cr(VI) into the environment, the European Commission has set-up restrictions in several directives. These European directives have triggered studies and new analytical protocols

for Cr(VI) determination and Cr speciation in solid matrices: packaging material,[15] cement,[16] materials in the automotive industry,[17] steelmaking solid waste,[18] fly ash,[19] paint samples[20] and airborne Cr(VI) compounds.[21,22]

Within the framework of the Landfill Directive (2003/33/EC) knowledge of the composition of the waste is the first step in the acceptance procedure for a safe disposal.[6] In accordance with the criteria for acceptance of waste at landfills some European member states have implemented leaching limit values for Cr(VI). For this reason European standard EN 12506 was developed for the analysis of Cr(VI) in water eluates from solid waste material.[7]

Enforcement of Packaging Directive 62/94 has required the development of reliable reference methods for the determination of *heavy metals* in glass.[8] The International Commission on Glass developed in this framework a recommended procedure for the determination of Cr(VI) detectable down to 2 mg Cr(VI)/kg of glass.[9]

The European Directive 2003/53/EC restricts the use of cement and cement products, that contain, when hydrated, more than 2 mg/kg of soluble Cr(VI).[10] CEN/TC51 has recently proposed a method for the determination of the water soluble Cr(VI) content of cement.[11] Also within the framework of 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment a method for the determination of Cr(VI) is under development within the International Electrotechnical Commission.[12,13]

Several European member states have issued regulatory or reference values for Cr(VI) in soil for risk assessment purposes. In soil for agricultural use a maximum recommended concentration of 6.6 mg Cr(VI)/kg dry substance has been proposed in the Flemish Region of Belgium.[23] For the most sensitive type of land use the Swedish guideline value suggest a maximum concentration of 5 and 120 mg/kg dry substance for Cr(VI) and Cr(III) respectively.[24] In Italy the highest permissible Cr(VI) concentrations in soil are 2 and 15 mg/kg, depending on whether they are exploited for parkland or industrial uses.[25]

However for the determination of Cr(VI) in contaminated soil and solid waste material no European standard is available. For this reason, a state of the art document regarding Cr(VI) speciation was prepared by Working Group 3 of Technical Committee 292 (Characterisation of waste) of the European Committee for Standardisation (CEN/TC292/WG3).[26] In the document an overview of Cr(VI) speciation in solid materials has been given. As a result of the survey, it was decided by CEN/TC292/WG3 in co-ordination with Subcommittee 3 of Technical Committee 190 of the International Organisation for Standardisation (ISO/TC190/SC3) to propose a common standard for the determination of hexavalent chromium in solid material based on existing standards.

Picture 5: In- and outdoor meetings of CEN TC 292 WG 3 at Lofoten (Norway, left), Aix-en-Provence (France, middle) and Bokrijk (Belgium, right).

For the extraction of Cr(VI), US EPA method 3060A and ISO 16740 were considered, whereas for the determination of Cr(VI) in the extract solution, US EPA 7199, ISO 16740 and ISO 10304-3 were taken into account.[14,27,42,44]

As the scope of these standards did not cover solid material (with the exception of US EPA 3060A), a robustness study had to be carried out in order to optimise the selected methodology and to evaluate the applicability for soil and especially waste samples. This paper describes the results of the robustness study and the results of the subsequent interlaboratory validation study on the determination of Cr(VI) in solid material.

## Extraction of Cr(VI) from solid matrices

To quantify Cr(VI) concentrations in a solid matrix and verify their compliance with maximum contaminant limits, a preliminary extraction of Cr(VI) from the solid is necessary. Extractants should be able to solubilize all forms of Cr(VI) without inducing changes in the speciation of chromium. The extraction procedure is not required to be selective for Cr(VI) since the differentiation between oxidised and reduced Cr species may be obtained by using specific analytical methods.

Initial attention to the determination of Cr(VI) in solid matrices was given to Cr(VI) levels in workplace atmospheres. In 1977, the National Institute for Occupational Safety and Health (NIOSH) proposed a method for the determination of Cr(VI) in atmospheric particulate matter. In 1984, the US EPA proposed a protocol, known as Method 3060, which consisted of digesting 100 g solid sample in 400 mL hot, alkaline solution of 0.28 M $Na_2CO_3$ and 0.5 M NaOH (pH about 12) for 30 – 45 min.[28] Vitale *et al*. tested the accuracy of the hot alkaline digestion of soil samples and investigated the reasons for occasionally poor Cr(VI) spike recoveries.[29] In their study they confirmed the ability of the method to extract soluble and insoluble Cr(VI) forms and concluded that very poor Cr(VI) spike recoveries were observed only in strongly reducing samples. They proved that method-induced oxidation of Cr(III) might occur with freshly precipitated $Cr(OH)_3$. To help interpret recovery data, they suggested the use of ancillary soil chemical parameters, including redox potential, pH, $S^{2-}$ and total organic carbon concentrations as indicators of the redox state of samples. In the case of samples characterised by strong reducing conditions, poor Cr(VI) recoveries should not be attributed to deficiencies of the used analytical methods without any additional proof. It is more likely that they are an indication on the potential of samples to reduce Cr(VI) spike and on their inability to sustain the existence of Cr(VI) in the original sample.

James *et al*.[30] compared five different extractants for Cr(VI) from soil: distilled water (pH 5.7), phosphate buffer (pH 7.0), carbonate-hydroxide solutions (pH 12) with and without heating, and hydroxide solutions (pH 13) with sonication. Their findings suggested that a carbonate-hydroxide solution heated at 85 °C was the most effective extractant for operationally defining Cr(VI) in soil. In 1996 US EPA revised the Method 3060 for extracting Cr(VI) from soil, sludges, sediments and solid wastes.[27] This new method (3060A), that was adopted as basis for the European standard, consisted of an alkaline digestion at 90 – 95 °C for 60 min according to the findings by James *et al*.[30]. This method consists of placing 2.5 g of a field-moist and homogenised sample in a 250 mL digestion vessel to which 50 mL of digestion solution (0.28 M $Na_2CO_3$/0.5 M NaOH), 400 mg of $MgCl_2$ and 0.5 mL of 1.0 M phosphate buffer (0.5 M $K_2HPO_4$/0.5 M $KH_2PO_4$) are added. The addition of $Mg^{2+}$ in a phosphate buffer to the alkaline extraction solution will prevent risks of Cr(III) oxidation, which otherwise may lead to Cr(VI) overestimate, particularly in samples with high Cr(III)/Cr(VI) ratios.

Although the US EPA revised Method 3060A gives maximal dissolution of all forms of Cr(VI) in solid samples while minimizing method-induced oxidation and reduction, species transformation may still occur. To correct for species transformation in the analysis of Cr(VI) in solid samples, speciated

isotope dilution mass spectrometry can be used as described by Huo and Kingston.[31] EPA RCRA Method 6800 [Speciated Isotope Dilution Mass Spectrometry (SIDMS)] addresses the correction for such degradations or conversion.[32]

Cr(III)-Cr(VI) interconversions may take place when reactants, which are able to reduce Cr(VI) or oxidise Cr(III) are present. The experimental conditions adopted for the extraction of Cr(VI) from solid matrices control these possible interconversions. Cr(VI) may react with many inorganic reductants such as Fe(II) and sulphide; a number of organic compounds including carboxylic and hydroxo-carboxylic acids, aldehydes, phenols, humic acid, *etc*. are also able to reduce Cr(VI). Humic material and Fe(II) are common components in soil and sediments and can be easily released from these solids into strong alkaline solutions. However at pH values higher than 10, the risk of reduction of Cr(VI) is strongly diminished.

Contrary to the diminished risk of reduction of Cr(VI) with increasing pH, the risk of oxidative processes converting Cr(III) to Cr(VI) tends to increase with increasing pH. Cr(III) aging is also strongly and positively affected by increase in pH and temperatures, thus reducing as matter of fact the potential oxidation of Cr(III). The term aging refers to the change in physical and chemical properties of freshly precipitated metal hydroxides and metal oxide hydrates as a function of time.[33] Aging processes include changes in the physical state (recrystallization), chemical structure (formation of new crystalline phases accompanied by changes in atom connectivity), and composition (hydrolytic polymerization).

Molecular oxygen and manganese oxides are possible oxidants during the digestion of solids. The US EPA method 3060A took into account the possibility that native Cr(III) in solid matrices could be oxidised under alkaline conditions and suggested that, in the case the oxidation was suspected, $Mg^{2+}$ was added to the alkaline extracting solution to suppress the oxidation.[27] It was hypothesised that the suppression was due to Cr(III) coprecipitation with $Mg^{2+}$ or to sorption of $Mg^{2+}$ on Mn oxides rendering them less prone to oxidise Cr(III).[29] $Mg^{2+}$ was also proved to play a strong negative effect on the rates of oxidation of Cr(III) with $H_2O_2$ because of its influence on the aging of Cr(III).[34] This effect was supposed to be due to the formation of a solid phase of the type $Cr_xMg_{(1-x)1.5}(OH)_3$ that, similarly to the mixed solid phase $Cr_xFe_{(1-x)1.5}(OH)_3$, controls the solubility of Cr(III).[35] This effect of $Mg^{2+}$ is probably observed also in the case of the oxidation of Cr(III) with $O_2$ and $MnO_2$ and substantiates the US EPA choice of adding this ion to suppress the oxidation of Cr(III) during the alkaline digestion of solids. A similar influence on Cr(III) aging was also proved in the case of carbonate.[34]

Based on these considerations concerning the kinetics of Cr(III) oxidation, a value of pH around 10, high temperature and high concentrations of $Mg^{2+}$ and carbonate ions would minimise risks of Cr(III) conversion to Cr(VI) during the digestion of solid samples.

## Determination of Cr(VI) in extracts

The photometric diphenylcarbazide (DPC) method is the most common method for determining Cr(VI) in aqueous solutions.[36] Nevertheless, this method suffers from the presence of interfering compounds, some of which are explicitly reported in published protocols.[37,38] In addition to species containing molybdenum, mercury, iron, vanadium, which give a positive interference, the presence of reductants able to compete with DPC under acid conditions may lead to underestimation of Cr(VI) concentrations. Hydrogen peroxide, which reduces Cr(VI) to Cr(III) under acid conditions, is one of the possible reductants in aqueous solutions. These also include Fe(II), sulphide, sulphite and a number of organic compounds. However, the presence of effective concentrations of reductants of

Cr(VI) is not common in the analysis of aqueous samples, while it becomes much more probable in the case of the application of the DPC method to soil and waste extracts.

Strong alkaline conditions favour the dissolution of Fe(III) species and humic-like matter that interfere in the determination of Cr(VI) by the DPC method. The dissolution of Fe(III) is driven by the formation of negatively charged Fe(III) hydrolysis products such as $Fe(OH)_4^-$ while the release of humic matter is connected with the formation of humates, which are soluble under strong alkaline conditions.[39,40]

To separate Cr(VI) from positive interferences ion chromatography (IC) can be used.[41] The ion chromatographic method obviates most of problems due to dilution of the sample with the eluent stream, passage through a guard column and Cr(VI) separation on an anion exchange column. An ion chromatography method followed by a post column derivatisation of Cr(VI) by DPC was published as US EPA 7199 and ISO 16740.[14,42] Moreover when applying derivatisation of Cr(VI) with DPC, the use of the ion chromatography method is advocated to overcome interferences from reductants during the post column reaction.
An ion chromatography method followed by direct spectrophotometric detection of Cr(VI) at 365 nm was published as ISO 10304-3.[44]

## Experimental

### Collection and preparation of the samples

For the robustness study, three soil samples and three waste samples were selected, homogenised and divided into subsamples by means of a rotating sample divider into 100 mL brown glass bottles (containing 50 -100 g of sample). A description of the samples and sample pretreatment is given in Table 1a.

| Code | Sample origin | *Sample pretreatment* |
|---|---|---|
| **Soil 1** | sandy soil, collected at a depth from 2 to 9 m from a site with galvanising industry (Belgium) | *A: air-dried, sieved (< 1 mm) and homogenised* |
| | | *B: air-dried, sieved (< 1mm), ground with a ball mill to pass (> 95 %) a 125 µm sieve and homogenised* |
| **Soil 2** | loamy soil, collected along high way berm of E17 at a depth of 1.5 – 2.5 m (Belgium) | *air-dried, sieved (< 1 mm), ground with a ball mill to pass (> 95 %) a 250 µm sieve and homogenised* |
| **Soil 3** | sandy soil with a very low content of organic matter, excavated during a remediation campaign on the terrain of a former electroplating plant (Germany) | *A: air-dried homogenised fraction 0.5 - 2.0 mm* |
| | | *B: air-dried fraction 0.5 - 2.0 mm, ground with a ball mill to pass (> 95 %) a 250 µm sieve and homogenised* |
| **Waste 1** | paint sludge (Italy) | *air-dried, crushed and sieved to < 2 mm, further completely ground to particle size < 250 µm and homogenized* |
| **Waste 2** | fly ash (France) | *sieved (< 250 µm) without additional drying and homogenized* |
| **Waste 3** | filter cake (Belgium) | *air-dried, sieved (< 1 mm) and homogenised.* |

Table 1a: Description of the samples and the sample pretreatment.

For indications regarding the major matrix components, all samples were analysed with an Energy Dispersive - X-Ray Fluorescence (EDXRF) screening method (Table 1b). The high performance X-LAB2000 (Spectro Analytical Systems, Kleve, Germany) spectrometer was equipped with a 400 W Pd end-window tube and a Si(Li) detector cooled with liquid nitrogen. For signal optimization the used

targets were $Al_20_3$ and Pd as Barkla polarizer, an HOPG crystal as Bragg polarizer and a Mo target as secondary target. The software was also provided with a quantitative programme set up with geological samples. For laboratory analysis, all samples were analyzed as powders (dried and finely ground) and placed in XRF sampling cups (Bruker AXS, Karlsruhe, Germany) provided with a 2.5 µm Mylar foil (Chemplex, Tuckahoe, NY, USA).[43] For the determination of the elements C, H, N, S a Truspec elemental analyser (LECO Instrumente GmbH , Mönchengladbach, Germany) was used.

| Element | Dimension | Soil 1 | Soil 2 | Soil 3 | Waste 1 | Waste 2 | Waste 3 |
|---|---|---|---|---|---|---|---|
| TIC | % | 0.29 | 1.15 | 1.03 | 2.62 | 0.59 | 0.34 |
| TOC | % | 0.05 | 1.14 | 0.59 | 0.06 | 0.10 | 0.14 |
| H | % | < 0.1 | 1.04 | - | < 0.1 | < 0.1 | 1.45 |
| N | % | 0.066 | 0.066 | - | 0.830 | 0.047 | 0.105 |
| S | % | 0.203 | 0.444 | 0.588 | 1.0 | 3.77 | 11.3 |
| Al | % | 0.7 | 2.5 | 1.0 | 1.8 | 1.3 | < 0.1 |
| Ca | % | 2.2 | 9.3 | 7.3 | 11 | 17 | 19 |
| Fe | % | 0.46 | 6.5 | 1.7 | 5.8 | 0.81 | 8.0 |
| K | % | 1.0 | 0.47 | 0.99 | 0.21 | 4.1 | 0.016 |
| Mn | % | 0.007 | 0.062 | 0.034 | 0.120 | 0.036 | 0.100 |
| Si | % | 31 | 15 | 24 | 2.6 | 3.5 | 0.061 |
| Ti | % | 0.10 | 0.20 | 0.14 | 0.033 | 1.30 | 0.008 |
| As | mg/kg | 2.2 | 26 | 5.4 | < 2 | 34 | 11 |
| Ba | mg/kg | 298 | 378 | 424 | 993 | 1220 | < 18 |
| Br | mg/kg | < 1 | 1.2 | < 1 | 121 | 891 | < 1 |
| Cd | mg/kg | < 3 | < 3 | 7 | < 3 | 267 | < 3 |
| Cl | mg/kg | 626 | < 55 | 129 | 5160 | 162000 | 63 |
| Co | mg/kg | < 8 | 100 | < 8 | 75 | 18 | 138 |
| **Cr** | **mg/kg** | **46** | **8700** | **972** | **14800** | **592** | **18600** |
| Cu | mg/kg | 7.6 | 58 | 68 | 6910 | 1020 | 350 |
| Hg | mg/kg | < 2 | < 2 | < 2 | 2.5 | 2.6 | < 2 |
| Mo | mg/kg | < 2 | < 2 | < 2 | 181 | 31 | 735 |
| Ni | mg/kg | 7.8 | 457 | 22 | 2640 | 63 | 11300 |
| P | mg/kg | 375 | 970 | 410 | 13400 | 1380 | 224 |
| Pb | mg/kg | 7.6 | 196 | 109 | 1810 | 3700 | 29 |
| Sb | mg/kg | < 5 | 6.2 | 7.6 | 38 | 977 | 5.3 |
| Sn | mg/kg | < 9 | < 9 | 27 | 767 | 1320 | 13 |
| Sr | mg/kg | 67 | 97 | 170 | 396 | 359 | 104 |
| Zn | mg/kg | 14 | 293 | 159 | 2770 | 15000 | 55 |
| Zr | mg/kg | 180 | 175 | 150 | 1350 | 195 | < 11 |

Table 1b: Matrix composition of the samples.



**Analytical methods**

The following digestion equipments were evaluated during the robustness study:

- a thermostatically controlled hotplate with a magnetic stirrer (Ikamag RCT, IKA Labortechnik, Germany);
- a thermostatically controlled heating block with a magnetic stirrer and reflux condenser (Behrotest DET 6 MAG, Behr Labortechnik, Germany );
- an ultrasonic-assisted leaching system, where the ultrasonic radiation was applied by means of a Branson 5210 ultrasonic bath (47 kHz, 185 W, The Netherlands).

For the determination of Cr(VI) in solid material the following alkaline digestion procedure was applied: Approximately 2.5 g of the homogenised sample was placed in an appropriate digestion vessel. 50 mL of digestion solution (0.28 M $Na_2CO_3$/0.5 M NaOH), 400 mg of $MgCl_2$ and 0.5 mL of 1.0

M phosphate buffer (0.5 M $K_2HPO_4$/0.5 M $KH_2PO_4$) were added to the solid sample. The samples were heated to (92.5 ± 2.5) °C for at least 60 minutes under continuous stirring (or, in case of ultrasonic agitation, at 20 or 60°C). After digestion, the vessels were allowed to cool to room temperature and the solutions were filtered using a 0.45 µm membrane filter (regenerated cellulose Porafil membrane filter, Macherey-Nagel, Düren, Germany).

The determination of Cr(VI) in the alkaline extracts was performed after ion chromatographic separation by spectrophotometric detection either at 365 nm (direct UV detection) or at 540 nm after post-column derivatisation with 1,5-diphenylcarbazide in acid solution according to ISO 16740 and ISO 10304-3.[14,44] In parallel, Cr(VI) was determined by species-specific isotope dilution mass spectrometry according to Tirez *et al*..[15] The total Cr concentration in the alkaline digestion solutions was measured with ICP-AES after adjusting the pH < 2 with nitric acid.

## Results and discussion

### Robustness study

*Objectives*

Based on a survey of procedures in use in the different European member states it could be noticed that a harmonization of digestion equipment and measurement method was needed.[26] The robustness study was performed in order to study the equivalency of different methods for the determination of Cr(VI) in waste and soil using alkaline extraction and to produce a set of validation samples with a homogeneous Cr(VI) load.

Regarding the evaluation of the extraction methodology, the objectives of the robustness study implied the evaluation of hotplate, heating block and ultrasonic bath as digestion equipment. For the determination methods of Cr(VI) in the extract solution, the robustness study implied the evaluation of ion chromatographic separation and spectrophotometric measurement either at 365 nm or at 540 nm after post column derivatisation with 1,5 diphenylcarbazide and direct determination of chromium in the alkaline extract with inductively coupled plasma-atomic emission spectrometry (ICP-AES). The robustness study was performed within 3 laboratories (VITO, BAM and FENICE S.p.A.).

*Digestion equipment – soil samples*

Hotplate digestion was compared with ultrasound-assisted leaching on soil 1A/B and soil 3A/B (see Table 1a) in two different laboratories. Both laboratories reported differences between hotplate digestion at 92.5 °C and ultrasound-assisted leaching at respectively 20 °C and 60 °C on both soil samples. The recovery of Cr(VI) in the ultrasound-assisted leaching at 20 °C and 60°C was less than 50 % and 75 %, respectively, of the recovery of Cr(VI) with hotplate digestion. These results are in agreement with the comparison of five extraction methods on soils published by James *et al*..[30] The efficiency of extraction of different Cr(VI) forms ($K_2CrO_4$, $SrCrO_4$, $BaCrO_4$ and $PbCrO_4$) using hotplate digestion and ultrasonic extraction has also been studied in the frame of the determination of Cr(VI) in workplace air.[21] It was found that all these Cr(VI) forms (representing water-soluble, sparingly soluble and insoluble forms) were completely dissolved when hotplate digestion was employed, but that less than quantitative recovery for barium chromate was obtained using ultrasonic extraction.

The measured Cr(VI) content in soil 1 after hotplate digestion amounted to 2 mg/kg, while the total Cr content measured with EDXRF and ICP-AES after digestion with an acid mixture of $HNO_3$/HCl/HF according to EN13656 [45] amounted to 46 mg/kg. The measured Cr(VI) content in soil 3 after hotplate

digestion amounted to 400 mg/kg, while the total Cr content measured with EDXRF and ICP-AES after digestion with an acid mixture of $HNO_3$/HCl/HF amounted to 800 mg/kg.

The comparison between hotplate and heating block digestion was performed in one laboratory on soil 3A/B. The results are summarized in Table 2.

| | Soil 3A | Soil 3B | | |
|---|---|---|---|---|
| | mg Cr(VI)/kg | mg Cr(VI)/kg | Recovery $K_2Cr_2O_7$ spike % | Recovery $PbCrO_4$ spike % |
| **Heating block** | 359 ± 10 (n=3) | 394 ± 4 (n=9) | 99 – 102 | 100 – 101 |
| **Hotplate** | 352 ± 26 (n=4) | 402 ± 7 (n=4) | 96 – 100 | 96 – 98 |

Table 2: Results of the robustness study comparing hotplate and heating block digestion methods.

Both digestion equipments gave comparable results and quantitative recoveries even for the insoluble Cr(VI) spike $PbCrO_4$. The grinding of the sample to a particle size of less than 250 µm (soil 3B) was reported to yield a significant better precision between the subsamples. It was also noticed that the addition of $MgCl_2$ and phosphate buffer suppressed the (minor) oxidation of an added $CrCl_3$ spike (respectively 0,7 and 0.2 % oxidation of 1000 µg Cr(III) added to 50 mL of the alkaline digestion solution).

The determination of Cr(VI) on soil 1 revealed that approximately 20 % of a soluble Cr(VI) spike (250 µg, added as $K_2Cr_2O_7$) was not recovered. Duplicate analysis with both heating block and hotplate showed a (79 ± 2)% recovery. In order to control this reduction process on soil 1, the Cr(VI) in soil 1A/B was also determined by species-specific isotope dilution mass spectrometry. The measured Cr(VI) content on soil 1 amounted to 5 mg/kg. The used method allows the direct determination of biases during digestion and confirmed that only 77 % of the added isotopically enriched $^{53}$Cr(VI) spike was recovered in soils 1A/B. Moreover, also a 10 - 15 % oxidation of the isotopically enriched $^{50}$Cr(III) spike was observed on soil 1A/B. This underpins observations that reduction reactions of Cr(VI) by organic matter or other reducing reagents may occur simultaneously with oxidation of Cr(III).[46] The observed higher Cr(VI) content (5 versus 2 mg/kg) was attributed to incomplete suppression of oxidation due to addition of only 1/10 of the prescribed amount of $MgCl_2$ to the alkaline digestion solution. The diminished added amount of $MgCl_2$ was applied in order to reduce possible interferences of chloride during species-specific isotope dilution mass spectrometry measurement.
The determination of Cr(VI) in soil 2 indicated no particular problems regarding the digestion and possible oxidation/reduction processes. The measured Cr(VI) content in soil 2 after hotplate digestion amounted to 2000 mg/kg, while the total Cr content measured with EDXRF amounted to 8700 mg/kg. Soil 1B and 2 were selected as validation samples for the interlaboratory trial.

*Digestion equipment – waste samples*

The results of the determination of Cr(VI) on the filter cake sample (waste 3) showed large discrepancies. The addition of Cr(III) spike to control possible oxidation processes revealed that up to 90 % of the spike was oxidised during digestion. The measured Cr(VI) content in waste 3 after hotplate digestion amounted to 1000 mg/kg, while the total Cr content measured with EDXRF and ICP-AES after digestion with an acid mixture of $HNO_3$/HCl/HF amounted to 20,000 mg/kg. As stated above one must consider that when Cr(VI) is stabilised with respect to pH, Cr(III) is in an unstable environment. The determination of Cr(VI) in a matrix in which the Cr(III) content is more than 20 times that of Cr(VI) remains ambiguous. Prolongation of the digestion time from 1 to 2 and 3 hours showed an increase in the Cr(VI) content of about 25 % and 90 %, respectively. Also the drying of the

sample affected the Cr(VI) content drastically. Drying of this sample at different temperatures (40, 60, 80, 105 and 200°C) showed an increase of the apparent Cr(VI) content up to 10000 mg Cr(VI)/kg, suggesting an increase of oxidation potential with drying. In order to confirm the oxidation processes on waste 3, the Cr(VI) was determined by species-specific isotope dilution mass spectrometry. This method confirmed that on the air dried sample 20 % of the added isotopically enriched $^{50}$Cr(III) spike was oxidised during digestion, while the recovery of the added isotopically enriched $^{53}$Cr(VI) spike amounted to 95 %.

The determination of Cr(VI) in waste sample 1 indicated no particular problems regarding the digestion and possible oxidation/reduction processes and was therefore selected as validation sample for the interlaboratory trial. Waste sample 2 was also considered to be a representative waste sample and was retained for the validation.

*Direct determination of Cr(VI) in the alkaline extract*

When it is assumed that no species of chromium other than Cr(VI) are present after digestion then direct determination will be possible. Based on a study performed by the Danish Hydraulic Institute (DHI), the concentration of Cr(VI) in the alkaline digestion solution of soils equals the total chromium concentration and can be determined directly with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or atomic absorption spectrometry (AAS).[47] Practically, in order to prove that Cr(VI) is the only soluble form of chromium present in the alkaline digestion solution, spiking of the sample with Cr(III) followed by the same digestion procedure as applied to the test portion is required. Due to the high element concentrations, *e.g.* of sodium, in the alkaline digestion solution the calibration strategy must be adapted appropriately. In many cases matrix matching of the calibration solutions and/or dilution of the sample together with addition of internal standards or using the standard addition method is necessary. The filtration of the alkaline digestion solution before acidification is essential, as “active” chromium hydroxide, an exclusively hydrogen-bonded, layered array of $Cr(OH)_3(H_2O)_3$ units, instantaneously dissolves in acid to form $Cr(H_2O)_6^{3+}$.[33] One minute after its precipitation in the pH range 8.5-9.7, acidification yields > 99 % of $Cr(H_2O)_6^{3+}$. When precipitates of “active” chromium hydroxide are aged in buffered aqueous suspension, the amount of $Cr(H_2O)_6^{3+}$ recovered after rapid acid dissolution decreases with time.

The filtration of the alkaline digestion solution is also necessary to prevent possible losses of Cr(VI). Although completely extracted, for $BaCrO_4$ and $PbCrO_4$ there is a risk that these compounds can reprecipitate during neutralisation. Huo *et al*. have studied the processes responsible for possible losses of Cr(VI).[48] They found that $CO_3^{2-}$ is essential in the dissolution of $BaCrO_4$ and that the precipitation of $BaCO_3$ greatly decreases the concentration of the free $Ba^{2+}$, driving the dissolution of $BaCrO_4$ and releasing $CrO_4^{2-}$ as a free ion in solution. The precipitated $BaCO_3$ is removed at the filtration step. When neutralising the solution, $CrO_4^{2-}$ cannot precipitate because nearly all Ba has been removed during filtration.

On the other hand, the dissolution of $PbCrO_4$ in the alkaline digestion does not require $CO_3^{2-}$, because the process is driven by the formation of $Pb(OH)_2$ and $Pb(OH)_n^{2-n}$. Although much of the Pb can be removed after extraction as $Pb(OH)_2$ by filtration, certain complexed Pb species can still remain in the filtrate. During neutralisation and due to the continuously decreasing concentrations of $OH^-$ and $CO_3^{2-}$, the Pb species are converted from $Pb(OH)_n^{2-n}$ to $PbCrO_4$. Therefore some of the dissolved $PbCrO_4$ reprecipitates during neutralisation, resulting in the loss of Cr(VI) from solution.

The direct determination of Cr(VI) in the alkaline digestion solution by ICP-AES was evaluated during the robustness study. For the measurements the digestion solutions were diluted in 10 % (v/v) nitric acid (ultra pure) and were placed in an ultrasonic bath for at least 15 minutes to degas. The calibration solutions were prepared in 10 % v/v nitric acid solution (ultra pure). A 10 mg/l rhodium

containing solution of 10 % (v/v) nitric acid was added on-line as internal standard and mixed with the sample solution before introduction in ICP-AES (20 % internal standard / 80 % sample). The chromium emission line 205.522 nm was used as analytical detection line after correction with internal standard. A ratio of 0.99 ± 0.04 between direct determination of Cr(VI) in 22 different alkaline digestion solutions with ICP-AES versus ion chromatography with detection after post column derivatisation with 1,5-diphenylcarbazide was observed.

*Conclusion robustness study*

From the results of the robustness study it was concluded that hotplate and heating block digestions gave comparable results on all samples if continuously stirring was performed and the temperature was controlled. In contrary, ultrasonic bath extraction (at 25°C and 60°C) gave significantly lower recoveries of Cr(VI). The alkaline extracts were analysed with ion chromatography followed with either direct spectrophotometric detection or detection after post column derivatisation with 1,5-diphenylcarbazide. No significant differences could be observed between both detection methods. Direct determination of the total chromium content in the alkaline digestion solution of the different materials with ICP-AES gave comparable results when dilution and internal standard correction were performed.

In accordance with the results of the robustness study it was decided within CEN/TC292/WG3 and ISO/TC190/SC3/WG1 to limit the normative scope of the draft standard for digestion to hotplate and heating block equipment. The quantification of Cr(VI) in the alkaline digestion solution can be performed after ion chromatographic separation and either by direct spectrophotometrical measurement at 365 nm (direct UV detection) or after post-column derivatisation with 1,5-diphenylcarbazide in acid solution at 540 nm.
It was considered that the processing of Cr(III) and Cr(VI) spikes to estimate the accuracy of the method is a prerequisite when analysing unknown sample matrices. Spike recovery experiments not only reveal the quantitative recovery of the Cr(VI) spike, but also assist in the interpretation regarding the oxidation-reduction potential of the sample. Nevertheless, as could be shown for soil 1, waste 2 and waste 3, the determination of Cr(VI) in a matrix in which the Cr(III) concentration is more than 20 times that of Cr(VI) may remain ambiguous.



**Interlaboratory trial**

*Objectives*

The samples soil 1B, soil 2, waste 1 and waste 2 were retained from the robustness study and were considered as an appropriate set of validation samples with a homogeneous Cr(VI) load for the interlaboratory trial. These four samples and a quality control solution were sent to the participating laboratories listed in the acknowledgements (soil 1B was renamed soil 1 in the interlaboratory trial). The quality control sample consisted of a Cr(VI) spiked alkaline digestion solution with a Cr(VI) concentration of 424 µg/L and was intended to control the quality of the detection method. Data sets of participants for the soil and waste samples were accepted for further statistical evaluation only in the case that the results obtained for this control solution did not deviate more than 10% from the assigned value. For the four test materials, every participating laboratory was obliged to give results obtained at least by one of the methods proposed to be included into the analytical protocol of the planned new European standard (Table 3, methods A - D). Additionally, participants were requested to perform recovery experiments with Cr(III) and Cr(VI) spikes on each of the delivered samples. The amounts of added spikes had to be chosen according to the contents of Cr(VI) in the samples under investigation (same order of magnitude).

Data obtained with alternative digestion and detection methods could be reported as well (Table 3, methods E - O). The average results of the Cr(VI) determinations per method and per sample are summarised in Figure 1.

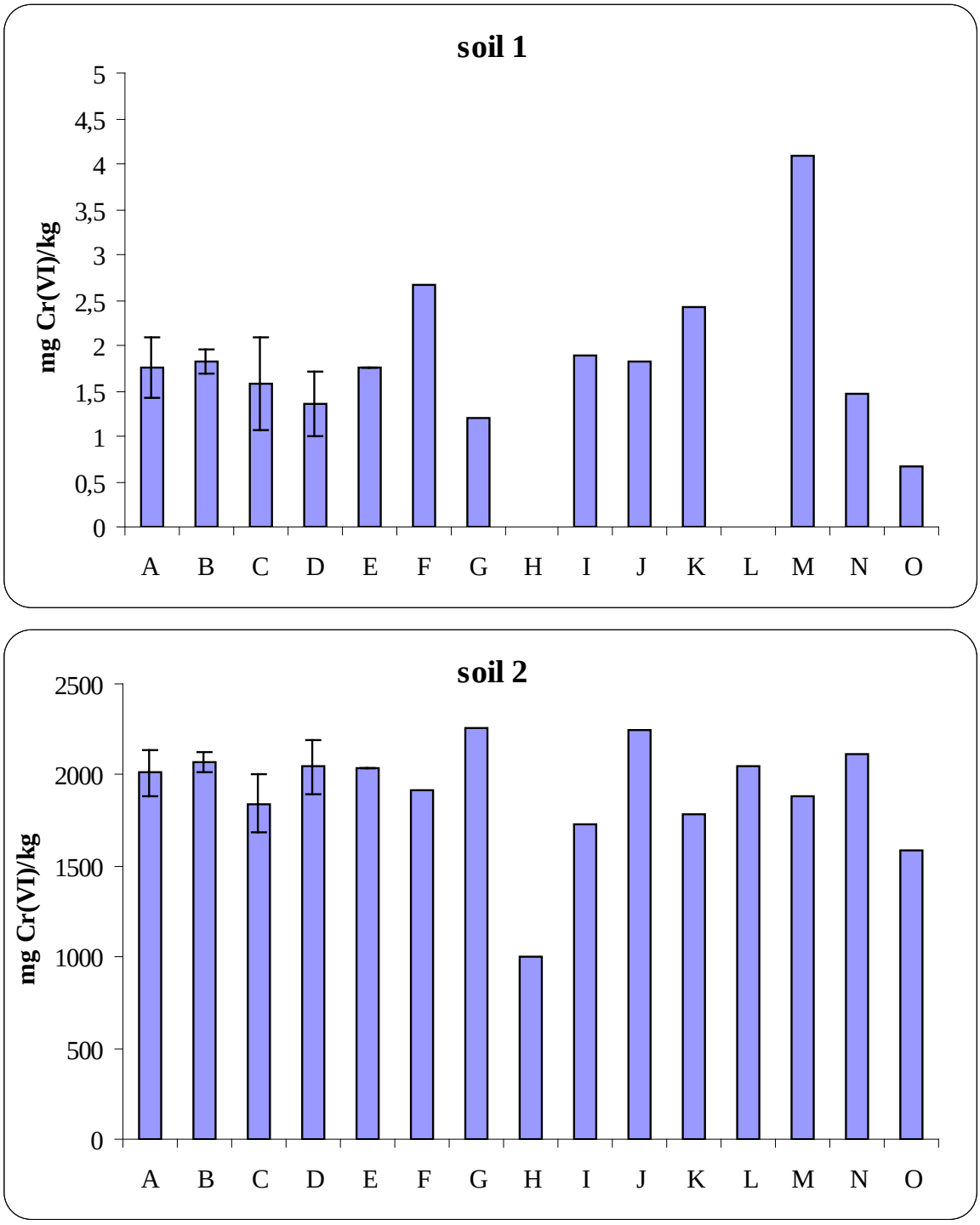


Figure 1a: Overview of accepted Cr(VI) results on soil 1 and soil 2 according to the different combinations of digestion and determination methods (see Table 3). For methods A-D, the error bar represents the 95% confidence interval of the mean calculated according to $C.I. = \pm t_{95\%, n-1} * s/\sqrt{n}$, with $t$ being a factor derived from Student´s t-distribution, $s$ the standard deviation and $n$ the number of all accepted individual results.

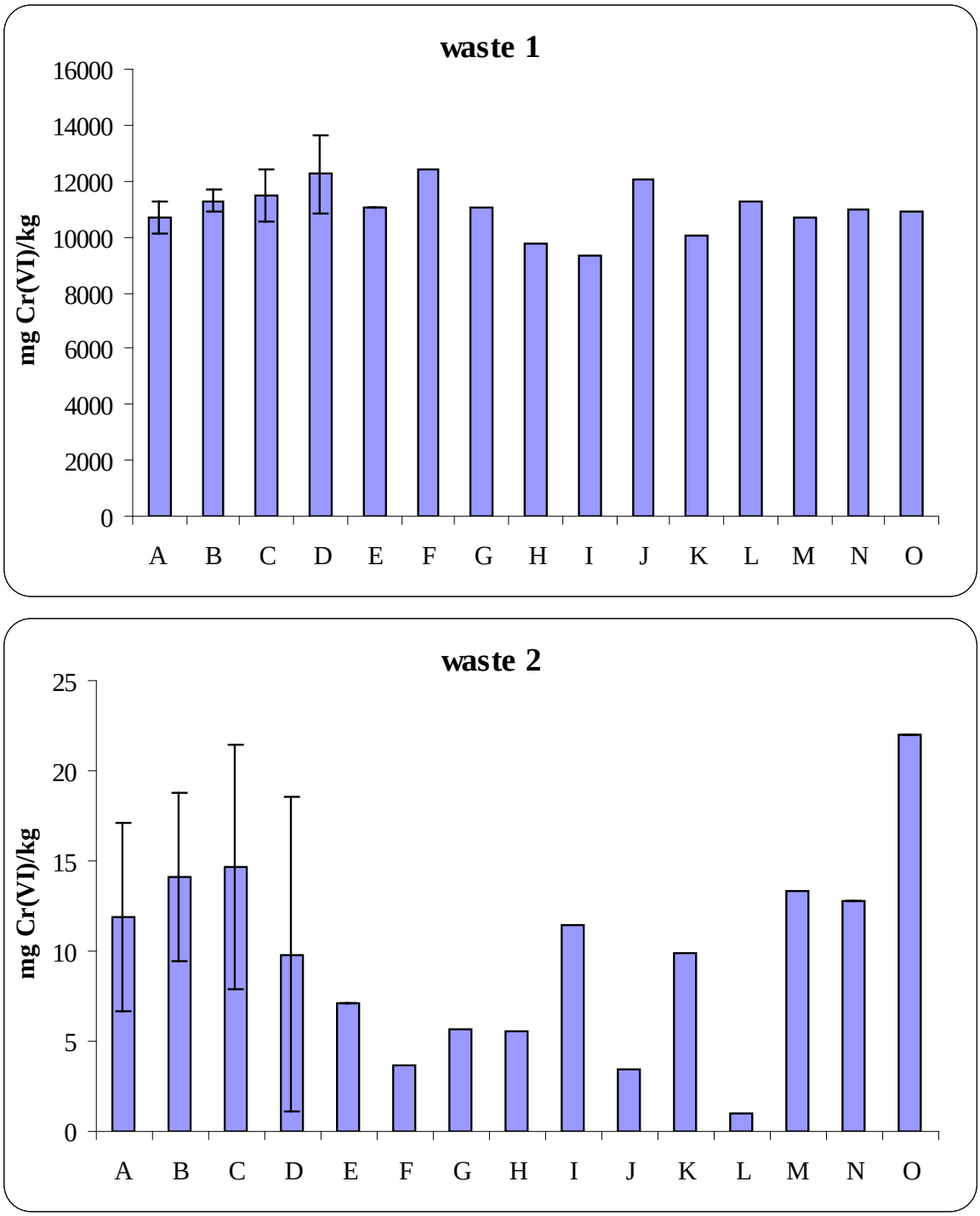


Figure 1b: Overview of accepted Cr(VI) results on waste 1 and waste 2 according to the different combinations of digestion and determination methods (see Table 3). For methods A-D, the error bar represents the 95% confidence interval of the mean calculated according to $C.I. = \pm t_{95\%, n-1} * s/\sqrt{n}$, with $t$ being a factor derived from Student´s t-distribution, $s$ the standard deviation and $n$ the number of all accepted individual results.

| Code | N | Digestion | Method of determination |
|---|---|---|---|
| **Method A** | 4 | hotplate | IC with direct spectrophotometric detection |
| **Method B** | 9 | hotplate | IC with spectrophotometric detection after post-column derivatisation with DPC |
| **Method C** | 5 | heating block | IC with direct spectrophotometric detection |
| **Method D** | 5 | heating block | IC with spectrophotometric detection after post-column derivatisation with DPC |
| **Method E** | 1 | hotplate | ICP-AES |
| **Method F** | 2 | hotplate | ET-AAS |
| **Method G** | 3 | hotplate | direct spectrophotometric detection |
| **Method H** | 1 | hotplate, water | IC with direct conductivity detection |
| **Method I** | 1 | heating block | ICP-AES |
| **Method J** | 1 | heating block | ET-AAS |
| **Method K** | 1 | heating block | IC-ICP-MS |
| **Method L** | 1 | heating block | direct spectrophotometric detection |
| **Method M** | 2 | closed vessel micro-wave | IC with spectrophotometric detection after post-column derivatisation with DPC |
| **Method N** | 1 | closed vessel micro-wave | IC with direct spectrophotometric detection |
| **Method O** | 1 | ultrasonic | ICP-AES |

Table 3: Combinations of digestion and determination methods used by laboratories participating in the interlaboratory trial (N = number of laboratories).

*Evaluation and interpretation – proposed methods*

The data for methods A - D were statistically evaluated according to ISO 5725-2[52] using commercial software (Prolab, Quo data GmbH, Dresden, Germany) and are summarized in Table 4.

Table 4: Performance characteristics of an international interlaboratory comparison on Cr(VI) determination (calculations according to ISO 5725-2).

| Sample | N | n | *w*(Cr(VI)) [mg/kg] | SR [mg/k | VR [%] | Sr [mg/kg | Vr [%] | R [mg/k | r [mg/kg] |
|---|---|---|---|---|---|---|---|---|---|
| **Soil 1** | 15 | 45 | 1.69 | 0.43 | 25.19 | 0.22 | 13.08 | 1.18 | 0.61 |
| **Soil 2** | 19 | 57 | 2007 | 205 | 10.22 | 88 | 4.36 | 568 | 242 |
| **Waste 1** | 19 | 57 | 11360 | 1308 | 11.51 | 788 | 6.94 | 3622 | 2183 |
| **Waste 2** | 13 | 39 | 12.90 | 8.97 | 69.55 | 1.59 | 12.31 | 24.85 | 4.40 |

| | |
|---|---|
| N | number of accepted laboratories |
| n | number of accepted results |
| *w*(Cr(VI)) | mass fraction of Cr(VI) calculated from N laboratory means |
| SR | reproducibility standard deviation |
| Sr | repeatability standard deviation |
| VR | relative reproducibility standard deviation |
| Vr | relative repeatability standard deviation |
| R | reproducibility limit |
| r | repeatability limit |

In Tables 5 to 8 an overview of the Cr(VI) determination is given per sample and per combination of digestion and detection method (methods A - D).

Table 5: Data for Cr(VI) determination and spike recoveries on soil 1 (low contaminated topsoil).

| Method | N | n | $w$(Cr(VI)) [mg/kg] | $SD_w$ [mg/kg] | $CV_w$ [%] | rec. Cr(VI) [%] | $SD_{rec\cdot Cr(VI)}$ [%] | rec. Cr(III) [%] | $SD_{rec\cdot Cr(III)}$ [%] |
|---|---|---|---|---|---|---|---|---|---|
| A | 3 | 9 | 1.75 | 0.46 | 26.32 | 98.0 | 7.9 | 3.5 | 5.1 |
| B | 7 | 21 | 1.83 | 0.23 | 12.61 | 94.8 | 11.7 | -1.7 | 12.4 |
| C | 2 | 6 | 1.58 | 0.56 | 35.13 | 95.5 | 10.6 | 3.6 | 0.8 |
| D | 3 | 9 | 1.36 | 0.51 | 37.25 | 96.5 | 2.7 | 1.1 | 3.7 |

| | |
|---|---|
| N | number of accepted laboratories |
| n | number of accepted results |
| $w$(Cr(VI)) | mass fraction of Cr(VI) calculated from N laboratory means |
| $SD_w$ | standard deviation calculated from N laboratory means |
| $CV_w$ | coefficient of variation of laboratory means |
| rec. Cr(VI) | mean recovery of Cr(VI) spike |
| $SD_{rec\cdot Cr(VI)}$ | standard deviation of recoveries of Cr(VI) spike |
| rec. Cr(III) | mean recovery of Cr(III) spike detected as Cr(VI) |
| $SD_{rec\cdot Cr(III)}$ | standard deviation of recoveries of Cr(III) spike detected as Cr(VI) |

Table 6: Data for Cr(VI) determination and spike recoveries on soil 2 (high contaminated topsoil).

| Method | N | n | $w$(Cr(VI)) [mg/kg] | $SD_w$ [mg/kg] | $CV_w$ [%] | rec. Cr(VI) [%] | $SD_{rec\cdot Cr(VI)}$ [%] | rec. Cr(III) [%] | $SD_{rec\cdot Cr(III)}$ [%] |
|---|---|---|---|---|---|---|---|---|---|
| A | 4 | 12 | 2010 | 209 | 10.41 | 98.5 | 5.1 | 3.0 | 3.6 |
| B | 8 | 24 | 2073 | 102 | 4.92 | 99.1 | 16.9 | 1.4 | 10.7 |
| C | 4 | 12 | 1843 | 269 | 14.57 | 101.2 | 12.2 | 4.9 | 2.8 |
| D | 3 | 9 | 2044 | 221 | 10.82 | 101.1 | 10.8 | 1.3 | 5.0 |

Table 7: Data for Cr(VI) determination and spike recoveries on waste 1 (paint sludge).

| Method | N | n | $w$(Cr(VI)) [mg/kg] | $SD_w$ [mg/kg] | $CV_w$ [%] | rec. Cr(VI) [%] | $SD_{rec\cdot Cr(VI)}$ [%] | rec. Cr(III) [%] | $SD_{rec\cdot Cr(III)}$ [%] |
|---|---|---|---|---|---|---|---|---|---|
| A | 4 | 12 | 10695 | 838 | 7.84 | 96.9 | 5.5 | 2.4 | 2.8 |
| B | 8 | 24 | 11299 | 867 | 7.67 | 95.5 | 5.6 | -1.7 | 8.5 |
| C | 4 | 12 | 11478 | 1327 | 11.56 | 97.9 | 13.0 | 1.7 | 6.0 |
| D | 3 | 9 | 12249 | 1796 | 14.66 | 96.7 | 7.6 | 4.2 | 3.4 |

Table 8: Data for Cr(VI) determination and spike recoveries on waste 2 (fly ash).

| Method | N | n | $w$(Cr(VI)) [mg/kg] | $SD_w$ [mg/kg] | $CV_w$ [%] | rec. Cr(VI) [%] | $SD_{rec•Cr(VI)}$ [%] | rec. Cr(III) [%] | $SD_{rec•Cr(III)}$ [%] |
|---|---|---|---|---|---|---|---|---|---|
| A | 2 | 6 | 11.91 | 6.16 | 51.70 | 67.9 | 53.9 | 25.5 | 26.2 |
| B | 5 | 15 | 14.09 | 8.88 | 63.03 | 90.3 | 46.1 | 13.8 | 20.3 |
| C | 3 | 9 | 14.64 | 10.09 | 68.93 | 74.0 | 38.0 | 6.6 | 7.7 |
| D | 3 | 9 | 9.83 | 13.08 | 133.04 | 49.1 | 55.8 | 3.1 | 7.1 |

The performance characteristics for Cr(VI) determination in the case of both soils and waste 1 were acceptable. However, for waste 2 the large relative reproducibility standard deviation suggests strong matrix effects. This indicates that for unknown matrices supplementary quality control data are needed in order to assess the validity of the analytical results.

The spike recoveries obtained with methods A - D are good in the case of the two soil samples (recovery Cr(VI) spike > 95 %, recovery Cr(III) spike < 5 %). Method B yielded for both soils the most reproducible results. Especially for soil 1 (low contaminated) this can be related to the superior sensitivity of the detection method (generally, the direct UV detection is less sensitive than the detection after post-column derivatisation with 1,5-diphenylcarbazide).

For the two waste samples the spike recoveries obtained with methods A - D were considered good only in the case of the paint sludge (recovery Cr(VI) spike > 95 %, recovery Cr(III) spike < 5 %). However, for the fly ash sample the spike recovery data are unsatisfactory. The ranges of recoveries for Cr(VI) and Cr(III) are unrealistically large and can be attributed to the poor reproducibility of the determination due to the reducing tendency of the sample matrix. The latter was deduced based on additional tests applying spiking with isotopically enriched chromium species in the digestion procedure. Based on these results, sample heterogeneity as a major cause of poor recoveries could be excluded. In this case no valid Cr(VI) content can be reported on the fly ash sample and any test report should include a remark on the recoveries of the spiked samples. Fly ash matrices generally contain Al, Si, Fe, Na, Ca, K, S, Zn, Ti and Cl as major components (see Table 1b). It is probable that oxidation/reduction reactions will occur in this matrix as no universal condition exist which can deal with the numerous potential mechanisms for redox-chemistry involving chromium. Similar problems regarding the determination of Cr(VI) in fly ash have been reported by Karwas *et al*. and Hua *et al*..[50,51]

*Evaluation and interpretation – alternative methods*

The direct determination of total chromium in the alkaline digestion solutions of the different materials according to methods E, F, I and J (Table 3) gave results comparable to those obtained with the selective methods A - D. Given as overall averages of the results obtained with methods E, F, I and J, the following Cr(VI) contents were found: 1.81 ± 0.06 mg/kg for soil 1, 2070 ± 250 mg/kg for soil 2 and 11400 ± 1300 mg/kg for waste 1. For soil 1 direct spectrophotometric determination of Cr(VI) in the alkaline digestion solution after complexation with diphenylcarbazide was obviously hampered by co-extracted interfering substances and is therefore not recommended (methods G and L).

The use of a closed vessel micro-wave system (methods M and N) with temperature control and continuous stirring as alternative heating device was reported by 2 laboratories. The closed vessel method has been reported for determination of Cr(VI) in fly ash samples and is assumed to prevent Cr(III) from oxidizing to Cr(VI) to a larger degree compared to hotplate method where the extraction

solution is exposed to ambient air.[19] The reported results from one laboratory were in good agreement with the methods using hotplate and heating block equipment (soil 1: 1.48 mg/kg; soil 2: 2100 mg/kg; waste 1: 10970 mg/kg). The Cr(VI) results reported from the other laboratory were only in agreement for waste 1 (10180 mg/kg) and in moderate agreement for soil 2 (1620 mg/kg); for soil 1 a four fold higher Cr(VI) content was recovered (6.8 mg/kg). The observed difference for soil 1 may be explained by partial Cr(III) oxidation (total Cr content of soil 1: 46 mg/kg) as was also noticed during the robustness study when the addition of $MgCl_2$ during digestion was omitted.

The results reported with the ultrasonic assisted leaching method (method O) confirmed the lower recoveries that were found in the robustness study. For soil 1 and soil 2, respectively, 40 % and 80 % of the average contents summarized in Table 4 were found. For waste 1 the reported result (10909 mg/kg) was in agreement with the average mean content (11360 mg/kg). These results are in line with the results reported by one of the participating laboratories applying hot water extraction (method H; soil 1: < 1 mg/kg; soil 2: 1007 mg/kg; waste 1: 9770 mg/kg), where also less effective solubilisation can be expected compared to the alkaline digestion. Comparable results found for waste 1 can be considered as an indication that for this sample the Cr(VI) was readily available. Spiking experiments with soluble Cr(VI) ($K_2Cr_2O_7$) have shown similar recoveries when using hot water or alkaline digestion, however for recovery of insoluble Cr(VI) species ($BaCrO_4$ and $PbCrO_4$) an alkaline digestion at elevated temperatures is needed.[30] The soluble and exchangeable fractions of Cr(VI) are useful parameters for estimating the mass fraction of Cr(VI) in soil that may leach to groundwater or be absorbed by plants and micro-organisms. However, quantifying insoluble forms of Cr(VI) is pertinent to environmental hazards associated with, *e.g.,* airborne, respirable dust, colloid and solute movement in groundwater and possible leaching from landfilled waste.



## Summary

An European standard for the determination of Cr(VI) in solid material has been elaborated in the framework of an international co-operation and finally validated in the course of an interlaboratory comparison.[52] The procedure is derived from the alkaline digestion prescribed by US EPA method 3060A and determines an operationally defined content of Cr(VI), including easily and sparingly soluble chromates. Although the method is one of the most rigorous with respect to extraction efficiency, an interpretation of obtained results with regard to the potential of the original sample to sustain the existence of Cr(VI) is needed. Especially, when the Cr(VI) content is less than 5% of the total chromium amount, the determination of Cr(VI) may remain ambiguous. The accuracy of the determination of Cr(VI) in solid matrices, and especially in waste, remains a challenging field from the point of view of minimal species interconversion on the one hand and maximum amount of Cr(VI) extracted on the other.

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- BAM, Division I.1, Berlin, Germany
- CESI, Piacenza, Italy
- Deutsche Metrohm GmbH & Co. KG, Filderstadt, Germany
- Eurolab Srl, Nichelino To, Italy

- FENICE S.p.A., Centro Servici Ecologici, Cascine Vica Rivoli, Italy
- FISIA ITALIMPIANTI S.p.A., Laboratorio Chimico e Biologico, Genova, Italy
- Forschungs- u. Qualitätszentrum FQZ Brandenburg GmbH, Eisenhüttenstadt, Germany
- Health & Safety Laboratory, Inorganics & Fibres Section, Buxton/Derbyshire, UK
- INERIS, Verneuil en Halatte, France
- Institut Alpha, Wasser- und Umweltanalytik, Ulm, Germany
- Institut Pasteur de Lille, Departement Eaux Environnement, Lille, France
- Metrohm Belgium, Berchem, Belgium
- Syndial - Attivita Diversificate, Centro Igiene e Protezione Ambiente, Ferrara, Italy
- Ultra-Traces Analyses Aquitaine (UT2A), Helioparc Pau-Pyrenees, Pau, France
- VITO, Milieumetingen – MIM, Mol, Belgium

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### 3.3.3. HEXAVALENT CHROMIUM IN AMBIENT AIR

VITO's interest for the determination of Cr(VI) started in 1997, with the certification of the Cr(VI) and total leachable Cr contents in welding dust loaded on a filter (CRM 545) [131]. This project was carried out under the Standards, Measurements and Testing Programme (SM&T, formerly BCR) of the European Commission in order to improve and control the quality of measurement of Cr(VI) in workplace atmosphere.

Besides in workplace atmospheres, elevated concentrations of hexavalent chromium can also be of concern in ambient air in urban areas close to industrial zones. In 2008, VITO was commissioned by the Flemish Environment Agency VMM to develop a monitoring method for the determination of the concentration level of Cr(VI) in ambient air. A multi-disciplinary approach, including X-ray absorption near-edge spectroscopy (XANES), was used for the validation of the monitoring method. XANES has proven to be well-suited for determining elemental speciation because it can directly and non-destructively analyse particulate matter samples at low concentration levels [136].

Thereafter, in 2010, a monitoring campaign was organised at 2 locations in an industrial zone at Genk-Zuid (Belgium). The results of the validation and the monitoring campaign were published in a local newspaper (see press cutting *Het Belang van Limburg*, 04/03/2011) and the scientific literature (see paper: Determination of hexavalent chromium in ambient air: a story of method-induced Cr(III) oxidation ?, *Atmospheric Environment*, 2011).

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ALGEMENE LUCHTKWALITEIT GENK-ZUID BETER

# Nog te veel chroom in Genkse lucht

GENK

**Ondanks een verhoging van de productie is de algemene luchtkwaliteit in Genk-Zuid verbeterd. Minder positief is dat de gemiddelde waarden van het gevaarlijke chroom 6 hoger liggen dan aanvankelijk geraamd. Een en ander blijkt uit de jongste meetresultaten van de VMM.**

De cijfers werden bekendgemaakt door de provinciale stuurgroep Leefmilieukwaliteit Genk-Zuid. Het gaat om de resultaten gemeten tijdens het laatste kwartaal van vorig jaar. Tot dan waren alleen de waarden gemeten van de totale hoeveelheid chroom in de lucht. Deze keer werden de metingen opgedeeld in het meer stabiele en ongevaarlijke chroom 3 en het toxische en gevaarlijke chroom 6. De hoogste concentraties daarvan werden aangetroffen in de Etienne Fabrylaan. De straat waar tot voor ruim drie jaar basisschool De Sleutel lag. De school verhuisde net omwille van de te hoge concentraties zware metalen, afkomstig van het nabije Aperam (voorheen Arcelor Mittal). Chroom 6 kan kanker aan longen en luchtwegen en andere aandoeningen veroorzaken.

**Investeringen**

Het staalverwerkende bedrijf Aperam gaat tegen het einde van dit jaar drie miljoen euro investeren in maatregelen die de uitstoot van nikkel en chroom moet verlagen. Volgens de Vlaamse Instelling voor Technologisch Onderzoek (VITO) zouden de maatregelen leiden tot 50 procent minder nikkel en 30 procent minder chroom in de lucht. De Vlaamse Milieumaatschappij zal metingen blijven uitvoeren in Genk-Zuid.

**Pcb's**

Burgemeester Wim Dries van Genk ziet zowel een positieve als negatieve tendens. "Het is goed dat er een algemene daling is van kwalijke stoffen in onze lucht in Genk-Zuid", zegt Dries. "Ik ben ook blij dat Aperam behoorlijk wat gaat investeren om de uitstoot van chroom en nikkel te verminderen. Ik maak me wel zorgen om de uitstoot van chroom 6, vooral in de omgeving van de Etienne Fabrylaan. De gezondheid van de mensen in Genk-Zuid primeert. Er zijn ook verhoogde waardes van pcb's vastgesteld rond het schrootbedrijf Stelimet. Dat is minder kwalijk voor de woonomgevingen. Maar we gaan de milieuinspectie toch vragen om er op toe te zien dat die waarden weer normale proporties aannemen."

Chris NELIS

Arts Harrie Dewitte

**"Chroom 6 gevaarlijker voor kinderen"**

Gemeenteraadslid en huisarts Harrie Dewitte (pvda+), die zich jaren geleden al in het dossier vastbeet, weet dat chroom 6 vooral gevaarlijk is voor kinderen. "Tijdens de voorgaande metingen gingen we uit van een gemiddelde van één procent chroom 6 in Genk-Zuid", zegt Dewitte. "Dat blijkt nu zo'n drie procent te zijn met piekwaardes van 20 procent. Heel beangstigend voor kinderen omdat die veel sneller ademen dan volwassenen en twee maal zoveel lucht binnen krijgen. Bovendien bedraagt de lichaamsverhouding van een volwassene ongeveer het vijfvoud. Daardoor lopen kinderen tien maal meer risico. Ik ben wel tevreden met de algemene daling en met de plannen van Aperam." CN

The data of the monitoring campaign suggested that (a variety of) environmental factors promoted Cr(VI)-Cr(III) inter-conversion. Recent studies (2013) have further examined the environmental factors affecting stability of Cr species in ambient PM in basic filter matrix under typical sampling conditions [137]. Enriched isotope spikes ($^{53}$Cr(VI) and $^{50}$Cr(III)) were used to monitor the Cr(VI)-Cr(III) inter-conversion. Some factors that were examined included major air pollutants, *i.e.*, $SO_2$, $O_3$ and $NO_2$, as well as temperature, humidity, and PM type (diesel exhaust particulate matter and secondary organic aerosol).

The chamber study characterized concurrent, competing Cr reactions that affect speciation during sampling with basic filters, *i.e.*, one pathway drives Cr(VI) reduction while the other drives Cr(III)

oxidation. A suite of interrelated environmental factors that affect competing Cr speciation was identified, including $SO_2$, stable reactive oxygen species (ROS), oxidizable PM matrix components, temperature, and humidity. Cr speciation under basic matrix depends on the oxidative capacity of PM matrix: reducing components drive Cr(VI) reduction, whereas stable ROS, such as organic peroxides drive Cr(III) oxidation. In another study, conversion of Cr(III) during sampling could be attributed to the reaction of Cr(III) with dissolved Mn and also reactions with gaseous oxidants, such as $O_3$ and particle-bound reactive oxygen species [138]. This combination of factors lead to Cr(VI) reduction and Cr(III) oxidation with significant day-to-day and seasonal variations in the field (summarised in Figure 33). The use of basic, $NaHCO_3$-pretreated filter medium will not prevent Cr(VI) reduction under sampling conditions.

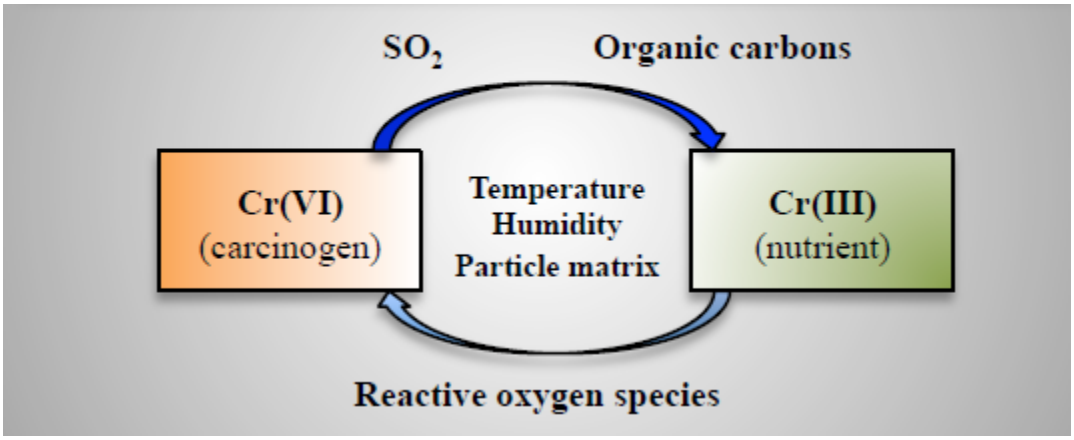


Figure 33: Inter-conversion between Cr(VI) and Cr(III) during air sampling in basic filter medium (courtesy of [137].

The SIDMS method (see § 3.3.1) would be one promising approach to improve the measurement accuracy since enriched isotope ($^{53}$Cr(VI) and $^{50}$Cr(III)) can be applied to the samples to allow simultaneous monitoring of Cr(VI) reduction and Cr(III) oxidation. However, there are still concerns regarding the use of the SIDMS method. The critical prerequisite for using this method is that the spiked isotope species should have the same chemical properties as the target component in the samples such that the spiked species mimic the species in the air samples. Composition of ambient Cr(III) and its conversion under sampling and extraction conditions need to be examined prior to Cr(VI) concentration correction via SIDMS method. Huang *et al.*, the author of the paper reporting on the examination of environmental factors affecting stability of Cr species in ambient PM, states that work about Cr(III) solubility on conversion will be reported in future publications [137].

# Determination of hexavalent chromium in ambient air: a story of method-induced Cr(III) oxidation ?

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(Reference list of this paper, see p. 148)

*Abstract*

*The accuracy of the determination of Cr(VI) in ambient particulate matter remains a challenge from the point of view of minimal Cr species interconversion. Knowledge of this method-induced oxidation and reduction is particularly relevant for the determination of Cr(VI) in ambient particulate matter, as the level of observed Cr(III) oxidation (average of 1.7 % in this study) can contribute significantly to the monitored range of measured Cr(VI) in $PM_{10}$. For Cr concentrations in $PM_{10}$ > 10 ng Cr/m³, this method-induced oxidation could lead to false positive exceeding of an air quality guideline value of 0.2 ng Cr(VI)/m³ in $PM_{10}$. The median daily Cr(VI) concentration in $PM_{10}$ measured over a monitoring period of more than 2 months at two locations close to a stainless steel factory amounted to 0.9 ng Cr(VI)/m³ and 0.27 ng Cr(VI)/m³. Average daily Cr(VI)/Cr ratios in $PM_{10}$ of 3.5 % and 2.6 % were measured at these locations. The described monitoring for the determination of Cr(VI) in ambient air via alkaline impregnated filters is sensitive (method detection limit of 0.015 ng Cr(VI)/m³) and reproducible (precision of the method ~25 %). The average Cr(VI) recovery of 75 % strongly indicates the effects of ambient sampling conditions and ambient particles on the Cr(VI) recoveries. The stability of the Cr(VI) and the Cr(III) spike on 0.12 M $NaHCO_3$ impregnated filters observed with XANES, indicates that the alkaline extraction of the filter in combination with the sampled air matrix is likely to induce the Cr conversions. The XANES spectra shows further that a Cr-spinel is the predominant component of Cr in ambient air $PM_{10}$ at the monitored locations.*



## Introduction

Understanding the concentrations, composition, and sources of atmospheric particulate matter (PM) is crucial since inhaling these particles can cause a wide array of negative health effects, including mortality and morbidity due to cardiovascular and pulmonary disease (Werner *et al.*, 2007). There are many characteristics that can affect the toxicity of PM, including its physical and chemical properties. While PM contains an enormous variety of organic and inorganic chemical species, certain classes of these compounds are of particular interest because of their toxicity. For example, transition metals such as Ni and Cr have been linked to adverse health effects through field and laboratory studies (Cleven *et al.*, 1992; Stern,1998).

The focus in this work is on Cr, which has two predominant oxidation states in the atmosphere: +3, which is an essential nutrient in low doses, and +6, which is highly toxic and carcinogenic (Cleven *et al.*, 1992; Stern,1998; Goldoni *et al.*,2006; Caglieri *et al.*, 2006).

Airborne Cr has been analyzed by many different techniques including UV−VIS spectroscopy, inductively coupled plasma−mass spectrometry, atomic absorption spectroscopy, and X-ray

techniques (Unceta *et al.*, 2010; Ashley *et al.*, 2003). All these methods, except the X-ray techniques, encounter two limitations: only the total Cr content can be determined, or wet extraction/separation steps are required to distinguish between Cr(VI) and Cr(III). For example, the standard methods of ISO, US EPA, NIOSH and OSHA for determination of Cr(VI) and Cr(III) in industrial hygiene particle samples all require an extraction step (Unceta *et al.*, 2010; Ashley *et al.*, 2003; Ashley *et al.*, 2009; Boiano *et al.*, 2000; Christensen *et al.*, 1999; Dyg *et al.*, 1994; Wang *et al.*, 1997; Steinsberger *et al.*, 1994). The experimental conditions adopted for the extraction of Cr(VI) from particles significantly influence the reliability of the final results owing to possible undesired Cr(VI)-Cr(III) interconversions (Pettine *et al.*, 2005).

From this point of view X-ray absorption near edge structure (XANES) has two main advantages for analysis of Cr and other metals: (1) no sample preparation (*e.g.*, extraction) is required, and (2) the technique can distinguish between different compounds of the same metal, including different oxidation states (*e.g.*, Cr(VI), Cr(III), and Cr(0)) as well as different compounds with the same oxidation state (*e.g.*, $Cr_2O_3$ vs $Cr_2S_3$) (Werner *et al.*, 2007). However for prolonged environmental monitoring purposes, XANES is not a feasible option due to the requirement of a synchrotron X-ray source.

For this reason, most papers dealing with environmental monitoring of Cr(VI) in particulate matter fall back on a workable extraction. The aim of this paper is to highlight the relevance of Cr(III) oxidation observed during a Cr(VI) monitoring campaign in respect to the accurate risk assessment of hexavalent chromium in ambient air.



**Determination of Cr(VI) in particulate matter in ambient air via extraction**

The first methods for the determination of hexavalent chromium in aerosols via extraction were developed to assess the toxicity of aerosols produced by metallurgical and engineering processes, such as steel making, cutting, grinding and welding. Ever since then the kinetics and thermodynamics of the Cr(VI)-Cr(III) equilibrium have played a major role for new method developments. In 1983 it is reported by Gray *et al.* that in the fumes generated from stainless steels, the hexavalent chromium content appears to rise to a maximum some time after formation of the aerosols and then partly decay again (Gray *et al.*, 1983). A few years later Zatka gives a theoretical background to the observed oxidation of Cr(III) to Cr(VI) during the determination of hexavalent chromium in welding fumes (Zatka, 1985).

An extensive review on the characterisation of the Cr(VI)/Cr(III) ratio in ambient air aerosols was published in 1992 by Cleven *et al.* It is stated that any data on Cr(VI) before 1987 are probably too high because of chromium species interconversion. A review on different digestion methods from soil was presented in 1995 by James *et al.*. Since then, there is a consensus on the use of an alkaline digestion solution to achieve minimal species interconversion and maximum extraction efficiency of hexavalent chromium on solid materials. This in turn has lead to many standardised methods using the alkaline digestion as reviewed by Unceta *et al.* in 2010.

Sampling of Cr(VI) in particulate matter in ambient air can roughly be divided in procedures using impingers/denuders and procedures using (impregnated) filters (Cleven *et al.*, 1992). In the case of the use of impingers, the Cr(VI) determination can be performed directly in the impinger solution. In the case of collection of PM on a filter, an extraction is needed prior to analysis. For the determination of Cr(VI) in the extraction solution, different analytical methods have been applied. For a discussion on possible detection methods we refer to Unceta *et al.*, since most of the possible interconversions occur during sampling and extraction.

In the first field evaluation studies to determine the environmental levels of airborne hexavalent chromium using an impinger train, it is reported that the oxidation of Cr(III) to Cr(VI) does not occur to a significant extent (0.7 %)(Sheehan *et al.*, 1992). In different field studies using the impinger method for monitoring airborne hexavalent chromium, ratios of Cr(VI) to total chromium from 0 up to 25 % were observed; however, no assessment of Cr(III) oxidation is reported (Bell *et al.*, 1997; Finley *et al.*, 1993; Metze *et al.*, 2004). In more recent studies using impinger trains, the species transformation from Cr(III) to Cr(VI) was evaluated. By Krystek *et al.* the oxidation of Cr(III) to Cr(VI) was reported to be less than 2 %, Li *et al.* reported an average of 13 % conversion of Cr(III) to Cr(VI) in solutions containing air sample matrix (Krystek *et al.*, 2007; Li *et al.*, 2002). Also an increasing rate of conversion of Cr(III) with time in an alkaline solution was observed (3 % after 24 h to 10 % after 72 h)(Li *et al.*, 2002).

An elaborate research on the fate of hexavalent chromium in the atmosphere, including sampling on an alkaline impregnated filter was published by Grohse *et al.* in 1988. The potential oxidation of Cr(III) with $MnO_2$ is theoretically discussed and it is recommended that further testing should be performed. In some field studies using filters to collect the airborne particulate matter, however, no assessment of Cr(III) oxidation is reported, while ratios of Cr(VI) to total chromium from 20 – 30 % were observed (Borai *et al.*, 2002; Talebi *et al.*, 2003). In a recent paper Cr(VI) is reported to constitute up to 50 % of the total chromium in Polish urban aerosols (Swietlik *et al.*, 2011).

For both sampling methods, impingers and filters, automated measurement systems have been described for continuous measurement of Cr(VI) in airborne particulate matter. However, no indication is given on the potential oxidation of Cr(III) to Cr(VI) during the measurement (Samanta *et al.*, 2001; Khlystov *et al.*, 2006; Isakov *et al.*, 2007).

Because of the several directives and recommendations in Europe and the US to limit and regulate the presence of Cr(VI) in the environment, governmental funded research has been performed to develop standard operating procedures for the determination of Cr(VI) in airborne particulate matter (Ashley *et al.*, 2003). The US EPA funded the development of a standard operating procedure for the analysis of hexavalent chromium at ambient atmospheric levels by Ion Chromatography (IC) using impregnated filters (SOP CARB 039, 2006). Within the US national monitoring program, more than 1400 measurement were performed over 22 locations in 2005. The average concentration amounted to 0.044 ng Cr(VI)/m³ and the highest concentration was reported in Washington DC, 2.97 ng Cr(VI)/m³ (ERG, 2006). In this standard operating procedure the quality control measures imply solely the control on possible Cr(VI) reduction.

A similar approach was performed by the Austrian Environmental Agency to monitor the Cr(VI) content in $PM_{10}$ in the city of Vienna in 2007. The range of Cr(VI) in $PM_{10}$ amounted 0.04 – 0.23 ng Cr(VI)/m³ and represented about 1 % of the total Cr content. No indication is given on the potential oxidation of Cr(III) to Cr(VI) during the procedure (Hagendorfer *et al.*, 2007).

For an evaluation of Cr(VI) in ambient air in the Netherlands near wood preservation plants and at a regional site, the National Institute of Public Health and the Environment developed an impinger/denuder system (Mennen *et al.*, 1998). Preliminary tests without a denuder showed that conversion of Cr(III) exceeded 10 %. With the introduction of a denuder to remove reactive gases, the conversion from Cr(III) ranged from 0.7 to 3 %.

With the introduction of speciated isotope dilution mass spectrometry (SIDMS), possible species interconversions occurring during the digestion can be mathematically corrected (Kingston, 1995). SIDMS uses the concept of spiking the sample with known amounts of enriched isotopes that have been chemically converted into the same forms of the species to be analysed.

This approach has been reported to be successful, especially to quantify the reduction of Cr(VI), where the addition of enriched "soluble" ($K_2Cr_2O_7$) and "insoluble" ($PbCrO_4$) Cr(VI) compounds were added to quantify the order of magnitude of reduction (Kingston *et al.*, 1998; Huo *et al.*, 1998; Tirez *et al.*, 2003; Tirez *et al.*, 2007). With respect to the correction for Cr(III) oxidation, the SIDMS method suffers some additional limitations. The correction is limited by the knowledge of the form in which Cr(III) is present in the particulate matter. Cr species in the environment include both soluble and insoluble forms; particularly, most Cr(III) in ambient air is present as insoluble forms and the conversions are expected to be lower for these insoluble Cr species. Also the surface of the particulate matter and the way in which Cr(III) is included will influence the solubility of Cr(III) during the extraction. Moreover, it has been observed that when using the procedure as described in the SIDMS patent (Kingston, 1995) for the preparation of the enriched Cr(VI) spike, traces of $H_2O_2$ in the spike solution may, after the addition to the sample in an alkaline environment, lead to possible oxidation of Cr(III)(Tirez *et al.*, 2003). This implies that the matrix of the spike solutions which are added to the extraction solution may introduce supplementary artefacts.

Using an isotope dilution mass spectrometric method, Nusko *et al.* reported that the Cr(III)/Cr(VI) ratio was found to be about 0.3 in aerosol particles. In a study on Cr(VI) in house dust using enriched Cr spikes, recovery for Cr(III) of 95 ± 10 % and for Cr(VI) of 90 ± 6 % were reported on blanks (Stern *et al.*, 2010). An average conversion rate of < 5 % in either direction was observed. However spiking of the sample matrices with the enriched isotopes resulted in inconsistent recovery of both isotopes for which no reason could be given. In a recent paper by Meng *et al.* on the further development and evaluation of a method for hexavalent chromium in ambient air using enriched isotopes, the Cr(III) conversion was further studied. The conversion from the enriched Cr(III) spike to Cr(VI) in a pH 4 $HNO_3$ extraction solution was on average 2.6 % for blank filters and 5 % for a NIST 1648 particles coated on a filter. No correction is finally made for Cr(III) conversion because of the expected difference in oxidation between the enriched Cr(III) spike and the Cr(III) present in the sample (Meng *et al.*, 2011).

In summary it can be stated that for the determination of Cr(VI) in particulate matter in ambient air via extraction, there is enough evidence that all methods reported so far in literature suffer to a greater or lesser extent from method-induced Cr(III) oxidation. This oxidation sets limits to the lower limit of Cr(VI) detection relative to the total Cr(III) content of the particulate matter.

**Determination of Cr(VI) in particulate matter in ambient air via XANES**

X-ray based techniques are generally regarded as reference methods for solid state speciation since they enable the identification and quantification of chromium oxidation states while being non-destructive. The most employed techniques are X-ray absorption near-edge spectroscopy (XANES), X-ray Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) (Unceta *et al.*, 2010). Whereas XPS and XANES will enable quantification of the redox status of chromium, only the nature of the crystalline phases under which chromium is present can be reached by XRD. Detection limits of XPS and XRD are usually about 0.1 wt. %. XPS enables chromium speciation if Cr(VI) represents at least 10 wt. % of total chromium.

A number of studies have been published on chromium speciation with XANES in combustion aerosol particles and in airborne fine particles (Werner *et al.*, 2007; Huggins *et al.*, 2004; Goodzari *et al.*, 2008; Wang *et al.*, 2007; Galbreath *et al.*, 2004; Huggins *et al.*, 2000; Galbreath *et al.*, 1994). A great advantage of XANES is that it can distinguish between different compounds of the same metal, including different oxidation states (*e.g.*, Cr(VI), Cr(III), and Cr(0)) as well as different compounds with the same oxidation state (*e.g.*, $Cr_2O_3$ vs $Cr_2S_3$). However, because of the fitting procedure to determine the fraction that each Cr species contribute to the total amount of Cr, any species that accounts for less than ~5 % is within the uncertainty of the resolving power of the fitting program

(Werner *et al.*, 2007). The ranges of Cr(VI) in particulate matter have been reported to range from 6 to 43 % of the total Cr content in $PM_{2.5}$ from coal combustion (Galbreath *et al.*, 1994). In particulate matter reference material NIST 1648 and 1650 the oxidation state of chromium is predominantly (> 95 %), if not entirely, in the trivalent state of the chromium (Huggins *et al.*, 2000). In particulate matter collected close to an iron and steel industrial area, the main chemical component of Cr in PM was chromite and oxides of trivalent chromium (Wang *et al.*, 2007).

The speciation of chromium in airborne fine particles in combination with atmospheric transformations have been extensively studied with (micro-)XANES by Werner *et al.* and Nico *et al.*. These studies demonstrated that aerosols contain a suite of different Cr(III) species, as well as more reduced Cr species. The major component was in all cases a Cr-Fe spinel, suggesting that the chemistry and toxicity of this phase will likely play a key role in the Cr associated health effect of ambient PM. In the study of the redox dynamics of mixed metal (Mn, Cr and Fe) ultrafine particles, two reaction pathways, one reductive and one oxidative, were found to be operating simultaneously during simulated atmospheric aging. The presence of Mn within the particles enhanced the importance of the oxidative pathway, leading to more net Cr oxidation during aging, implying that Mn can mediate oxidation by removal of electrons from other particulate matter (Nico *et al.*, 2009).

In summary XANES has proven to be an appropriate speciation method for Cr in particulate matter in ambient air, however due to the linear fitting process the method is limited to detect fractions of Cr species that contribute to more than ~ 2 - 5 % of the total amount of Cr.



## Materials and Methods

### Cr(VI) - Cr(III) measurements via XANES

*Preparation of the pure phase Cr compounds*

In total, 6 reagent-grade Cr compounds were purchased: $Cr_2O_3$ (Alfa Aesar GmbH & Co., Karlsruhe, Germany); $Cr_3C_2$ (Sigma-Aldrich NV/SA, Bornem, Belgium), $FeCr_2O_4$ (Norkem, Grootebroek, The Netherlands), $Cr_2S_3$ (Merck, Darmstadt, Germany), $Cr_2(SO_4)_3$ (Alfa Aesar) and $K_2Cr_2O_7$ (Merck). These samples were mixed with boron nitride (BN, an inert and weakly absorbing binder) and pressed into self-supporting pellets. For metallic Cr, a 3 µm thick Cr foil was used to collect the Cr K edge XANES spectrum.

*Sampling*

XANES analysis was performed on the following particulate matter samples:

1. sample X: two 0.12 M $NaHCO_3$ impregnated ashless cellulose filters (grade 40, Whatman International Ltd., Maidstone, UK) were spiked with 25 µl of a 1000 µg $ml^{-1}$ $Cr(NO_3)_3.9H_2O$ solution (Spex Certiprep Inc., Metuchen, USA). Both filters were measured directly via XANES after spiking. Subsequently one filter was sampled with a Tecora Bravo Plus sampler (TCR Tecora Srl., Milan, Italy) for 16 h at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on 25/06/2009 (sampled volume : 12.8 $m^3$). The other filter was preserved under argon atmosphere in an exsiccator for 16h. Thereafter both filters were analyzed.
2. sample X2: two 0.12 M $NaHCO_3$ impregnated ashless cellulose filters (Whatman) were spiked with 25 µl of a 1000 µg $ml^{-1}K_2Cr_2O_7$ solution (Merck). Both filters were measured directly via XANES after spiking. Subsequently one filter was sampled with a Tecora Bravo Plus sampler (TCR Tecora Srl, Milan, Italy) for 16 h at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on 26/06/2009 (sampled volume: 12.8 $m^3$). The other filter was preserved under argon atmosphere in an exsiccator for 16h. Thereafter both filters were analyzed.

3. samples X3 and X4*:* ambient particulate matter ($PM_{10}$) collected on a 150 mm diameter PTFE filter (TE 38.5 µm, Schleicher&Schuell, 's-Hertogenbosch, the Netherlands) during 72 h with Digitel DHA-80 high volume samplers (Digitel Elektronik AG, Hegnau, Switzerland) in a rural area in Flanders (Mol, Belgium). Sampling was performed on 22/06/2009 and the filters were stored in a sample holder under ambient conditions until measurement on 25/06/2009.


Picture 6: Digitel DHA-80 high-volume samplers and Partisol speciation sampler in a rural area (Mol, Belgium), with details of the Partisol speciation sampler filter holder ($PM_{10}$).

4. Samples X5 and X6: ambient particulate matter ($PM_{10}$) collected on a 47 mm diameter PTFE filter (Schleicher&Schuell) with a Partisol speciation sampler (Partisol Plus model 2300 filter sampler, Thermo Fisher Scientific Inc, Waltham, USA). The sampling was performed at a monitoring site of the Flemish Environment Agency (Belgium), which is located at 100 m from a stainless steel factory and in the vicinity of a residential area. Sampling was performed in the period from 28/04 to 4/05/2009 (sampled air volume ~ 43 $m^3$, 3 days of continuous sampling on each filter). The filters were stored in a sample holder under ambient conditions until measurement on 25/06/2009.

Picture 7: Sampling location and a Partisol speciation sampler used for the simultaneous sampling on 4 filters.

*XANES data collection*

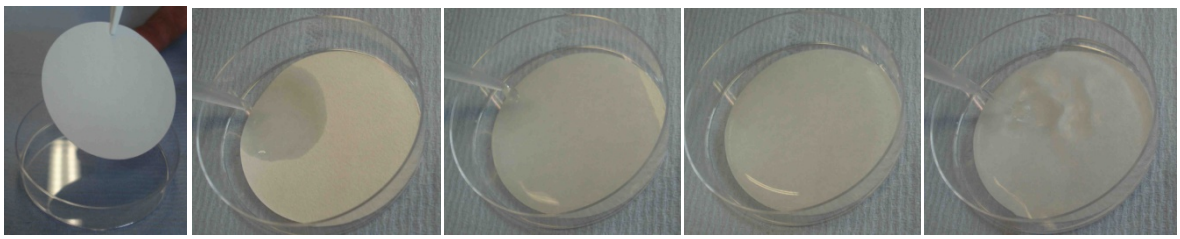
The Cr K edge XANES measurements were performed at the XAS station of the Dutch-Belgian CRG beamline (DUBBLE BM26A) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) (Nikitenko *et al.*, 2008). This XAS instrument is located at a bending magnet port (magnetic field strength B=0.4 Tesla, critical energy $E_c$=9.6 keV) of the 6 GeV electron storage ring and is equipped with a Si(111) double crystal monochromator. The higher harmonics were suppressed by a Si reflecting strip on a flat mirror behind the monochromator. The intensity of the incoming and transmitted X-ray beams was measured with ionisation chambers (Oxford Instrument). The fluorescence XAS spectra were collected with a $LN_2$ cooled energy dispersive (ED) nine channel monolithic Ge detector. The spectra were normalized by subtracting the pre-edge background and dividing the absorption data by the edge step at 50 eV above the Cr K edge position. The spectra on the Cr reference compounds were recorded in transmission mode. The fluorescence mode was used for the filter samples. The dimensions of the incoming beam were 4 mm horizontally by 0.5 mm vertically.

Picture 8: XANES measurements at the XAS station of the Dutch-Belgian CRG beamline (DUBBLE BM26A) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France).

**Cr(VI) – Cr(III) sampling and measurements for the monitoring campaign**

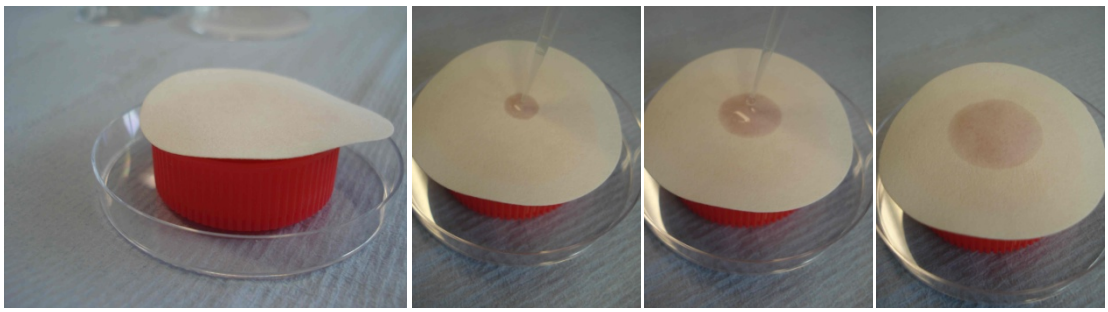
Preparation of the filters

Ashless cellulose filters (grade 40, 47 mm, 8 µm, Whatman International Ltd., Maidstone, UK) were selected for sample collection. Single filters were pretreated with 8 ml of 0.12 M $NaHCO_3$ (Alfa Aesar, Karlsruhe, Germany) in closed petri dishes (55 x 14 mm, VWR, Leuven, Belgium) for 16 h. The filters were dried under $N_2$ atmosphere in an exsiccator.



Picture 9: Impregnation of the filters.

The addition of Cr(VI) spike on the filter at a level of 20 ng Cr(VI)/filter was performed by using an automatic pipette of 40 µl of a 0.5 µg Cr(VI) $ml^{-1}$ $K_2Cr_2O_7$ stock solution (Merck). The addition of Cr(III) spike on the filter at a level of 1000 ng Cr(III)/filter was performed by using an automatic pipette of 40 µl of a 25 µg Cr(III) $ml^{-1}$ $Cr(NO_3)_3$ stock solution (Spex Certiprep Inc., Metuchen, USA).



Picture 10: Addition of Cr(VI) spike on the filter.

For the determination of total Cr, sampling was performed on Teflon filters (Teflon 47 mm, 2.0 µm, Pall Corporation, Sint-Stevens-Woluwe, Belgium).

*Sampling*

Ambient particulate matter ($PM_{10}$) was collected at 24 hour intervals over a period from 04/10/2010 until 09/12/2010 at two locations in the Flemish region of Belgium. Location 1 was situated at 190 m of a stainless steel factory in the predominantly downward wind direction. Location 2 was situated in the same wind direction, but 850 m further away. On location 1 sampling was performed each day from 9 am to 9 am on the next day. On weekdays samples were recovered immediately after sampling and transported to the laboratory (~ 2 h) in a cooled transport (< 5°C). Sampling in the weekend was performed automatically, but samples were left on the instrument and collected on Monday mornings. Sampling of $PM_{10}$ at location 2 was performed on weekdays only.


Picture 11: Ambient particulate matter (PM10) sampling location 1 (GK11) and location 2 (GK05).

In order to evaluate concentrations and conversions between Cr-species, 5 separate samplings were performed simultaneously at each location every day. Samples (a)-(d) were taken with a Partisol speciation sampler. Sample (e) for the determination of total Cr was sampled with a Partisol Plus model 2025 filter sampler:

a) a 0.12 M $NaHCO_3$ impregnated ashless cellulose filter
b) a 0.12 M $NaHCO_3$ impregnated ashless cellulose filter (duplicate sample of (a))
c) a 0.12 M $NaHCO_3$ impregnated ashless cellulose filter spiked with 20 ng Cr(VI)
d) a 0.12 M $NaHCO_3$ impregnated ashless cellulose filter spiked with 1000 ng Cr(III)
e) a teflon filter (PTFE) for the determination of total Cr

*Extraction and Analysis*

The filters were analyzed within 24 hours after sampling for filters collected during weekdays and otherwise kept in a freezer in the laboratory (-18°C) until measurement. For the alkaline extraction of the filter a temperature controlled ultrasound-assisted leaching system was used (Branson 5210, 47 kHz, 185 W, Soest, the Netherlands). For the determination of Cr(VI) in particulate matter collected on a filter, the following alkaline digestion procedure was applied. The filter was placed in a 15 ml tube (VWR), 10 mL of 0.02 M $NaHCO_3$ digestion solution was added. The filters were extracted at 15 °C ± 2.5 °C for 60 minutes. After digestion, the solutions were filtered using a 0.45 µm membrane filter (PTFE filtercaps, Dionex, California, USA).

The determination of Cr(VI) in the alkaline digestion was performed after ion chromatographic separation and measured spectrophotometrically at 530 nm after post-column derivatization with 1,5-diphenylcarbazide in acid solution according to SOP CARB 039 (SOP CARB 039, 2006; Dionex application 179). The ion exchange chromatography system consisted of a Dionex DX-120 system coupled to an UV-VIS spectrophotometer (Spectrasystem UV 1000, Thermo, Breda, The Netherlands) and 2 HPLC pumps (Model 426, Alltech, Deerfield, USA). The ion exchange chromatography system conditions are summarized in table 1. Calibration standards were prepared daily with deionized water (18.2 MΩ $cm^{-1}$) using the Milli-Q system (Millipore, Brussels, Belgium) and from a 1000 µg $ml^{-1}$ $K_2Cr_2O_7$ standard stock solution (Merck). The laboratory quality controls were prepared from a 1000 µg $ml^{-1}$ Cr(VI) standard solution (Merck).

| | |
|---|---|
| Eluent | 250 mM $(NH_4)_2SO_4$ /100 mM $NH_4O_H$ |
| Guard column | Ionpac NG1 dionex |
| Pre-column | Ionpac AG7 dionex |
| Analytical column | Ionpac AS7 dionex |
| Measurement wavelength | 530 nm |
| Eluent flow rate | 1,5 ml/min |
| Post column reagent flow rate | 0,5 ml/min |
| Sample volume | 1000 µl |
| Knitted reaction coil | 750 µl |

Table 1: IC-DPC settings for the determination of Cr(VI) in extraction solutions.

The elemental concentration of Cr on the filters was measured with polarized Energy Dispersive XRF (EDXRF Spectro, X-lab 2000). The calibration of the XRF spectrometer was performed by an in-house developed aerosol generation system based on the ultrasonic nebulization of a multi-element solution and collection of the aerosols on a filter (Vanhoof *et al.*, 2003).

## Results and discussion

### XANES measurements

*Stability of Cr(III) and Cr(VI) spiked filters*

The transmission XANES spectra on the Cr reference powders pressed in BN pellets are given in figure 1. Comparison with literature shows that the XANES spectrum for $Cr_2O_3$ contains two pre-edge peaks (Wang *et al.*, 2007). However, in our spectrum, the intensity of the second pre-edge peak around 5995 eV is more intense, which suggests that a small fraction of the Cr atoms was oxidized to Cr(VI) or traces of Cr(VI) were present in the reagent-grade $Cr_2O_3$ compound.

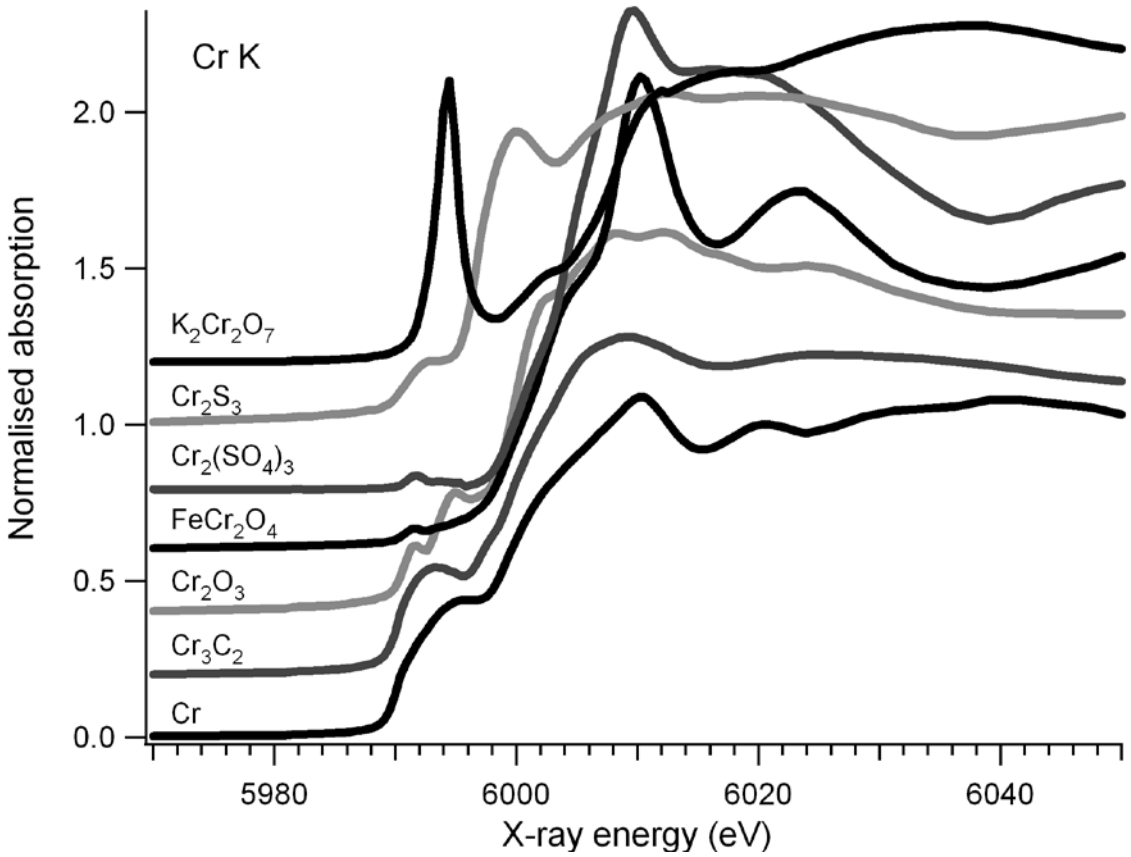



Figure 1: Normalized Cr K transmission XANES spectra for the Cr reference compound pressed in BN pellets (vertically shifted for clarity, bottom shows zoomed view around the absorption edge).

The Cr K fluorescence spectra for the filter spiked with a Cr(III) solution of $Cr(NO_3)_3$ (sample X1) is given in figure 2. The spectrum of the filter stored for 16 h under argon condition is identical to the freshly loaded filter. The filter that was sampled under ambient air conditions shows a small broadening of the white line peaks. This points towards a possible broadening of the corresponding electron levels or a higher structural disorder. However, no indication for oxidation to Cr(VI) is observed.

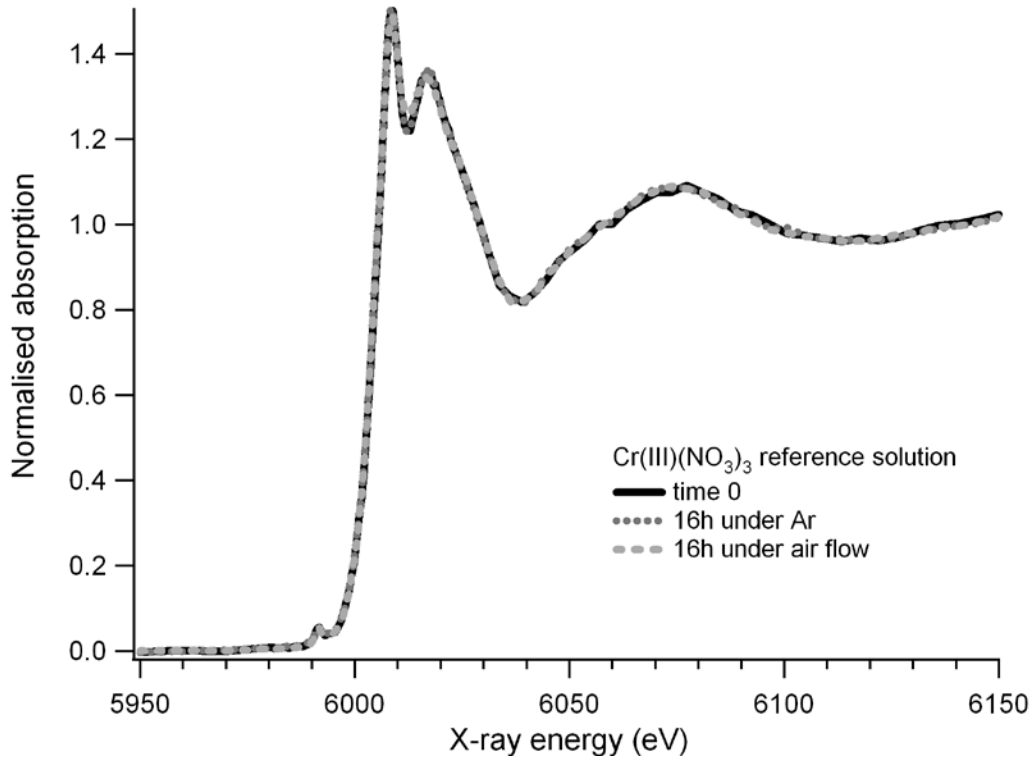



Figure 2: Normalized Cr K fluorescence XANES spectra of the 0.12 M $NaHCO_3$ impregnated ashless cellulose filters spiked with 25 µl of a 1000 µg $ml^{-1}$ $Cr(NO_3)_3.9H_2O$ solution (sample X1).

The Cr K fluorescence spectra for the freshly loaded Cr(VI) reference solution (sample X2) after 16 h storage under argon conditions, after 16 h under ambient air and after subsequent 11 h irradiation with the X-ray beam are given in figure 3.

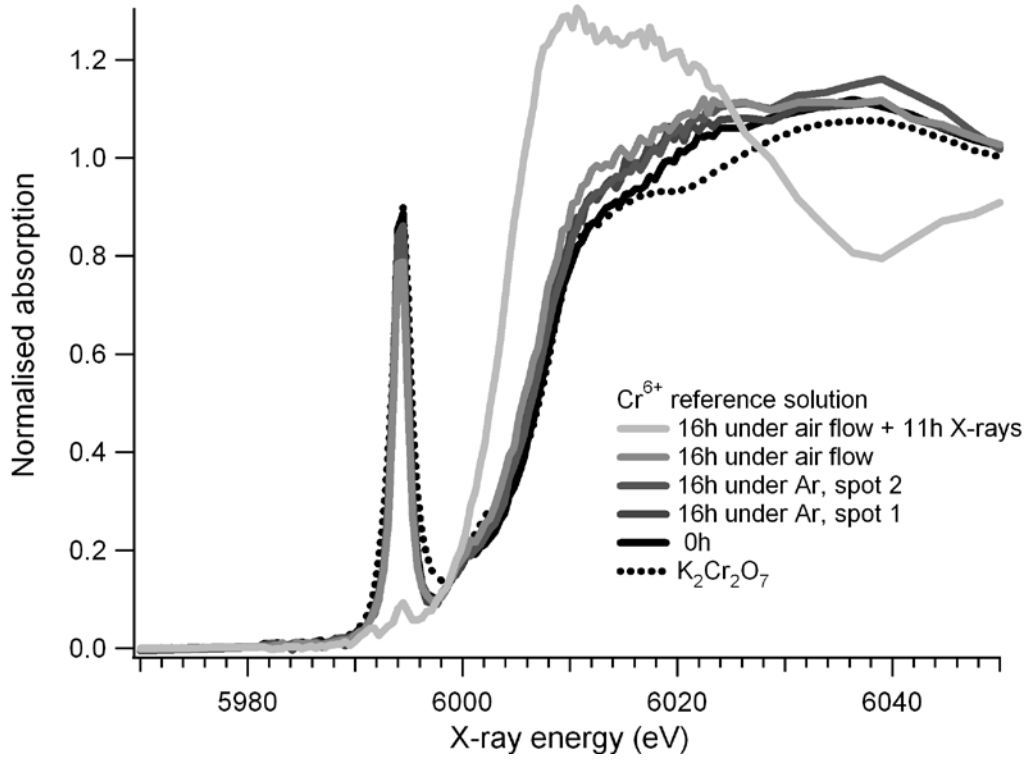



Figure 3: Normalized Cr K fluorescence XANES spectra of the 0.12 M $NaHCO_3$ impregnated ashless cellulose filters spiked with 25 µl of a 1000 µg $ml^{-1}$ $K_2Cr_2O_7$ solution (sample X2).

By comparing the intensity of the Cr(VI) pre-edge with the pre-edge peak intensity of the freshly prepared Cr(VI) spiked filter, an estimate of the Cr(VI) fraction can be obtained. Both storages under argon and under ambient air did not significantly change the Cr(VI) fraction. On the freshly prepared Cr(VI) filter and the filter stored under argon, 2 subsequent XANES scans were recorded with a collection time of about 18 min each. For both filters, the Cr(VI) fraction in the second scan decreased to 0.90, showing a reduction under influence of the X-ray irradiation. A second location on the filter stored under argon was analysed, giving the same result. The sample stored for 16 h under ambient air has a Cr(VI) fraction of 0.84, showing a partial reduction of the Cr(VI) under ambient air storage. The time dependence Cr(VI) reduction under X-ray radiation was studied in more detail on the under ambient air stored filter by recording XANES spectra every 11 min up to a total irradiation time of 11 hours, a selection of these spectra is given in figure 4. From the time plot of the obtained Cr(VI) fraction, the standard deviation on the Cr(VI) fraction was estimated to be 0.02. An almost complete reduction of Cr(VI) on the filter under influence of the X-ray radiation can be observed.

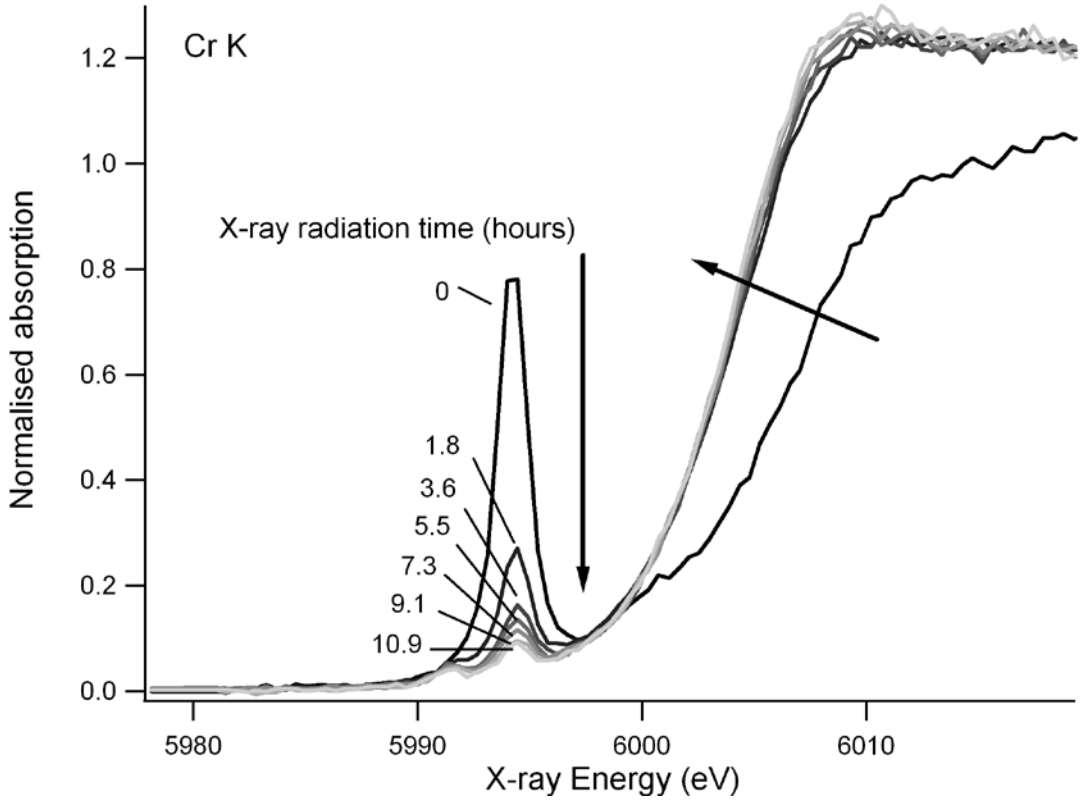



Figure 4: Normalized Cr K fluorescence XANES spectra of the 0.12 M $NaHCO_3$ impregnated ashless cellulose filter spiked with 25 µl of a 1000 µg $ml^{-1}$ $K_2Cr_2O_7$ solution (sample X2) during X-ray irradiation over 11h (spectra were recorded every 11 min, only a selection is shown in this figure).

In summary the XANES data show that the Cr(III) spike and the Cr(VI) spike are stable (> 95%) on the impregnated filters after 16 h sampling under ambient air conditions. Prolonged X-ray irradiation of the filter converted the spiked Cr(VI) to Cr(III).

*XANES analysis of ambient particulate matter*

The Cr K fluorescence XANES spectra for the air filters X3 and X4 sampled in a rural area in Flanders (Mol, Belgium) are given in figure 5. The main component is identified as $FeCr_2O_4$. The observed noise on the X3 and X4 spectra are due to the low Cr content on the filters, respectively 0.4 and 0.45 µg Cr/filter. The purchased reagent grade $FeCr_2O_4$ compound was also measured with XRD. These results reveal that this compound contains a spinel-structure which is isomorphous with $Fe_3O_4$. Based on the gradient in the diffraction lines, lattice parameters with values of 8.30 Å and 8.27 Å were

calculated. The structure is related to a AlCrFeMgO spinel, suggesting that Cr is infiltrated in a spinel-structure. This could explain the small differences observed in the XANES spectra between the reference $FeCr_2O_4$ compound and the filter samples.

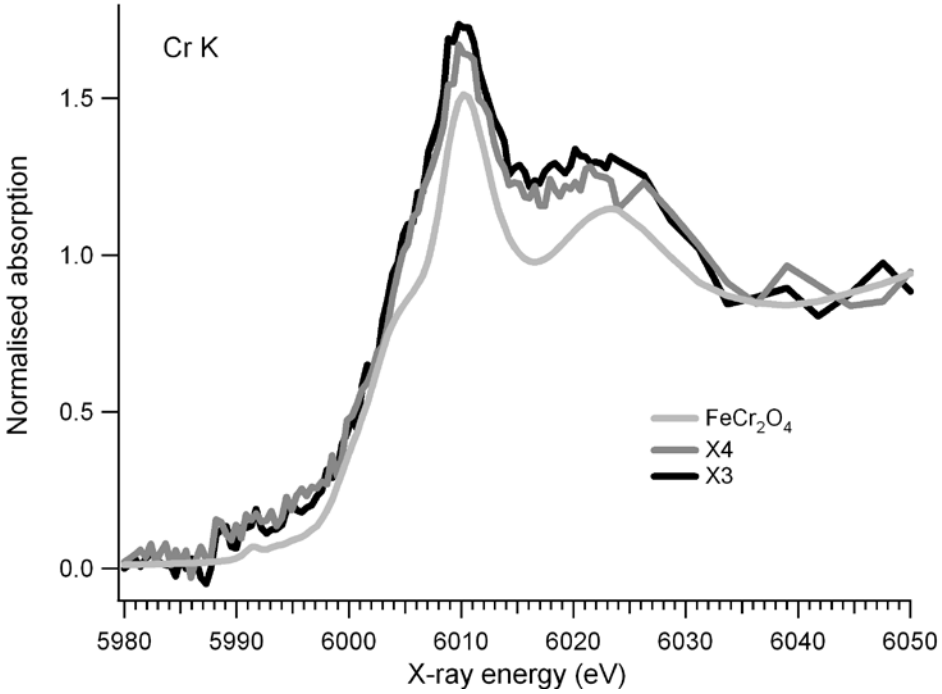



Figure 5: Normalized Cr K fluorescence XANES spectra for the X3 and X4 ambient air filters (rural area) compared with the $FeCr_2O_4$ reference compound (transmission mode).

The Cr K fluorescence spectra from the X5 and X6 filters are given in figure 6. The main identified component is the $FeCr_2O_4$ form.

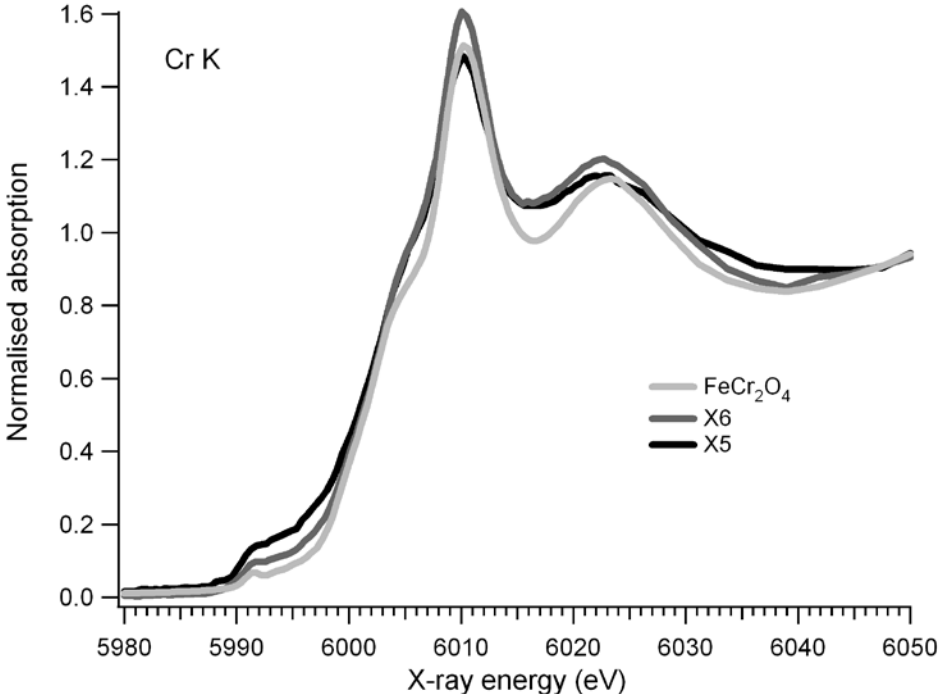



Figure 6: Normalized Cr K fluorescence XANES spectra for the X5 and X6 ambient air filters (near anthropogenic Cr source) compared with the $FeCr_2O_4$ reference compound (transmission mode).

The total Cr content of X5 and X6 was respectively 1.8 µg Cr/filter (42 ng Cr/m³) and 4 µg Cr/filter (79 ng Cr/m³). These results are in agreement with literature data suggesting that a Cr-Fe spinel is the major component of Cr in ambient air $PM_{10}$ (Werner *et al.*, 2007; Huggins *et al.*, 2000; Wang *et al.*, 2007).

**Monitoring campaign**

*Laboratory quality controls*

With the optimized settings of the ion exchange chromatography system as described in table 1, the method detection limit (calculated as prescribed in SOP CARB 039) was 0.022 µg Cr(VI) $l^{-1}$ (this corresponds to 0.015 ng Cr(VI)/m³). This analytical method is highly sensitive and more cost effective for monitoring purposes compared to, *e.g.,* IC-ICP-MS (Tirez *et al.*, 2003; Meng *et al.*, 2011). To control the daily performance of the ion exchange chromatography system, a calibration blank and 3 calibration verification standards were analyzed. To control the daily performance of the extraction, an extraction blank and two extraction solutions spiked with respectively 2 µg/l Cr(VI) and 100 µg/l Cr(III) were analyzed. To control the filter impregnation procedure, an impregnated blank filter, an impregnated filter spiked with 20 ng Cr(VI) and an impregnated filter spiked with 1000 ng Cr(III) were extracted and analyzed in every measurement run. The results of these quality control measurements are summarized in table 2.

| Quality control | value |
|---|---|
| calibration blank | < 0.1 µg Cr(VI)/l (n = 37) |
| calibration verification standard 0.1 | 0.103 ± 0.015 µg Cr(VI)/l (2s, n = 35) |
| calibration verification standard 0.5 | 0.507 ± 0.018 µg Cr(VI)/l (2s, n = 36) |
| calibration verification standard 5 | 5.02 ± 0.25 µg Cr(VI)/l (2s, n = 37) |
| extraction blank | < 0.1 µg Cr(VI)/l (n = 35) |
| extraction solution + 2 µg/l Cr(VI) | 2.02 ± 0.11 µg Cr(VI)/l (2s, n = 35) |
| extraction solution + 100 µg/l Cr(III) | < 0.1 µg Cr(VI)/l (n = 33)<br><0.5 µg Cr(VI)/l (n = 3) |
| impregnated blank filter | < 1 ng Cr(VI)/filter (n =32)<br><5 ng Cr(VI)/filter (n = 12) |
| impregnated blank filter + 20 ng Cr(VI) | 20.6 ± 5.5 ng Cr(VI)/filter (2s, n = 36) |
| impregnated blank filter + 1000 ng Cr(III) | 4.9 ± 3.9 ng Cr(VI)/filter (2s, n = 34) |

Table 2: Quality control measurements during the monitoring campaign.

The extraction showed a good recovery of the Cr(VI) spike 101 ± 5% (95% confidence level, 2s). The oxidation of the Cr (III) spike added to the alkaline extraction was in 90% of the samples <0.1% (not detectable) and in 10% of cases <0.5%. The impregnation of the filters was the most critical step with respect to contamination. The 20 ng Cr (VI) spike on the filter was recovered for 103 ± 27% (95% confidence level, 2s). The oxidation of the 1000 ng Cr (III) spike on the filter was on average 0.49 ± 0.39% (equivalent to 4.9 ng / filter). Raising the temperature of the ultrasonic assisted extraction from 15 to 70°C resulted in a 10 fold increase in observed oxidation of the Cr(III) spike.

*Field quality controls*

Based on the daily duplicate sampling and analysis of sample (a) and (b) at both locations, a precision of ± 0.26 ng Cr (VI)/m³ (2s, N = 37) could be derived for concentrations < 1 ng Cr (VI)/m³. In the range > 1 ng Cr (VI)/m³, a relative precision of ± 24 % (2s, N = 30) was derived.

The recovery of Cr(VI) on the sampled impregnated filter (c) spiked with 20 ng Cr (VI) (equivalent to 1.43 ng Cr (VI)/m³ with the average sampling rate of 14 m³/24h) was calculated as: Recovery = ([sample c] - [mean (sample a, sample b)])/1.43 and is summarized in table 3. The average recovery, calculated for total Cr concentrations in ambient air up to ~ 250 ng / m³, amounted 75 % (N = 87). For total Cr concentrations in ambient air > 250 ng / m³, the rise in level of Cr(VI) concentration due to the added Cr(VI) spike (sample c) was less than ~ 20 % of the measured Cr(VI) concentration in the samples a and b and within the measurement uncertainty. The range of observed Cr(VI) recovery over the two locations amounted to 33 – 103 % (10-90 % percentile) during the monitoring period.

The difference between the average recovery of the Cr(VI) spiked laboratory quality control (103 %) and the Cr(VI) spiked field control (75 %) is in line with the literature data reported by Meng *et al.* and strongly indicates the effects of ambient sampling conditions and ambient particles on the Cr(VI) recoveries (Meng *et al.*, 2011). For example, Fe could contribute to the reduction of Cr(VI) to Cr(III) under typical atmospheric conditions through the following reactions: Cr(VI) + 3Fe(II) → Cr(III) + 3Fe(III).

| | N | mean | st. dev. | median | 10 percentile | 90 percentile |
|---|---|---|---|---|---|---|
| Recovery Cr(VI) spike (%)[1] | 87 | 75 | 39 | 78 | 33 | 103 |
| Cr(III) oxidation (%)[2] | 58 | 1.7 | 1.2 | 1.4 | 0.4 | 3.1 |

[1] calculated as Recovery = ([sample c] - [mean (sample (a),sample(b)])/1.43 for all days where [Cr] < 250 ng Cr/m³.
[2] calculated as oxidation = ([sample d] - [mean (sample (a),sample(b)])/71.4 for all days where [Cr] < 100 ng Cr/m³.
Table 3: Summary of the field quality control data of the Cr(III) and Cr(VI) spiked filters.

The oxidation of Cr(III) on the sampled impregnated filter (d) spiked with 1000 ng Cr (III) (equivalent to 71.4 ng Cr (III)/m³) was calculated as: oxidation = ([sample d] - [mean (sample a, sample b)])/71.4 and is summarized in table 3. The average oxidation (calculated for total Cr concentrations in ambient air up to ~ 100 ng / m³) amounted 1.7 % (N = 58).

For total Cr concentrations in ambient air > 100 ng / m³, the raise in level of Cr(VI) concentration due to the oxidation of the Cr(III) spike (sample d) was less than ~ 20 % of the measured Cr(VI) concentration in the samples a and b, and within the measurement uncertainty. The range of observed Cr(III) oxidation over the two locations amounted from 0.4 to 3.1 % (10-90 % percentile) during the monitoring period. The difference between the oxidation of the non-sampled Cr(III) spiked filter (0.49 %) and the sampled Cr(III) spiked filter (1.7%) is in accordance with literature data and indicates the importance of the air sampled matrix (Li *et al.*, 2002).

The stability of the Cr(VI) and the Cr(III) spike on impregnated filters observed with XANES indicates that the extraction of the filter in combination with the sampled air matrix is likely to induce the Cr conversions.

*Monitoring data*

The results of the Cr(VI) and total Cr data obtained during the monitoring campaign are represented in figure 7 and figure 8 and are summarized in table 4.

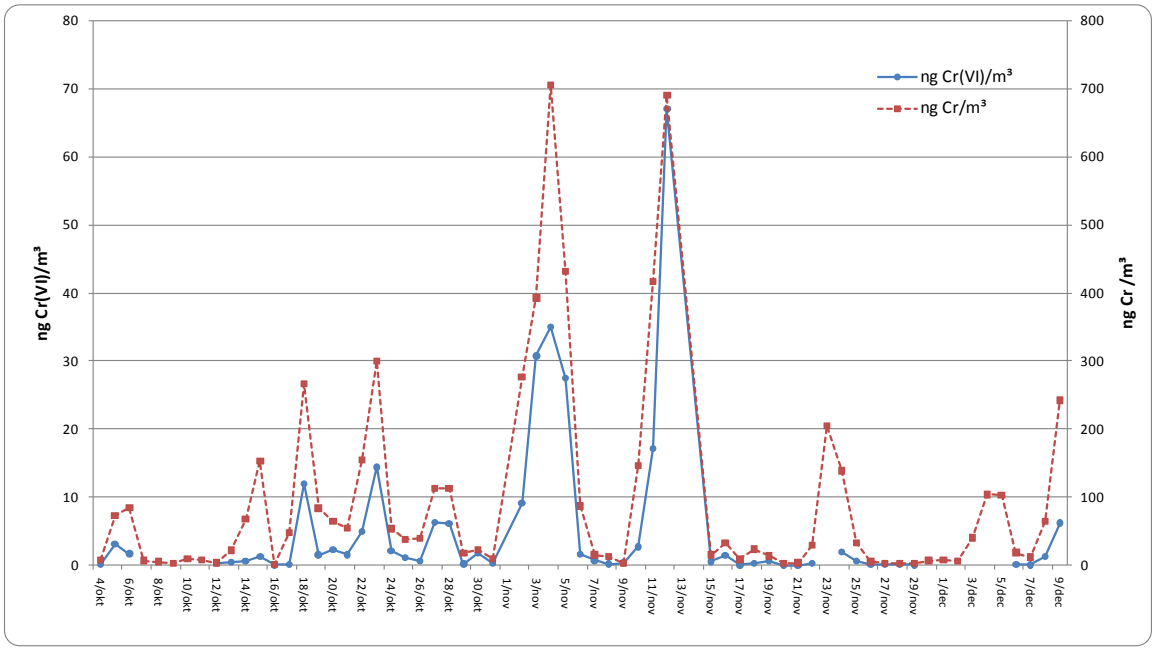



Figure 7: 24 h monitoring data of Cr(VI) and total Cr in PM10 at location 1 (near anthropogenic Cr source) over a period from 04/10/2010 to 09/12/2010.



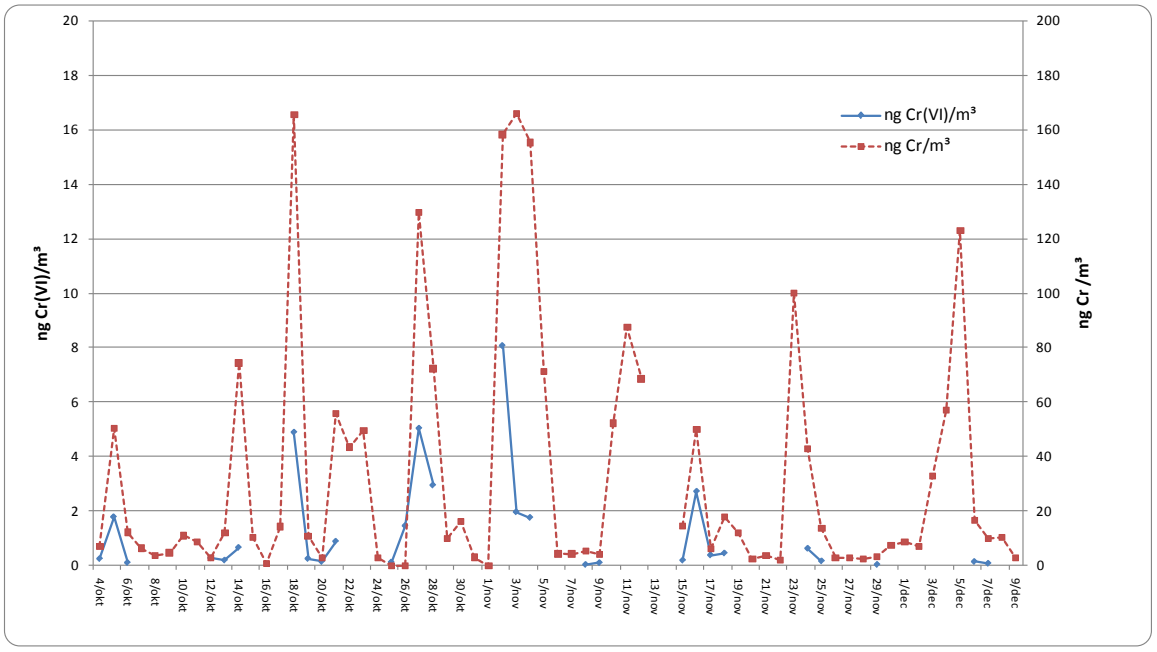



Figure 8: 24 h monitoring data of Cr(VI) and total Cr in PM10 at location 2 (further from anthropogenic Cr source) over a period from 04/10/2010 to 09/12/2010.

The Cr(VI) concentrations measured at location 1 (mean of 5.2 ng Cr(VI)/m³; median of 0.9 ng Cr(VI)/m³) and location 2 (mean of 1.2 ng Cr(VI)/m³; median of 0.27 ng Cr(VI)/m³) are on average above the air quality guideline value of 0.2 ng Cr(VI)/m³ in $PM_{10}$ recommended as an annual average by DEFRA (DEFRA, 2009). The mean daily Cr(VI)/Cr ratios measured at both locations were respectively 3.5 % and 2.6 %.

| | | N | mean | median | 10th percentile | 90th percentile |
|---|---|---|---|---|---|---|
| **Location 1 near anthropogenic Cr source** | ng Cr(VI)/m³ | 52 | 5.2 | 0.9 | 0.09 | 14 |
| | ng Cr/m³ | 64 | 96 | 33 | 3.7 | 274 |
| | daily Cr(VI)/Cr ratio (%) | 52 | 3.5 | 3.0 | 0.9 | 6.7 |
| **Location 2 further from anthropogenic Cr source** | ng Cr(VI)/m³ | 28 | 1.2 | 0.27 | 0.07 | 3.5 |
| | ng Cr/m³ | 60 | 34 | 11 | 2.9 | 102 |
| | daily Cr(VI)/Cr ratio (%) | 26 | 2.6 | 1.6 | 0.9 | 5.3 |

Table 4: Summary of the monitoring data of Cr(VI) and total Cr in PM10 at the two locations.

Highest concentrations of total Cr and Cr(VI) were observed when the wind was blowing from the industrial plant towards the monitoring sites. As expected, the highest concentrations were measured on the location close to the plant (location 1). However, in the light of the range of observed Cr(III) oxidation over the two locations (0.4 - 3.1 %), these results have to be interpreted carefully. It is assumed that the measured Cr(VI) is a combination of method-induced Cr(III) oxidation and actual Cr(VI) present in the $PM_{10}$ fraction. Cr(III) oxidation depends on many factors and may be induced in the air, on the filter and during the extraction. Basically, only the oxidation due to capture of the $PM_{10}$ fraction on the filter and due to the extraction are considered as method-induced artefacts. However, this method-induced oxidation sets limits to the Cr(VI) detection relative to the total Cr content of the particulate matter.

Correction for the Cr(III) conversion is ambiguous because of the expected difference in oxidation between the added Cr(III) spike and the Cr(III) present in the sample (most likely Cr spinel) (Meng *et al.*, 2011). With an average oxidation of 1.7 %, this would mean that for total Cr concentrations above ~ 10 ng Cr/m³, an air quality guideline value of 0.2 ng Cr(VI)/m³ in $PM_{10}$ would fall within the uncertainty on the Cr(VI) determination method. Daily $PM_{10}$ ambient air quality measurements by the Flemish Environmental Agency on 20 monitoring stations close to industrial areas in 2009 show that median values are in 80 % of the monitoring stations between 1.2 – 8.3 ng Cr/m³; However, in 20 % of the monitoring stations, median Cr concentrations in $PM_{10}$ > 10 ng Cr/m³ were measured (VMM, 2009). The level of Cr(VI)-Cr(III) interconversions observed at one location may not be extrapolated to another, due to potential differences in Cr sources in combination with differences in air matrix. With respect to the interactions between Cr-Mn as possible oxidative pathway, it can be mentioned that the Mn concentration measured in $PM_{10}$ at both locations fluctuated in a same way than the levels of Cr. At the highest Cr concentrations in $PM_{10}$ observed during the monitoring campaign, the measured Mn concentrations were between 1/2 to 1/3 of the Cr concentration.

The air quality guideline value of 0.2 ng Cr(VI)/m³ in $PM_{10}$ proposed by DEFRA was not derived from epidemiological studies at Cr(VI) ambient concentration levels, but derived by dividing the Lowest Observed Adverse Effect Level over a 40 year working lifetime by a factor of 1000 (DEFRA, 2009). Within this process of deriving toxicity based guideline values, the accurate measurement of Cr(VI) is crucial. Any enforcement of Cr(VI) regulatory values for ambient air in the future will require supplementary efforts with respect to method standardization.

## Conclusion and practical implications

The described monitoring method for Cr(VI) in ambient air via impregnated filters is sensitive (method detection limit of 0.015 ng Cr(VI)/m³) and reproducible (precision of the method ~25 %). The Cr(VI) recoveries (average 75 %) strongly indicate the effects of ambient sampling conditions and ambient particles on the Cr(VI) recoveries. The method – and in more general terms all methods via extraction – is susceptible to method-induced Cr(III) oxidation. Knowledge of the method-induced oxidation is particularly relevant for the determination of Cr(VI) in ambient particulate matter as the level of observed oxidation (average 1.7 %) is within the range of the level of measured Cr(VI) (average daily Cr(VI)/Cr ratios of 3.5 % respectively 2.6 %). For Cr concentrations in $PM_{10}$ > 10 ng Cr/m³, this method-induced oxidation could lead to false positive exceeding of the air quality guideline value of 0.2 ng Cr(VI)/m³ in $PM_{10}$.

The stability of the Cr(VI) and the Cr(III) spike on impregnated filters observed with XANES indicates that the alkaline extraction of the filter in combination with the sampled air matrix is likely to induce the Cr conversions.

In order to assess the toxicity of Cr containing $PM_{10}$ in general, we encourage that new research and monitoring programs in the field of determination of the Cr(VI) content in ambient particulate matter would report on Cr(VI) and Cr(III) interconversions.

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**References paper,** Determination of hexavalent chromium in ambient air: a story of method-induced Cr(III) oxidation?, *Atmospheric Environment*, 2011, **45**, 5332-5341.

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### 3.4. OXYHALIDE BY-PRODUCTS IN DRINKING WATER DISINFECTION

The first documented drinking water treatment can be found in Egyptian hieroglyphics, describing procedures to purify water [116]. The basic principles were the same then as they are today: boiling, chemical treatment and filtration. The importance of drinking water quality and its influence on human health was known, but the specific contaminations would not be identified for centuries. This situation was changed in the 19$^{th}$ century, when chlorine was introduced as a chemical disinfectant for water treatment. The introduction of chlorination to drinking water was followed by remarkable reductions in cholera, dysentery and typhoid worldwide.

Nowadays, water treatment by disinfection of drinking water is generally considered a major public health achievement of the 20$^{th}$ century. Consequently, the identification of water contaminants shifted from microbiological to chemical. The number of chemicals determined in drinking water has grown exponentially. However, from the hundreds of them present, only very few have been studied or have documented proof of their health effects.

Nearly half of the parameters monitored are being measured for operational reasons (*e.g.,* iron, ammonium, pH, chloride, dissolved organic carbon) and/or for reasons of customer satisfaction (*e.g.*, colour, taste, hardness). Of the health-related compounds, a number of metals and small groups of organic compounds and pesticides are being measured on a regular base in a majority of countries.

During the 1970s, it was discovered that chlorination of drinking water produced carcinogens, such as trihalomethanes, haloacetic acids and other. Since then, environmental regulatory agencies, as well as drinking water treatment technologists, have been carrying out extensive research for alternative disinfection methods that minimize the production of by-products with significant health risks. Ozonation has emerged as one of the most promising alternatives to chlorination.

In the last decade, the use of ozone in the treatment of drinking water to improve taste, odour and reduce the presence of organic micropollutants has been spreading. In the early 1980s, it became obvious that application of ozonation in drinking water treatment did not only result in the formation of oxygenated compounds but, in bromide-containing water, brominated organic compounds as well as bromate are formed.

Bromate is the most important inorganic oxyhalide by-product, the concentration of which has to be controlled in drinking water. Bromate is formed when water containing bromide is ozonated. From the theoretical and practical point of view, it can be seen that bromate formation can be influenced by many parameters, such as ozone dose, water pH, temperature and indigenous concentration of bromide. Furthermore, other subjects of interest and topics of advanced research are chlorite and chlorate [117].

Bromate has been identified as an animal and possible human carcinogen. The International Agency for Research on Cancer (IARC) classified bromate in group B-2 (the agent is possibly carcinogenic to humans). The United States Environmental Protection Agency (US EPA), as well as the Commission of the European Communities, has issued rules that require public water supplies to control previously unregulated microorganisms and cancer-causing disinfection by-products in final treatment drinking water [11]. According to these regulations, Maximum Admissible Level (MAL) is 10 µg/L for bromate and 1000 µg/L for chlorite.

The maximum admissible level for bromate has been primarily based on current analytical capability (not on toxicological considerations - the target concentration for bromate in drinking water is zero); thus, there is a need for on-going development and refinement of analytical technologies in order to permit rapid and reliable determinations at the sub-µg/L level.

Global and national agencies are continually striving to monitor bromate, chlorite and chlorate levels in drinking water to establish appropriate regulatory limits. In Flanders, the control of drinking water quality is organized in 81 different drinking water supply zones [118]. A drinking water supply zone is a geographically defined area within which water intended for human consumption comes from one or more sources and can be considered as being approximately of uniform quality.

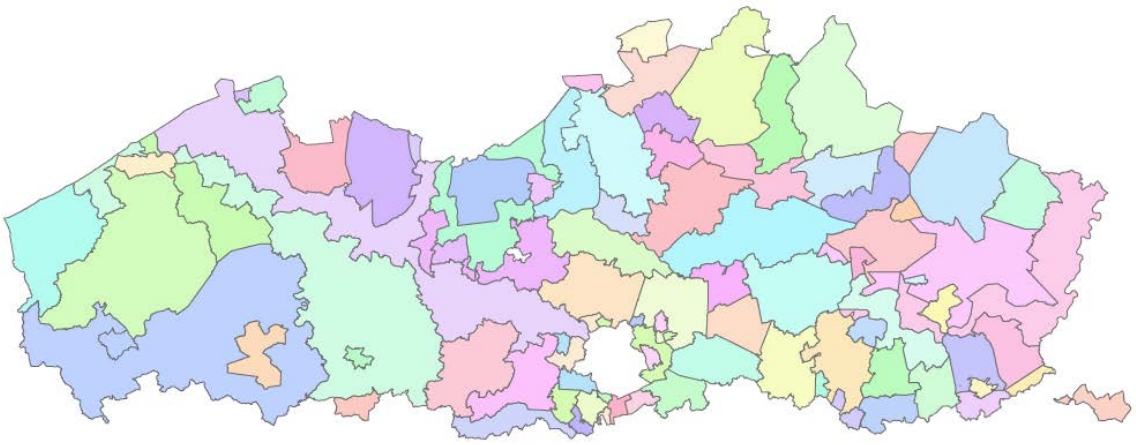

Figure 34: Overview of the 81 drinking water supply zones defined in Flanders [118].

For the 81 different drinking water supply zones in Flanders, approximately 1400 bromate control analyses of water collected from the tap are performed on a yearly basis in the audit monitoring program imposed by the European Directive [118]. For the chemical parameters, most exceedings of maximum admissible concentration in drinking water are observed for lead (69 out of 7900 analysis, year 2010). In general, the drinking water distributed in Flanders largely complies with the quality requirements set by the European Directive.

In support of routine determination of bromate in regulatory monitoring programs, the benefits of a user-friendly and low cost low pressure LC/ICP-MS set-up as compared to the more traditional HPLC/ICP-MS hyphenation was studied (see paper: Determination of bromate in drinking waters using low pressure liquid chromatography / ICP-MS, *J. Anal. At. Spectrom.*, 2013).

# Determination of bromate in drinking waters using low pressure liquid chromatography / ICP-MS

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(Reference list of this paper, see p. 165)

*Abstract*

*This paper describes a user-friendly method for bromate determination that can be implemented easily on any inductively coupled plasma - mass spectrometer present in drinking water laboratories. The method is applying low pressure liquid chromatography coupled to an ICP – quadrupole mass spectrometry instrument (ICP-QMS) or an ICP – sector field mass spectrometry instrument (ICP-SFMS) and is compared to that relying on high performance liquid chromatography (HPLC) coupled to an ICP-QMS instrument. The low pressure LC/ICP-MS method uses a low-pressure delivery six-port valve and a 5 cm anion exchange column, which allows a fully resolved separation of bromate in 13 min and achieves a limit of quantification of 0.2 µg bromate $L^{-1}$. The low pressure LC system is small, easy to install and its operation is fully integrated within the ICP-MS software. The method allows fit-for-purpose assessment of bromate, potentially present as a Br-containing disinfection by-product in drinking water, and meets all performance characteristic requirements set by the European Council for the monitoring of the quality of water intended for human consumption. A median bromate concentration of 0.5 µg $L^{-1}$ was obtained for 80 tap water samples collected during regulatory monitoring campaigns from 2009 until 2012 and covering different water supply areas in the Flemish region of Belgium.*



## Introduction

Water treatment by disinfection processes is considered a major public health achievement of the twentieth century.[1] In the 1970s, however, it was discovered that chlorination of drinking water produced carcinogens, such as trihalomethanes and haloacetic acids.[2] Since 1974, more than 500 disinfection by-products have been identified in drinking water. Since that time, environmental regulatory agencies and drinking water treatment technologists have performed extensive research on alternative disinfection methods that reduce the generation of organic by-products with significant health risks.

Ozonation has emerged as one of the most promising alternatives to chlorination.[1] In the early 1980s, it became obvious that the application of ozonation in drinking water treatment not only resulted in the formation of oxygenated compounds, but also in the formation of brominated organic compounds and bromate. Bromate has been identified as an animal, and possibly human, carcinogen.[3,4] The International Agency for Research on Cancer (IARC) has classified bromate in group B-2 (the agent is possibly carcinogenic for humans).

A Maximum Admissible Concentration (MAC) of 10 µg $L^{-1}$ bromate in drinking waters is recommended by the US EPA,[5] the Council of the European Union (in Directive 98/83)[6] and the WHO[7].

As the European Council recommends limits of detection (LoDs) for the determination of bromate in drinking water of less than 2.5 µg $L^{-1}$, this has necessitated the further development of more sensitive and/or alternative analysis approaches in the past 20 years. Most techniques currently available for bromate determination use ion chromatography (IC) as the underlying separation mechanism.[3,4] The methods for bromate determination using IC can be generally divided into: (a) direct methods (suppressed conductivity detection)[8], (b) indirect methods (UV/Vis detection after post-column derivatization)[9] and (c) hyphenated techniques (ICP–MS and MS detection)[10-14].

For all of the determination methods mentioned above, standardised methods that can achieve LoDs of less than 2.5 µg L−1 are available nowadays. For a critical comparison of available ISO, US EPA and other methods concerning ion chromatography determination of bromate, we refer to Hautman et al. and Michalski.[1,2]

The selection of the method used for bromate determination is guided by, among other, the availability of appropriate equipment, ease of use and expenditures. For the determination of trace elements in drinking water, most - if not all - of the drinking water laboratories are nowadays equipped with ICP-MS instrumentation. In spite of the excellent sensitivity, wide linear dynamic range and multi-element capability of ICP-MS, for hyphenated techniques such as HPLC/ICP-MS, the ease of use and expenditures are limiting factors for common use in routine drinking water laboratories. With the introduction of low pressure chromatography, a fast analytical method for speciation with ICP-MS detection becomes more feasible.[15] This low pressure LC system is small, easy to install and its operation is fully integrated within the ICP-MS software. Moreover, as the low pressure LC system makes use of an autosampler commonly used for elemental analysis, the system can be implemented easily on any inductively coupled plasma - mass spectrometer present in drinking water laboratories.

The work in this paper describes and compares the capabilities and limitations of HPLC/ICP-MS and low pressure LC coupled to an ICP – quadrupole mass spectrometry instrument (ICP-QMS) and coupled to an ICP – sector field mass spectrometry instrument (ICP-SFMS) for the determination of bromate in drinking water.

## Experimental section

### Instrumentation

*HPLC/ICP-MS*

Samples were analysed using a quadrupole-based ICP-MS instrument (Elan 6000, Perkin-Elmer, SCIEX, ON, Canada), equipped with an MCN-100 micro-concentric nebuliser (Cetac technologies, NE, USA) fitted onto a cyclonic spray chamber for sample introduction. During optimization of the instrument settings, solution was fed to the MCN-100 by means of a peristaltic pump. The speciation was carried out with a 100x2 mm P1 AAD 1 anion exchange DMEA microbore column (Institut für Anorganische Chemie, Universität Hannover, Germany). The separation column consisted of a high-capacity and high-performance PS/DVB-anion-exchanger functionalized with 2-(dimethylamino)-ethanol, which has been developed by Seubert *et al.*.[16] The eluent was pushed through the column at a flow rate of 400 µL $min^{-1}$ via a series 10 HPLC pump (Perkin-Elmer). A FIAS 400 (Perkin-Elmer) peristaltic pump was used for filling the 1000 µL sample loop. The sample loop was connected to an automated 6-port valve (LabPRO 6, Rheodyne, CA, USA). The operation of the entire measurement system, including sample uptake, filling of the loop, injection onto the column and ICP-QMS measurement, is computerized. Integration of the chromatograms (peak areas) was accomplished

with Turbochrom software (Perkin-Elmer). Before analysis, the instrument was preconditioned by aspirating the eluent for at least 1 hour.

Low pressure *LC/ICP-QMS*

Samples were analysed using a quadrupole-based ICP-MS instrument (Nexion 300S, Perkin Elmer), equipped with a µ-Flow nebulizer (PFA-400, Elemental Scientific Inc or ESI, NE, USA) coupled to a 50 mL baffled cyclonic spray chamber (Perkin Elmer). The speciation was carried out using a SC-DX chromFAST system (ESI) using a 50 x 4 mm anion exchange column (CF-Se-01, ESI).

The low pressure mobile phase was delivered to the column using an integrated FAST Valve and Precision Micro Peripump (FAST DXi) (see figure 1, right). The FAST system consists of a six-port injection valve and a vacuum pump connected to a 2500 µL sample loop. The adjustable injection time and pump rate control the amount of sample injected from the 2500 µL sample loop. The flow of eluent was delivered by a peristaltic pump (controlled by the ICP-MS software) using green/orange flared tubing (i.d. 0.38 mm). The operation of the entire measurement system, including sample uptake, filling of the loop, injection onto the column and ICP-MS measurement, is computerized. Integration of the chromatograms (peak areas) was accomplished with periSPEC Peak Area Finder Software (ESI).

Low pressure *LC/ICP-SFMS*

Samples were analysed using a single-collector double-focusing sector field ICP-MS instrument (ELEMENT II, ThermoScientific, Germany), equipped with a µ-Flow nebulizer coupled to a 50 mL baffled cyclonic spray chamber (Elemental Scientific Inc or ESI, NE, USA). The speciation was carried out using a SC-DX chromFAST system (ESI) using a 50 x 4 mm anion exchange column (CF-Cr-01, ESI). The low pressure mobile phase was delivered to the column using the peristaltic pump of the ICP-SFMS unit (see figure 1, left).

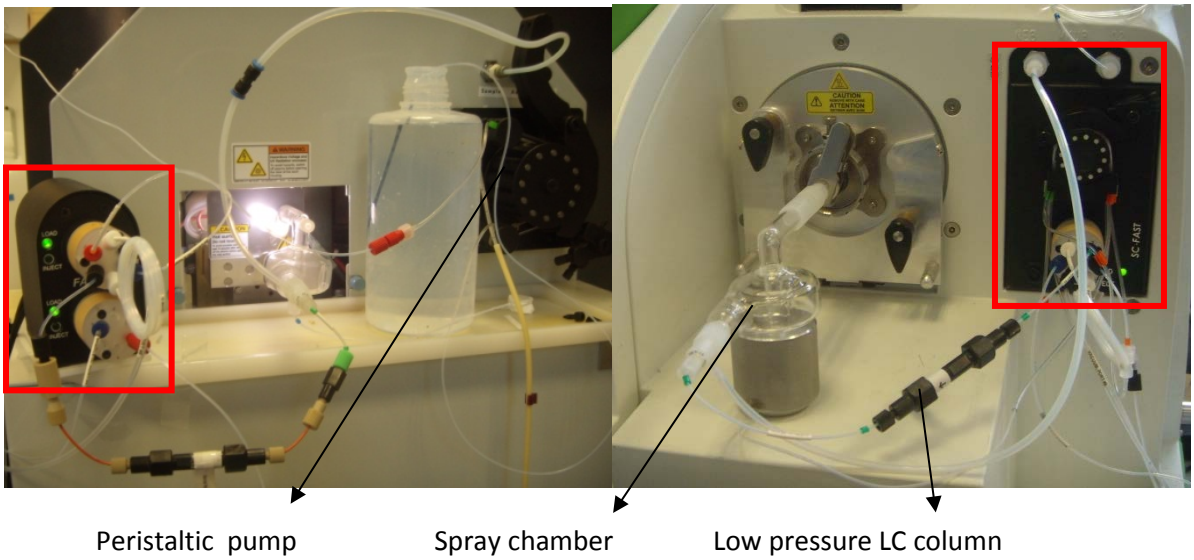


Figure 1: Low pressure LC/ICP-MS system: (left) ESI FAST system (in frame) consisting of a six-port injection valve and a vacuum pump connected to a sample loop; the system is installed on the sample holder of the ICP-SFMS instrument (ELEMENT II, ThermoScientific); the flow of the eluent is delivered by the peristaltic pump (controlled by the ICP-SFMS software); (right) FAST Valve and Precision Micro Peripump (FAST DXi) integrated in the ICP-QMS instrument (Nexion 300S).

**Standard solutions and reagents**

For the preparation of all solutions, ultra-pure water with a resistivity of 18 MΩ $cm^{-1}$ obtained from a Milli-Q water purification system (Millipore, MA, USA) was used.

Stock standard solutions were prepared from 1 g $L^{-1}$ bromide and bromate standard solutions purchased from Merck (Darmstadt, Germany). A quality control standard solution of 5 µg $L^{-1}$ $BrO_3^-$ was prepared from $KBrO_3$ purchased from Spex CertiPrep Inc. (New Jersey, USA). Bromoacetic acid was purchased from Merck, dibromoacetic acid and bromochloroacetic acid were purchased from Sigma Aldrich (Steinheim, Germany).

The eluent was prepared by dissolving $NH_4NO_3$ (Merck) in Milli-Q water. In case of low pressure LC/ICP-QMS, Ge (Spex CertiPrep Inc., NJ, USA) was added to the eluent (final concentration: 5 µg $L^{-1}$) to optimise the ICP-QMS instrument settings and to monitor signal drift during measurement. In case of low pressure LC/ICP-SFMS, Cs (Spex CertiPrep NJ, USA) was added to the eluent (final concentration: 10 µg $L^{-1}$).

**Sample treatment**

The samples were filtered through a 0.45 µm membrane filter (Schleicher & Schuell, Germany) to remove suspended solids and stored in the dark at 4 °C until analysis.

## Results and Discussion

**HPLC/ICP-QMS**

The HPLC/ICP-QMS optimisation was performed in 1999 and the protocol involved the use of a quadrupole-based ICP-MS instrument. The efforts to set up an HPLC/ICP-QMS system at that time were mainly devoted to the automation and a proper communication interface between the sample injection system, HPLC pump and ICP-QMS instrument.[17]

*Optimization of ICP-QMS*

Because the quadrupole-based ICP-QMS instrument used at that time (Elan 6000) was not equipped with a collision/reaction cell to remove interferences poly-atomic interferences, an evaluation of the potentially occurring interferences was necessary. The bromide isotopes at masses 79 and 81 have approximately the same relative abundance, but the signal of the latter suffers more from interference by a poly-atomic argon-containing ion. This interference results in an increase of the background signal; under the given instrumental settings, the height of the baseline in the chromatograms is: $^{79}Br$ (250 cps: $^{40}Ar^{38}ArH^+$) < $^{81}Br$ (14500 cps: $^{40}Ar^{40}ArH^+$). Although the baseline levels are stable during measurement, to a certain extent they generate a higher noise, resulting in less accurate results and a deterioration of the LoD. When selecting (a) suitable mass-to-charge ratio(s) (m/z) for monitoring, also the possibility of matrix-borne spectral interferences needs to be taken into account. In this case however, these interferences can be circumvented by adjusting eluent concentration and flow rate of the IC separation. Considering both the background levels and the isotopic abundances, $^{79}Br$ was selected for quantitative measurements.

*Optimisation of HPLC conditions*

Ammonium nitrate, which has the same elemental composition as nitric acid, is considered an optimal eluent in HPLC/ICP-QMS due to its following features: thermal volatility, hence no significant

salt deposition on the cones; no extra background interferences compared to $HNO_3$ in ICP-QMS; high concentration tolerance by ICP-QMS without causing pronounced non-spectral interference; possibility to adjust its pH value from acidic to slightly alkaline without impairing the ionic strength; no complexing capacity of $NH_4^+$ with anions or $NO_3^-$ with metals and no potential precipitation of analytes (unlike a carbonate mobile phase, which can induce the precipitation of $CaCO_3$).

The chromatographic anion exchange column offers the possibility of compressing bromate into a smaller zone at the top of the column when the sample is transferred from the sample loop onto the separation column. This can be seen in figure 2, where prior matrix matching of the sample with 100 mM $NH_4NO_3$ leads to peak broadening. The peak area is equal in both cases but the peak shape is superior when the samples are injected without addition of eluent. This effect has been referred to by Nowak *et al.* as the *relaunch effect*.[11] During the transfer of bromate and the other matrix anions from the sample loop onto the analytical column, the top of the column is mainly converted into a $Cl^-$ or $SO_4^{2-}$ form (major anions in drinking water). Because the anions have a much lower affinity to quaternary ammonium functional groups than nitrate (present in the eluent), the bromate is compressed into a smaller zone at the column top than it would have been when the column top was in the $NO_3^-$ form. Therefore, the resulting bromate peak in water has a much better peak shape than in the case of addition of $NH_4NO_3$ eluent to the sample, because in this case the column top would be in $NO_3^-$ form.



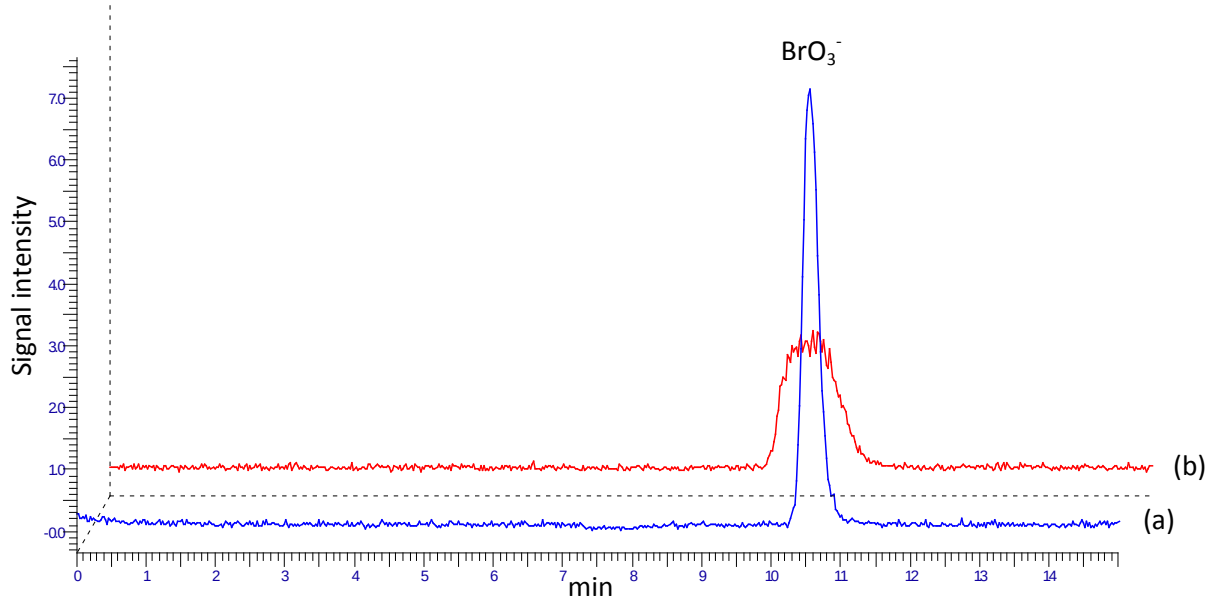


Figure 2: Compressing effect at the top of the column, measurement with HPLC/ICP-QMS of (a, blue) 10 µg $L^{-1}$ of $BrO_3^-$ in water and (b, red) 10 µg $L^{-1}$ of $BrO_3^-$ in 100 mM $NH_4NO_3$ solution (flow rate 400 µL $min^{-1}$, eluent 100 mM $NH_4NO_3$).

*Analytical characteristics and interferences*

The limit of quantification (LoQ) was calculated based on 7 consecutive measurements of a 100 ng $L^{-1}$ bromate and 100 ng $L^{-1}$ bromide standard solution. The LoQ calculated as six times the standard deviation on the 7 replicates amounted to 40 ng bromate $L^{-1}$ and 100 ng bromide $L^{-1}$. The peak of monobromoacetic acid, which can occur as another brominated disinfection by-product, overlaps slightly with the bromide peak, but is well separated from bromate, the compound of interest. This is shown in figure 3 and is in agreement with the data reported by Nowak and Seubert, using the same micobore column.[11]

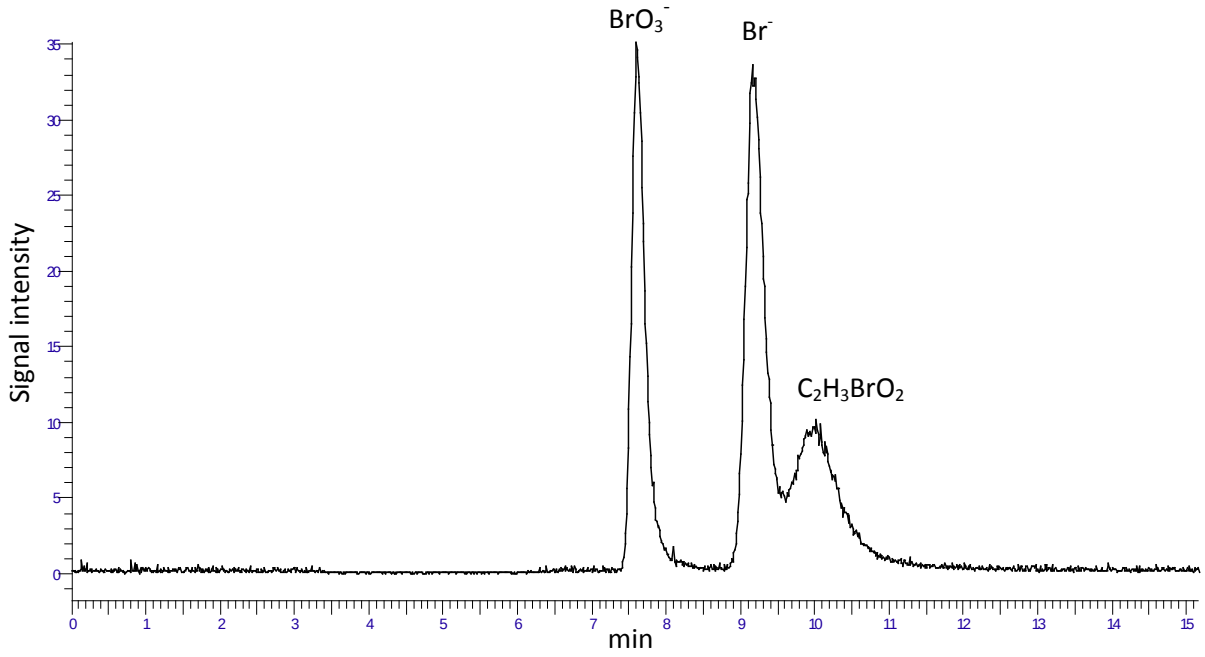


Figure 3: Standard solution containing 10 µg $L^{-1}$ of $BrO_3^-$, 10 µg $L^{-1}$ of $Br^-$ and 10 µg $L^{-1}$ of $C_2H_3BrO_2$ (monobromoacetic acid) measured with HPLC/ICP-QMS (flow rate 400 µL $min^{-1}$, eluent 100 mM $NH_4NO_3$).

**Low pressure LC/ICP-SFMS and LC/ICP-QMS**

The low pressure LC method uses a commercially available low-pressure flow injection switching valve system that is easy to use, is easily integrated and has compatible software that works well with both the ICP-MS and autosampler. The low pressure LC system is small and can be easily installed between the ICP-MS and the autosampler, or in case of the ICP-QMS instrument used in this work, even integrated in the instrument (see figure 1, right). A comparative study for the determination of bromate in drinking water was made between the low pressure LC system coupled to a sector field ICP-MS unit (ICP-SFMS, ELEMENT II) on the one hand and a quadrupole-based instrument (ICP-QMS, Nexion 300S) on the other.

*Optimisation of low pressure LC conditions*

For optimization, the same mobile phase as described above for the HPLC/ICP-QMS protocol was used and the flow rate was adapted to approximately 170 µL $min^{-1}$ (10 rotations per minute on the peristaltic pump). A fixed 100 µL sample loop was connected to the six-port injection valve. A low pressure LC/ICP-SFMS chromatogram is shown in figure 4. A calibration line up to 50 µg $L^{-1}$ of $BrO_3^-$ and $Br^-$ was constructed and it was observed that the sensitivity (slope) expressed as $^{79}$Br-signal *versus* µg Br $L^{-1}$ is ~ 15 % less for $^{79}$Br-bromide as compared to $^{79}$Br-bromate and this for both the ICP-QMS and the ICP-SFMS instrument. This is assumed to be an effect induced by the $NH_4NO_3$ eluent in combination with the nebulizer system (µ-Flow nebulizer coupled to a baffled cyclonic spray chamber). This difference was also observed when bromide and bromate standard solutions (obtained from different suppliers) were analysed directly without LC. The matrix of the eluent in combination with the nebulisation system have been shown to have an effect on $^{79}Br^+$ signal.[18,19] Kahen *et al*. hypothesized that gaseous $HBr_{(g)}$ formed during nebulisation diffuses away from the droplets and particles and can be removed from the injector gas stream by dissolution in the condensed low temperature eluent on the walls and subsequent drainage.[18] Difference in sensitivity between As species has also been observed when using desolvation systems as part of the nebulisation system in HPLC/ICP-QMS.[20-22,25] For accurate measurements, independent calibrations for each Br species are needed.

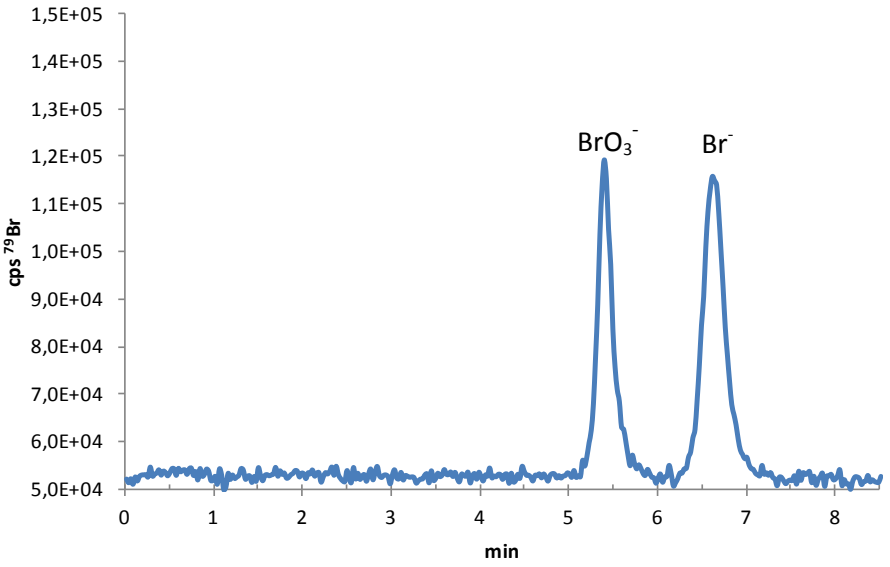


Figure 4: Standard solution containing 2.5 µg $L^{-1}$ of $BrO_3^-$ and 2.5 µg $L^{-1}$ of $Br^-$ measured with low pressure LC/ICP-SFMS ($^{79}Br$, 100 µL sample loop, flow rate of 170 µL $min^{-1}$, eluent 100 mM $NH_4NO_3$).



The known chromatographic interferences for the determination of bromate in drinking water via ICP-MS detection are bromoacetic acid, dibromoacetic acid, bromochloroacetic acid, bromide and the phosphate and/or sulphate matrix.[14] Under the chromatographic conditions mentioned above (flow rate of 170 µL $min^{-1}$, eluent 100 mM $NH_4NO_3$), complete overlap of the peaks of monobromoacetic acid and bromate was observed (the two most difficult brominated disinfection by-products to resolve due to their close pKa values).[10] This feature is also observed in the chromatograms presented by Guo *et al.* and in different US EPA methods using IC.[1,10,14] To chromatographically resolve the co-elution of monobromoacetic acid and bromate, the conditions were optimized to a flow rate of approximately 450 µL $min^{-1}$ (25 rpm) using 2 mM $NH_4NO_3$ as eluent. While the monobromoacetic acid and bromate peak were well separated, the bromide peak eluted only after 26 minutes (see figure 5).

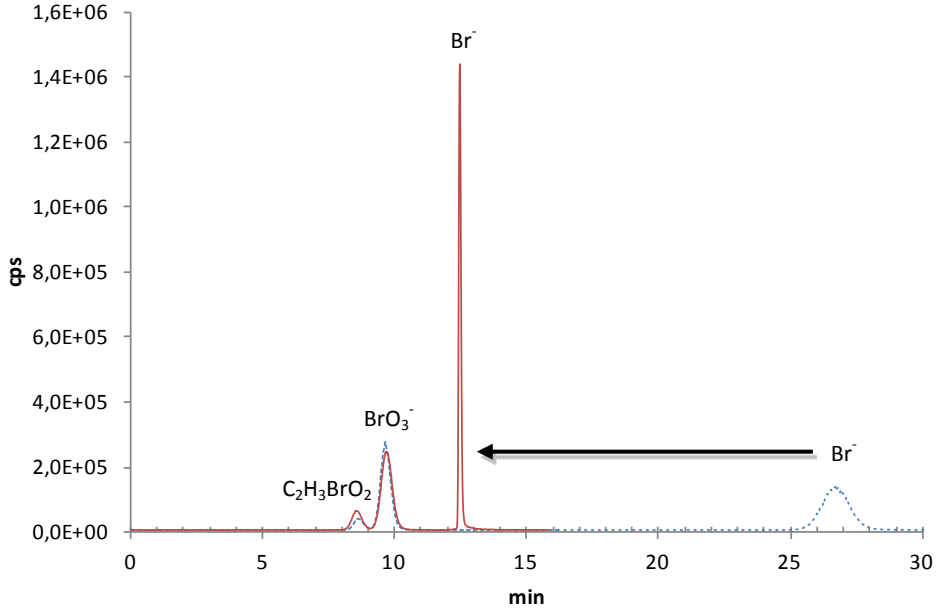


Figure 5: Standard solution containing 10 µg $L^{-1}$ of $C_2H_3BrO_2$, 50 µg $L^{-1}$ of $BrO_3^-$ and 50 µg $L^{-1}$ of $Br^-$ measured with low pressure LC/ICP-SFMS ($^{79}Br$, 100 µL sample loop, flow rate of 450 µL $min^{-1}$). Dotted line: eluent 2 mM $NH_4NO_3$; full line: eluent 2 mM $NH_4NO_3$ and secondary injection of 375 µL of 100 mM $NH_4NO_3$ after 620 s.

For comparison, the HPLC/ICP-QMS method developed by Guo *et al.* allows the determination of bromate and bromoacetic acids in 46 minutes.[10] The US EPA method 321.8 allows the determination of bromate in 12 minutes.[1,14] In order to speed up the analysis, a sample loop of 2500 µL was connected to the injection valve and the ESI FAST system was programmed with a 'gradient' mobile phase using 2 mM and 100 mM $NH_4NO_3$. In principle, the 2 mM is being constantly delivered at a flow rate of approximately 450 µL $min^{-1}$ (25 rpm). First, the sample solution is loaded in the 2500 µL sample loop using the vacuum pump and thereafter injected during 15 seconds (which corresponds to an injection volume of ~ 113 µL). Second, the sample loop is filled with the 100 mM $NH_4NO_3$ solution and 620 seconds after the injection of the sample solution, the 100 mM $NH_4NO_3$ solution is injected during 50 seconds (which corresponds to an injection volume of ~ 375 µL). The effect of using a '*gradient*' mobile phase using low pressure LC/ICP-SFMS is shown in figure 5. By using this automated second injection as gradient mobile phase, the chromatographic run was shortened to 13 minutes.

To resolve co-elution of bromate, bromide, bromoacetic acid, dibromoacetic acid, bromochloroacetic acid, phosphate and sulphate (matrix), the low pressure LC conditions were further optimized to a flow rate of approximately 340µL $min^{-1}$ using 5 mM $NH_4NO_3$ as eluent. First, the sample is loaded in a 1000 µL sample loop using the vacuum pump and injected during 180 seconds (~ 1000 µL). Second, the sample loop is filled with 50 mM $NH_4NO_3$ solution and fully injected 1200 seconds after the first injection (~ 1000 µL). A low pressure LC/ICP-QMS chromatogram of a standard solution containing possible interferences is shown in figure 6 ($^{74}Ge$, which has similar mass to $^{79}Br$, was used as internal standard).[23] Retention time shifts in ion chromatography are possible due to weak eluent strengths and high ionic strength matrices. For phosphate concentrations up to 100 mg $L^{-1}$ no interferences were observed, however for sulphate concentrations above 200 mg $L^{-1}$ peak broadening was observed for bromate.

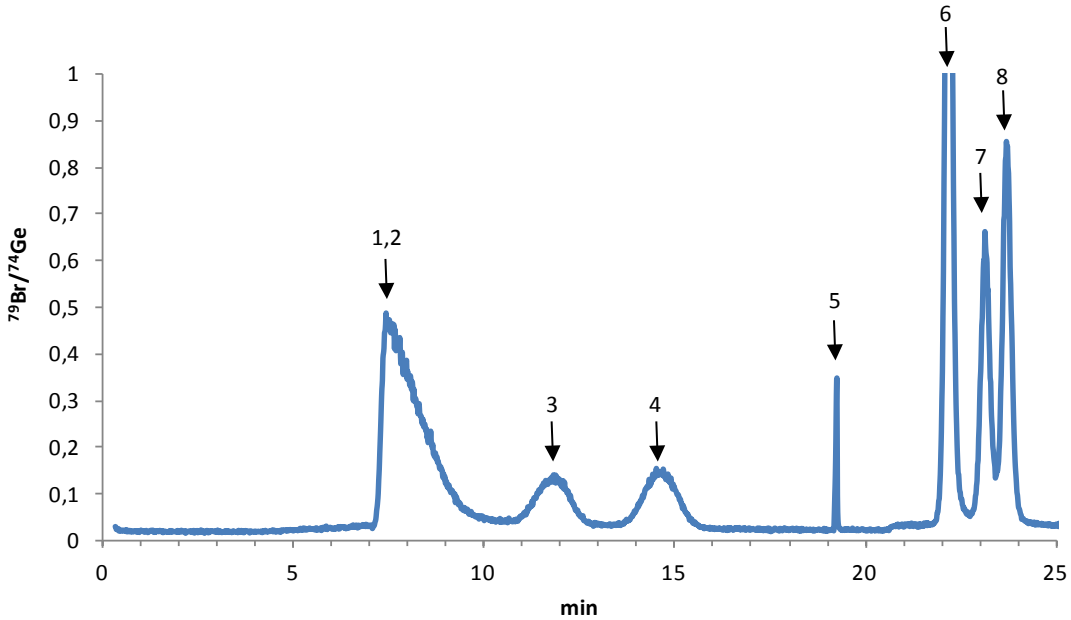


Figure 6: Low pressure LC/ICP-QMS chromatogram ($^{79}Br/^{74}Ge$ signal ratio) for a standard solution containing (1) 100 mg $L^{-1}$ of $PO_4^-$; (2) 100 mg $L^{-1}$ of $SO_4^-$; (3) 5 µg Br $L^{-1}$ of $C_2H_3BrO_2$; (4) 5 µg Br $L^{-1}$ of $BrO_3^-$; (5) secondary injection of 50 mM $NH_4NO_3$; (6) 5 µg Br $L^{-1}$ of $C_2H_2ClBrO_2$; (7) 5 µg Br $L^{-1}$ of $C_2H_2Br_2O_2$; (8)5 µg Br $L^{-1}$ of $Br^-$; 1000 µL sample loop, flow rate of 340 µL $min^{-1}$, 5 mM $NH_4NO_3$ and secondary injection after 1200 s of 1000 µL of 50 mM $NH_4NO_3$.

The flexibility of low pressure LC/ICP-SFMS can be used to develop fit-for-purpose methods. In the case only bromate is the analyte of interest, the 27 minutes lasting chromatographic run needed to separate bromide from dibromoacetic acid (figure 6) can be shortened to 13 minutes (figure 5). As

the Maximum Admissible Concentration (MAC) of 10 µg $L^{-1}$ bromate in drinking waters is rarely exceeded, one could further reduce the chromatographic run time to 8 minutes (see figure 4). In this case, monobromoacetic acid and bromate will co-elute and could lead to a false positive exceeding of the MAC. However, exceedings are rarely observed (see further) and – if needed – these samples could be easily re-analysed using a '*gradient*' mobile phase to resolve the co-elution of monobromoacetic acid.

According to the European drinking water directive, the performance characteristics of the method of analysis must, as a minimum, be capable of measuring bromate with a trueness of 25 %, a precision of 25 % and a limit of detection of 2.5 µg $L^{-1}$.

The flexibility of low pressure LC/ICP-MS can be used to develop a tailor-made method with predefined sensitivity by simply changing the sample injection time. This is demonstrated by injecting a solution of 10 µg $L^{-1}$ $BrO_3^-$ and 10 µg $L^{-1}$ $Br^-$ from the 2500 µL sample loop during 15 (113 µL), 30 (225 µL), 60 (450 µL), 120 (900 µL) and 240 (1800 µL) seconds. A correlation coefficient of $R^2 = 0.9995$ was derived between the measured peak area of bromate and the injection time. An overlay of the chromatograms, time shifted for the different durations of the sample injection time (*e.g.*, chromatogram for a sample injection time 120 s was shifted 105 s to the left), is shown in Figure 7. This feature can also be used to instrumentally "dilute" a sample out of calibration range by simply changing the injection time.

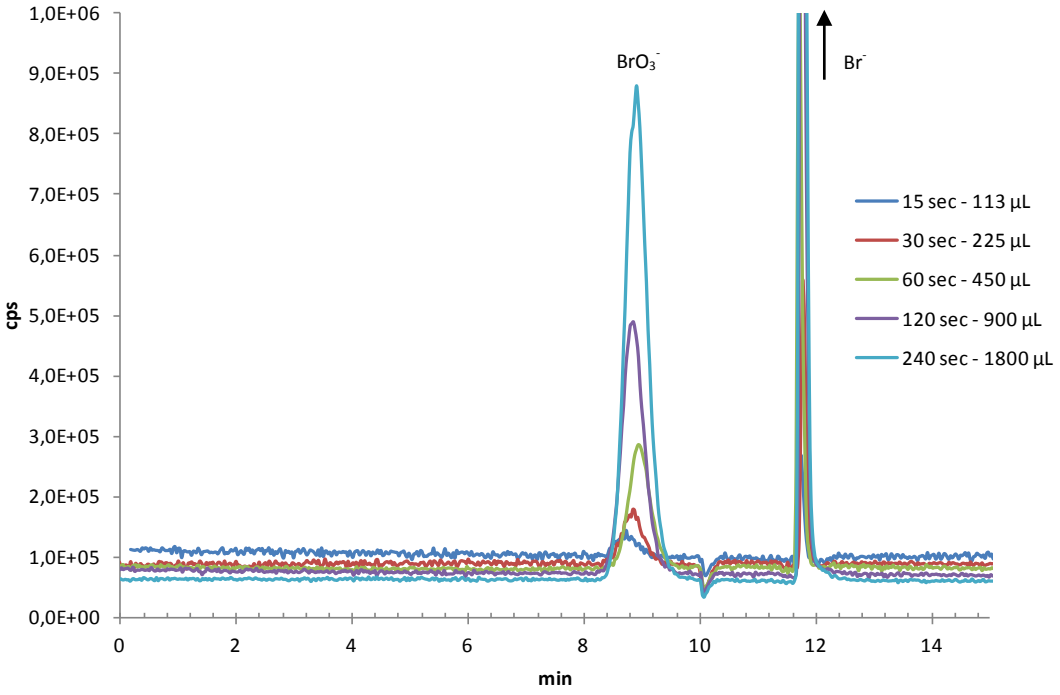


Figure 7: Effect of sample injection time (sample loop volume) on peak area; low pressure LC/ICP-SFMS measurement ($^{79}Br$) of a standard solution containing 10 µg $L^{-1}$ of $BrO_3^-$ and 10 µg $L^{-1}$ of $Br^-$, eluent 2 mM $NH_4NO_3$ and secondary injection after 620 s of 375 µL of 100 mM $NH_4NO_3$ (for the overlay of the chromatograms, a time shift to compensate for the difference in sample injection duration was made).

The LoQ attainable with low pressure LC/ICP-SFMS was calculated based on 7 consecutive measurements of a 0.5 µg $L^{-1}$ bromate-spiked tap water using a 900 µL sample loop (chromatographic conditions according to figure 7). An average concentration of 0.52 µg $L^{-1}$ bromate was measured, and the LoQ, calculated as six times the standard deviation on the 7 replicates, amounted to 0.17 µg $L^{-1}$ bromate.

The LoQ attainable with low pressure LC/ICP-QMS was calculated based on 7 consecutive measurements of a 0.5 µg $L^{-1}$ bromate-spiked tap water using a 1000 µL sample loop (chromatographic conditions according to figure 6). An average concentration of 0.51 µg $L^{-1}$ bromate was measured, and the LoQ, calculated as six times the standard deviation on the 7 replicates, amounted to 0.19 µg $L^{-1}$ bromate.

Notwithstanding the relative high first ionisation energy of Br (11.81 eV), resulting in a low degree of ionisation in the plasma, the calculated LoQ of both systems is similar and fit-for-purpose for the determination of bromate in drinking water.[26] The integrated peak area of a 0.5 µg $L^{-1}$ bromate spike solution (1000 µL sample loop) using ICP-QMS amounts to ~ 60000 cps and is a factor of ~ 10 lower as compared to ICP-SFMS (in low resolution mode). Despite the superior sensitivity of ICP-SFMS, the chromatographic baseline noise (low pressure LC system), the broadening of the bromate peak (related to the strength of the eluent) and the manual integration of the chromatograms (peak areas) at these low levels using the periSPEC Peak Area Finder Software (ESI) are likely to contribute to the standard deviation from which the LoQ is derived.

A drinking water sample was spiked with 12 µg $L^{-1}$ bromate and analysed 4 times via low pressure LC/ICP-SFMS (chromatographic conditions according to figure 7 and using a 900 µL sample loop). An average concentration of 11.9 ± 0.2 (st. dev.) µg $L^{-1}$ bromate was measured (recovery of 99 %). The standard deviation calculated on 7 determinations of quality control samples containing 0.5 and 5 µg $L^{-1}$ bromate, processed in different measurement runs, amounted to 0.502 ± 0.028 µg $L^{-1}$ and 4.92 ± 0.24 µg $L^{-1}$ bromate, respectively.

A drinking water sample was spiked with 2.5 µg $L^{-1}$ bromate and analysed 4 times via low pressure LC/ICP-QMS (according to chromatographic conditions described in figure 6). An average concentration of 2.52 ± 0.09 (st. dev.) µg $L^{-1}$ bromate was measured (recovery of 101 %). The standard deviation calculated on 4 determinations of quality control samples containing 1 and 5 µg $L^{-1}$ bromate, processed in different measurement runs, amounted to 0.999 ± 0.021 µg $L^{-1}$ and 4.93 ± 0.03 µg $L^{-1}$ bromate, respectively.

The performance characteristics in terms of trueness, precision and LoQ of low pressure LC/ICP-SFMS and LC/ICP-QMS are amply sufficient to meet the values specified in the European drinking water directive. According to these required performance characteristics for regulatory monitoring, there is still room left for further reduction in running costs, *e.g.*, by using Ge as internal standard to be relied on for Br quantification and thus omitting the daily external calibration procedure (Eickhorst *et al.* showed that the Br-to-Ge ratio was nearly constant over 4 months and almost independent of the ICP–MS instrument settings).[24] Moreover, next to Br determination, ICP-MS also offers the possibility of simultaneous Cl and I monitoring in the samples under investigation.[12,24]

**Bromate analysis in audit monitoring program**

The European Directive not only sets quality limits to water intended for human consumption, but also defines a check and audit monitoring program for the Member States. For the 81 different drinking water supply zones in the Flemish region of Belgium, approximately 1400 bromate determinations in water collected from the tap are performed on a yearly basis in the audit monitoring program.[27] Besides these legal monitoring requirements, the 17 different drinking water companies carry out supplementary bromate determinations at the level of the water production, water towers and main supplies. All these results are reported to the Flemish Environment Agency for an evaluation of the drinking water quality. Of the 1439 analyses of tap waters performed during the audit monitoring program in 2009, only 1 result (11.4 µg $L^{-1}$) exceeded the Maximum Admissible Concentration for bromate.[27] Of the 1477 tap waters analyzed during the audit monitoring program in 2010, not a single exceeding was observed for bromate.[28]

As a supplementary validation and verification of the results of the drinking water companies, a yearly analysis of about 20 tap waters randomly collected over the different drinking water supply zones in the Flemish region is carried out by our laboratory. The results of these bromate determinations of the last 4 years are summarised in figure 8. For the years 2009-2010, the analyses were performed with HPLC/ICP-QMS, for the years 2011-2012, the analyses were performed with low pressure LC/ICP-SFMS.

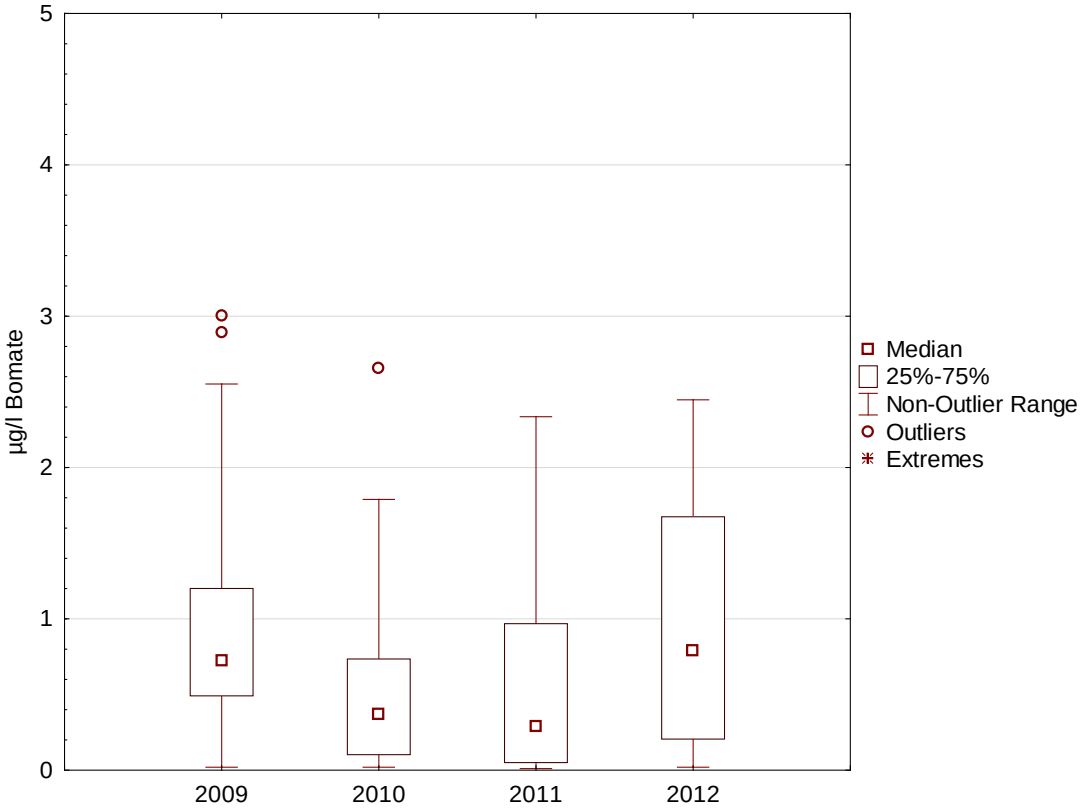


Figure 8: Box and Whisker plots of bromate concentrations yearly determined in 20 tap waters collected randomly over different water supply zones in the Flemish region of Belgium (2009-2010 analysis with HPLC/ICP-QMS; 2011-2012 analysis with low pressure LC/ICP-SFMS).

Partcipation in an interlaboratory trial for the determination of bromate in drinking water is performed on a yearly basis. When using HPLC/ICP-MS the bias in the interlaboratory trial amounted 4.2 and 1.4%, when using low pressure LC/ICP-SFMS the bias amounted -3.1 and -0.3% (average of 9 participating laboratories).

The overall median value in Flemish tap water is 0.5 µg $L^{-1}$ bromate and almost all measured concentrations are below the recommended LoD of 2.5 µg $L^{-1}$. In 2011, one result (24 µg $L^{-1}$, extreme value not shown in figure 8) exceeded the Maximum Admissible Concentration (10 µg $L^{-1}$). The maximum admissible level for bromate has been primarily based on current analytical capabilities (not on toxicological considerations - the target concentration for bromate in drinking water is zero); thus, there is a need for ongoing development and refinement of analytical technologies in order to permit rapid and reliable determinations at the sub µg $l^{-1}$level.

## Conclusion

Routine determination of bromate in regulatory monitoring programs is needed to monitor the level of brominated disinfection by-products in drinking water. The benefits of low pressure LC/ICP-MS as

compared to HPLC/ICP-MS are the ease of use and the availability of a low-cost system for fast and routine speciation analysis, which can be implemented and automated on any ICP-MS instrumentation easily. The methodology/technology described here shows that the complexity (and cost) of the instrumentation required for such analysis has been considerably reduced, without compromising performance characteristics in terms of LoQ and reliability of daily analysis results.

From the random sampling, organised as a supplementary validation and verification of the results of the drinking water companies, a median bromate concentration in Flemish tap water of 0.5 µg $L^{-1}$ was derived. One result exceeding the Maximum Admissible Concentration (10 µg $L^{-1}$) for bromate was observed on a total of 80 samples. Global and national agencies are striving to monitor bromate in drinking water in order to establish appropriate regulatory limits. Depending on the results of further research, a risk model could possibly provide a more definitive guideline value for oxyhalides in drinking water. For these reasons, there is a need for further improvement of the existing methods in terms of sensitivity, cost and reliability. Unquestionably, the analysis of inorganic oxyhalide disinfection by-products in drinking water will continue to lead to ongoing improvement in water quality in the future.

**Acknowledgements:**
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28. Flemish government agency, results of the quality controls of the in Flanders region distributed water intended for human consumption, 2010, http://www.vmm.be/. Accessed 20 Sept 2012.

## 3.5. SUMMARY AND CONCLUSION

In this chapter, speciation applications have been designed to determine chromate in solid materials, selenate and selenite in waste water and bromate in drinking water. All of the applications were driven by European legislation, *i.e.,* the restriction of hexavalent chromium in electrical and electronic equipment brought onto the European market, removal of oxy-anions from wastewater to ensure compliance with European environmental quality parameters and the control of the maximum level of carcinogenic disinfection by-products in European drinking water monitoring programs.

Referring to the quote by T.S. Eliot in the introduction (*Where is the wisdom we have lost in knowledge? Where is the knowledge we have lost in information?*), one must keep in mind that in the age of too much information, knowledge of and profound insight in the intrinsic quality of the analytical data becomes even more valuable when it comes to interpretation of the actual chemical status of our environment. The latter is especially illustrated in the conclusions formulated in the three different papers dealing with the determination of Cr(VI) in solid matrices, where research in the chromium species interconversion led to new analytical challenges and multi-disciplinary methods to be used. Quality control and quality assurance programs carried out along these speciation research projects were of utmost importance to derive the level of oxidation of Cr(III) and to assess the toxicity of Cr-containing solid materials. Correction for the species interconversion observed remains ambiguous when the chemical form of the species present in the sample (*e.g.*, $FeCr_2O_4$) is different from the added spike (*e.g.*, $Cr(NO_3)_3.9H_2O$). On the other hand, knowledge of the method-induced interconversion is particularly relevant for the determination of Cr(VI) in ambient particulate matter ($PM_{10}$) as the level of observed Cr(III) oxidation is within the range of the level of monitored Cr(VI) and could lead to false positives exceeding of the air quality guideline value.

While the relevance of elemental speciation in regulatory monitoring is not at stake, why is elemental speciation not done routinely with LC/ICP-MS in analytical laboratories? First, European Directives and legislation about elemental speciation are to a great extent still missing with the exception of those for a few species (*e.g.,* Cr(VI), organotin compounds, methylmercury) and therefore, routine laboratories lack the incentive to invest in the technologies. Second, for the determination of some species, *e.g.,* bromate, alternative cheap methods (as compared to LC/ICP-MS) are available for monitoring at the concentration level of the regulatory limit value. Third, the assumption of monitoring in a regulatory context is that only one or a few constituents of a sample - usually the analytes of interest - play a role in the measurement that is obtained. When applying standardized procedures in routine, users tend to have as little concern as possible about what other species in the sample might yield a false response or whether the method is applicable to all samples in the measurement run. However, and especially for solid samples, elemental speciation analysis is not considered as a course of action to always be followed and interpreted in the same way. These restrictions have often led to the current pragmatic approach in elemental speciation in regulatory context, *i.e.,* only in case the total concentration is above the limit value, an elemental speciation analysis is performed.

Speciation analysis nowadays is a modern and important analytical discipline, in which many questions have to be answered, especially in environmental chemistry and the life sciences. With the availability of commercial interfaces to easily hyphen different separation techniques (primarily LC, GC) to ICP-MS, one may forget the exciting research in the past aiming at, *e.g.*, coupling GC via a self-made heated transfer line to an ICP-MS unit [139]. Also, the efforts to set up an HPLC/ICP-MS system for the speciation of selenium in the year 2000, were mainly devoted to the automation and a proper communication interface between the sample injection system, the HPLC pump and the ICP-MS instrument. Ten years later and with the availability of a low pressure LC system, speciation analysis can be implemented easily on any ICP-MS instrument and this was demonstrated for the (routine)

determination of bromate in drinking water. Nowadays, LC/ICP-MS can truly be considered widespread sensitive and versatile speciation instrumentation. Recent approaches to determine Se species, specifically at ultratrace levels, have also focussed on a robust and work/time efficient method by online coupling of a preconcentration (trap) column to an IC-ICP-MS system [124]. Other novel approaches used ICP tandem mass spectrometry (ICP-MS-MS) with $O_2$ reaction/collision gas to completely remove severe interferences with the Se speciation originating from the plasma source and the biological sample matrix [125].

Speciation is also increasingly involved in multi-disciplinary approaches using so-called *orthogonal speciation schemes (e.g.,* ESI-MS and HPLC/ICP-MS) for (complex) species identification and/or quantification (*e.g.*, metallomics, pharmaceutical substances)[111]. Recent advances in this field, includes front-end modifications (*e.g.*, micro and capillary nebulizers) to adapt the ICP-MS instrument to the low flow rates (~ µl $min^{-1}$) and/or high organic content solutions delivered by the LC system. Also here, alternative instrumental approaches are needed in the search for lower detection limits. One such approach is based on the high resolving power provided by double focusing ICP-MS instruments (*e.g.*, in case of phosphoproteomics to separate the $^{31}P^{+}$ and $^{32}S^{+}$ peaks from those of polyatomic ions). A less expensive alternative is the use of reaction cells in ICP-QMS (*e.g.*, chemically resolve $^{31}P^{+}$ and $^{32}S^{+}$ from polyatomic ions by their oxidation to $^{31}P^{16}O^{+}$ and $^{32}S^{16}O^{+}$ after preferential reaction with oxygen gas supplied to the cell)[140].

# CHAPTER 4 TRACER EXPERIMENTS WITH STABLE ISOTOPES IN ENVIRONMENTAL STUDIES AND USE OF NATURAL ISOTOPIC VARIATION AS A PROXY

## 4.1. PERSPECTIVE ON ISOTOPIC TRACERS

As a first approximation, it can be stated that all elements have an isotopic composition that is invariant in nature. This is the result of thorough mixing of most nuclides prior to the formation of the solar system some 4.6 billion years ago [144]. Although isotopic abundances are assumed to be fairly constant in nature, variations do occur. These variations may result from the decay of naturally occurring and long-lived radionuclides (*e.g.*, $^{238}U$ -> $^{208}Pb$) or natural isotope fractionation effects [145]. Different isotopes of one and the same element display the same number of electrons and thus show to a very large extent the same chemical behaviour. Nevertheless, small differences in their physicochemical behaviour exist as a result of the difference in the number of neutrons in their nucleus, or in other words, their mass. Due to this relative difference in mass, different isotopes of the same element may take part to a slightly different extent in physical processes or in (bio)chemical reactions with natural mass fractionation as a consequence.

The capability to determine isotope abundances is an important asset of mass spectrometry. Inorganic mass spectrometry recently celebrated its 100$^{th}$ anniversary [146]. In 1910, Thomson demonstrated the existence of isotopes of chemical elements with the example of two abundant stable neon isotopes ($^{20}Ne$ and $^{22}Ne$). Thomson's student Francis William Aston continued the research, building the first full functional mass spectrometer (reported in 1919), which rapidly allowed him to identify no fewer than 212 of the 288 naturally occurring isotopes (or primordial isotopes found on Earth that have existed in their current form since before Earth was formed). In 1921, F. W. Aston became a fellow of the Royal Society and received a Nobel Prize in Chemistry in the same year *"for his discovery, by means of his mass spectrograph, of isotopes, in a large number of non-radioactive elements, and for his enunciation of the whole-number rule"*. Updates on the isotopic composition of the elements as determined by isotope ratio mass spectrometry are reported on a regular basis by the Commission on Isotopic Abundances and Atomic Weights (CIAAW) of the International Union of Pure and Applied Chemistry (IUPAC) [147]. The update involves a critical evaluation of the published literature and for each element, data from the "best measurement" of the isotope abundances in a single sample, along with a set of representative isotope abundances and uncertainties that accommodate known variations in normal terrestrial materials are reported.

The precise and accurate determination of isotope ratios is required for different application fields, such as: geochronological dating; provenance determination of, among other, objects of art and/or archeological or forensic relevance and agricultural products of animal or plant origin; the use of isotope ratios determined in natural chronological archives (*e.g.*, speleothem or coral) to serve as a paleoproxy, *e.g.*, for temperature or pH; determining isotope ratios of radioactive elements in the nuclear industry and for radioactive waste control; tracer experiments using highly enriched stable isotopes or long-lived radionuclides in environmental, biological or medical studies and the isotope dilution technique as a potentially primary method for the determination of element concentrations at trace and ultratrace levels.

In general, an important requirement for a technique used for studying (the sometimes extremely small) variations in the isotopic composition of an element is the possibility to perform analyses with

a very high precision and accuracy. While (gas source) isotope ratio mass spectrometry (IR-MS) is traditionally used for studying the isotopic composition of the "light" elements (*e.g.*, H, C, N, O and S), for a long time, thermal ionization mass spectrometry (TIMS) has been considered as the only technique that provided a sufficient precision to detect subtle variations in the isotopic composition of the "heavier" elements. Compared to TIMS, the first ICP-MS instruments offered a less demanding sample preparation and were relatively easy to operate. But on the other hand, they were also characterized by a rather poor isotope ratio precision ( ~ 0.2 to 0.5 %, while for TIMS precisions down to 0.005 % are attainable), a more pronounced bias and spectral overlap of the analyte signals with those of interfering ions [144,146]. Through the years, various modifications have led to a significant improvement in the isotope ratio precision attainable with single-collector ICP-mass spectrometers (down to 0.05% or slightly better). The first time that the isotope ratio precision typical for TIMS was approached, was in 1992, with the introduction of multi-collector (MC) sector-field ICP-mass spectrometers that are equipped with an array of Faraday collectors [144,145]. In contrast to the single-collector instruments, with which the analyte signals are monitored sequentially, MC-ICP-MS instruments are able to monitor the intensity of several ion beams simultaneously, as a result of which short term variations in signal intensity are affecting all isotopes to the same extent, such that these cause (practically) no detrimental effect on the isotope ratio precision. In this way, with the most recent MC instruments, isotope ratio precision down to 0.002 % RSD can be obtained.

In the context of this dissertation, only single-collector ICP-mass spectrometers have been used for isotope ratio measurements. With the attainable precision of this type of instrumentation, a variety of environment-related issues can be studied using (i) compounds in which a particular element shows an isotopic composition that is artificially made sufficiently different from the corresponding natural one or using (ii) elements for which the natural variations in the isotopic composition are quite pronounced (*e.g.*, B, Sr or Pb).

Single-collector ICP-mass spectrometers are very well suited for performing isotope dilution measurements for the determination of element (or species) concentrations at trace and ultratrace levels using artificially enriched stable isotopes [148]. As an example, the species-specific isotope dilution method for the determination of hexavalent chromium is discussed in § 3.3. Another example of the good accuracy and precision attainable with isotope dilution, are the results of the stability testing of human blood reference materials (BCR CRMs 634, 635 and 636), also performed with the Elan 6000 quadrupole-based ICP-MS unit. The average results of 24 independent analyses of each reference material are given hereunder (uncertainty expressed as a 95 % confidence interval).

| | Pb µg/L | Cd µg/L |
|---|---|---|
| BCR 634 – Certified | 46 ± 5 | 1.4 ± 0.4 |
| BCR 634 – measured | 51 ± 2 | 1.27 ± 0.04 |
| BCR 635 – Certified | 210 ± 24 | 6.6 ± 0.6 |
| BCR 635 – measured | 209 ± 13 | 6.5 ± 0.5 |
| BCR 636 – Certified | 520 ± 50 | 11.6 ± 0.6 |
| BCR 636 – measured | 512 ± 8 | 11.6 ± 0.2 |

In the context of bio-monitoring and with increasing awareness of the possible link between environmental exposure to certain metals and neuro-degenerative diseases, (ultra)trace determination of elements in human body fluids are increasingly being performed with ICP-MS. The analysis by ICP-MS can, however, be hampered by the existence of spectral (*e.g.*, $MoO^+$ on $Cd^+$) and non-spectral interferences and care must be taken with ambient low-level determination of trace elements in human body fluids (*e.g.*, problems with the accurate detemination of Cd in blood were reported in the first Flemish bio-monitoring program, 2002–2006)[149].

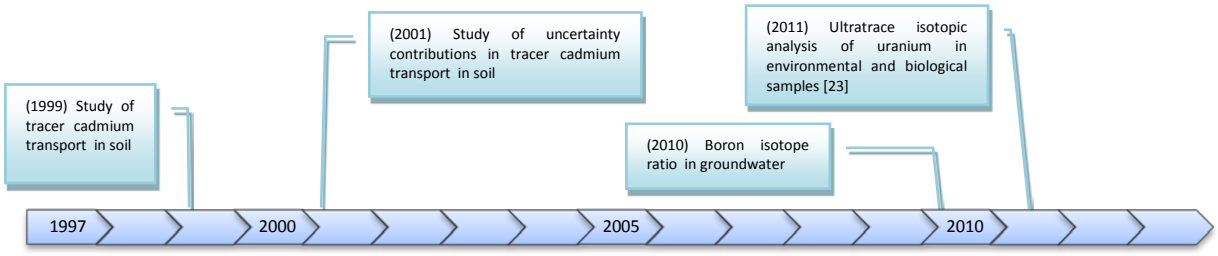
The focus in this dissertation, however, is on tracer experiments with stable isotopes in environmental studies and on the use of natural isotopic variation as a proxy. In the following paragraphs, the scientific papers related to the development of methods based on ICP-MS for the isotopic analysis of elements in an environmental context are introduced with emphasis on the connecting thread of the PhD dissertation, *i.e.,* the relation between the ICP-MS measurement, the environmental issue and the regulatory context. The scientific papers have been arranged chronologically in the following paragraphs (see timeline):

§ 4.2 Metal leaching from soils contaminated by historic smelter emissions

K. Tirez, P. Seuntjens and N. De Brucker, Full uncertainty calculation on quantitative determination of tracer and natural cadmium in soil column effluents with ICP-MS, *J. Anal. At. Spectrom*., 1999, **14**, 1475–1484.

§ 4.3 Sources of nitrate leaching

K. Tirez, W. Brusten, D. Widory, E. Petelet, A. Bregnot, D. Xue, P. Boeckx and J. Bronders, Boron isotope ratio ($\delta^{11}B$) measurements in WFD monitoring programs: comparison between double-focusing sector-field ICP (ICP-SFMS) and thermal ionization mass spectrometry (TIMS) , *J. Anal. At. Spectrom*., 2010, **25**, 964-974.




Timeline (1997 – 2013) showing the chronological order of the development of methods based on inductively coupled plasma-mass spectrometry (ICP-MS) for the determination and isotopic analysis of metals and oxy-anions in an environmental context.

**Interesting links:**

- **Isotopic Analysis, Fundamentals and Applications Using ICP-MS**, F. Vanhaecke and P. Degryse, 2012, ISBN 978-3-527-32896-3 - Wiley-VCH, Weinheim, 529 p.

## 4.2. METAL LEACHING FROM SOILS CONTAMINATED BY HISTORIC SMELTER EMISSIONS

The transport of *heavy metals* in soils depends on water flow and physicochemical processes, such as sorption and immobilisation due to mineral precipitation. Slow water flow and sorption result in residence times of several decades or centuries in soils [151]. Many efforts have been spent to model and evaluate heavy metal transport in soils at small scale, *i.e.,* from the lab scale columns up to the field scale, but only few assess metal leaching from large diffusely contaminated areas [152,153].

From a land management point of view, there is a clear need for models that allow predicting concentrations of metals leaching to groundwater in a spatially variable context. Such an instrument allows the land manager to plan measures, to prioritize actions, and to evaluate different scenarios of soil and land reclamation and rehabilitation.

A prominent example of regional groundwater pollution is the Kempen area at the Dutch-Belgian border. An area of approximately 700 km² is polluted with Cd and Zn due to historical non-ferrous smelting activities [154-156].

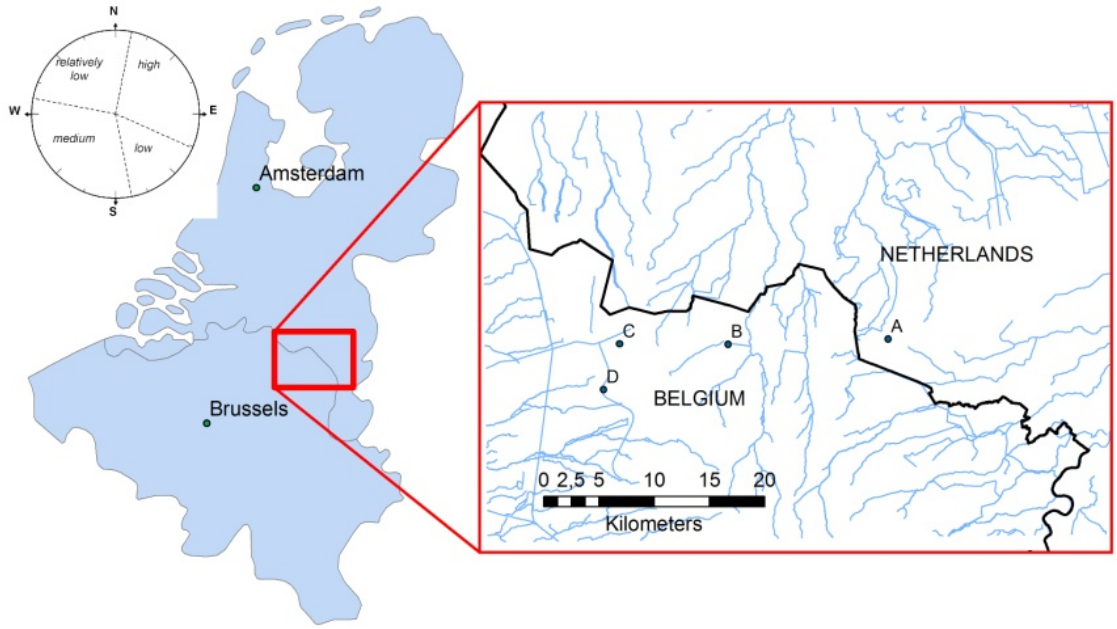



Figure 35: Map of the affected area with the location of the 4 smelter sites (A, B, C and D) and the 4 classes of wind direction [155].

Historical emissions of *heavy metals* due to non-ferrous ore processing, starting at the end of the 19$^{th}$ century, caused metals to leach into groundwater in vulnerable areas, mainly consisting of acid sandy soils and shallow groundwater tables.

In commission of OVAM, a spatially resolved model for leaching of Cd into groundwater was developed for the area [155]. This model uses land-use maps, historical information on emissions, atmospheric deposition data and soil data. Cd transport through the unsaturated zone can be simulated taking into account differences in soil type and land-use. This results in spatially resolved information on amount and timing of metals leaching into the groundwater at a regional scale. The model allows evaluating management scenarios on the long term and reveals general patterns and changes over longer periods of time (see maps below).

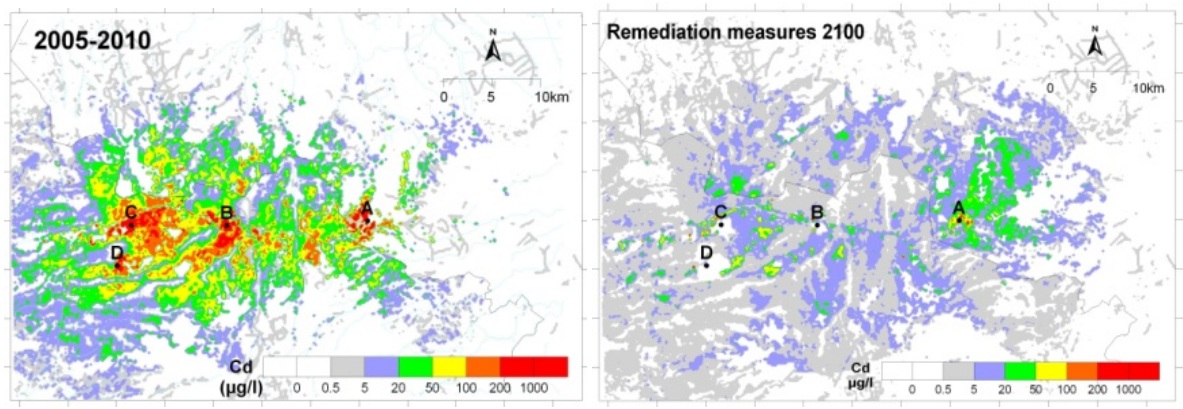



Figure 36: Map representing concentrations of Cd leaving the unsaturated zone in 2005 and map representing expected concentrations of Cd leaving the unsaturated zone in 2100 under the remediation measures scenario [155].

In order to validate the sorption models and to provide basic transport parameters for the leaching of Cd into groundwater, laboratory-scale migration experiments have been performed. For this purpose, soil migration experiments, in which a tracer (stable $^{111}$Cd isotope) was added on top of a contaminated soil and the column effluents were fractionally collected, were performed. The level of contaminant (natural) and tracer ($^{111}$Cd) cadmium in the soil column effluents was simultaneously determined by ICP-MS. For the calculation of the uncertainty on the quantitative determination of tracer and natural cadmium, a method was proposed, emphasising a practical, realistic approach of estimating uncertainties based on statistical assumptions (see paper: Full uncertainty calculation on quantitative determination of tracer ($^{111}$Cd) cadmium and natural cadmium in soil column effluents with ICP-MS, *J. Anal. At. Spectrom.*, 1999). In a subsequent paper (not presented in this dissertation), the total uncertainty budget was used as a method evaluation criterion for the determination of tracer ($^{111}$Cd) cadmium and indigenous cadmium in soil column effluents with ICP-MS (K. Tirez, M. Berglund, P. Seuntjens and N. De Brucker, *J. Anal. At. Spectrom*., 2001, 16, 307-314).

# Full uncertainty calculation on quantitative determination of tracer ($^{111}$Cd) cadmium and natural cadmium in soil column effluents with ICP-MS

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*Journal of Analytical Atomic Spectrometry*, 1999, **14**, 1475-1484.
(Reference list of this paper, see p. 193)

*Abstract*

*In laboratory-scale migration experiments a tracer (stable $^{111}$Cd isotope) is added on top of a contaminated soil and the column effluents are fractionally collected. This paper describes an analytical method for the simultaneous low level quantitative determination with inductively coupled plasma-mass spectrometry (ICP-MS) of contaminant (natural) and tracer ($^{111}$Cd) cadmium in soil column effluents by adaptation of the isotope dilution equation.*
*For the calculation of the full uncertainty on the quantitative determination of tracer and natural cadmium, a method has been proposed emphasising the practical, realistic approach of estimating uncertainties based on statistical assumptions. The GUM Workbench© program, the computations of which follow the rules of the 'ISO guide to the expression of uncertainty in measurement', was used. At low concentrations of cadmium (< 0.2 ng ml$^{-1}$ Cd) the uncertainty due to counting statistics is the major source of uncertainty. At higher concentrations the signal instability of the ICP-MS, partially due to the clogging of the sampling cone by calcium salts present in the leachant ($CaCl_2$), forms the largest contribution to the total uncertainty. For concentrations of 0.5 ng ml$^{-1}$ Cd and higher the expanded uncertainty U amounts to ± 4 % (coverage factor 2, 95 % probability).*



## Introduction

For the protection of our groundwater resources the understanding of the transport of pollutants in soil and groundwater is essential. In the "Kempen" Region of Belgium and the Netherlands, a large area of sandy soils is contaminated by a diffuse atmospheric deposition of *heavy metals*. A low pH and low organic carbon content in the acidic sandy soils enhance transport of mobile *heavy metals* from the soil surface through the unsaturated zone into the groundwater.[1-4] After 100 years of non-ferro industrial activity in the region, metals are slowly leaking from soil into the groundwater. Solute transport models are used to estimate the future risk of groundwater contamination and consequently support soil quality remediation.

During the last decade considerable research effort has been expended on clarifying transport processes simultaneously occurring in the soil.[5-8] Laboratory-scale migration experiments are frequently used to validate sorption models and to provide basic transport parameters. For the study of *heavy metal* transport mechanisms, stable isotopes, having nearly the same physicochemical properties as the pollutant of concern, can be used as a tracer. In these experiments a concentrated solution of metal tracer is brought on top of a soil column and leached out subsequently.

In this work, the stable $^{111}$Cd isotope was used to study the transport of cadmium in sandy soils. Both the pollutant (cadmium) and the added stable isotope tracer ($^{111}$Cd) are determined simultaneously in the soil column effluent. These measurements allow to discern between transport properties of cadmium residing for a prolonged period (years) in the soil and tracer spiked onto the column (days). In this way, the effect of contaminant aging on transport can be assessed.

The sensitivity of inductively coupled plasma-mass spectrometry (ICP-MS) combined with the possibility of different isotope measurements allows the determination of both cadmium fractions in effluents at very low concentrations. The isotope dilution technique has been widely used to obtain accurate and precise ICP-MS results. However, the isotope dilution formula cannot be used as such. In the experimental setup (figure 1), a known amount of stable isotope tracer is added on top of the soil column but is collected in different leached fractions. The exact amount of tracer in the different fractions is unknown and forms part of the investigation. Therefore, an external calibration has to be used in order to quantify the amount of tracer and natural cadmium in each collected fraction.

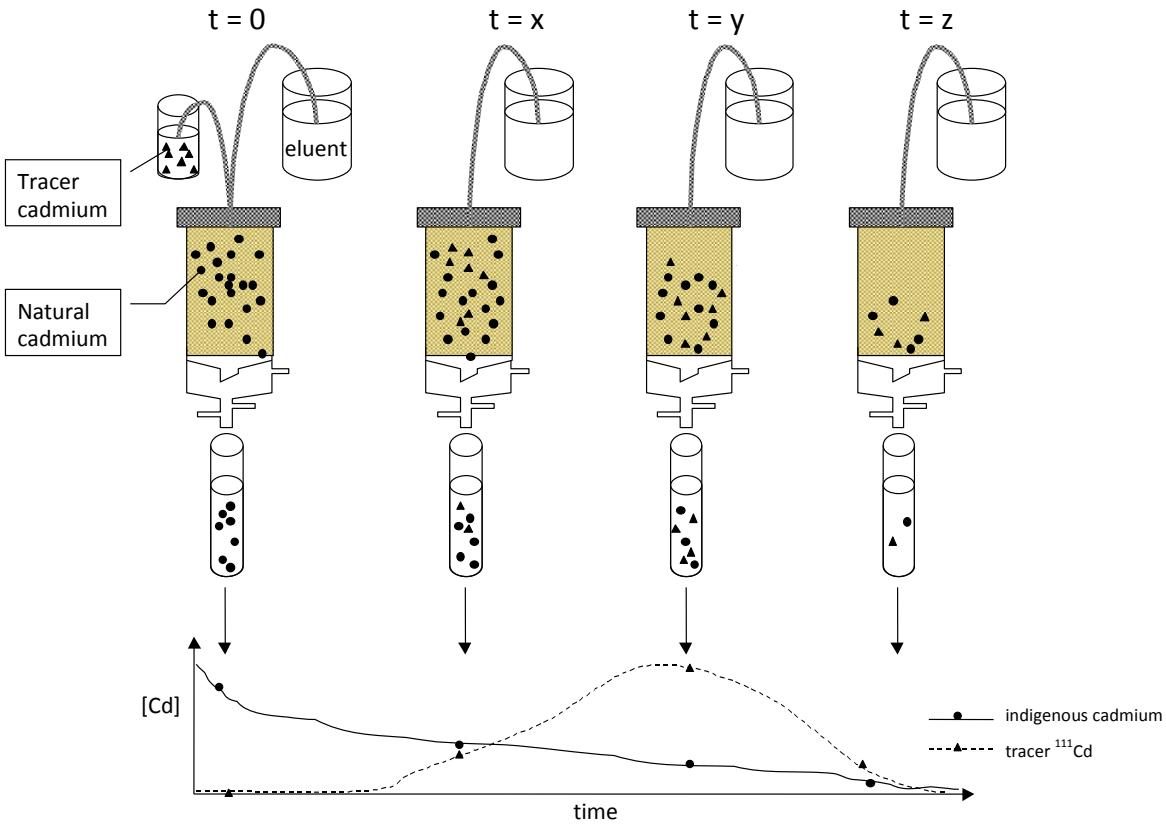


Figure 1: Laboratory-scale migration experiment set-up. Acrylic columns (Ø : 5,6 cm, 10 cm long) filled with undisturbed sandy soil. The concentration of cadmium on the y-axis is the total cadmium concentration in the soil column effluents of the indigenous (•) and added tracer (**Δ**) cadmium.

As the analytical results obtained are used for modelling groundwater contamination, the estimation of the total uncertainty is required. To quantify the combined uncertainty on the ICP-MS results, a commercial available software program (GUM Workbench©) was used. The analysis and computations of this program follow the rules of the 'ISO guide to the expression of uncertainty in measurement'9.

## Method of calculation

### Determination of tracer cadmium ($Cd_t$) and natural cadmium ($Cd_n$) in soil column effluents

For the simultaneous quantitative determination of tracer cadmium ($Cd_t$) and natural cadmium ($Cd_n$) in soil column effluents, a calculation method was deduced from the isotope dilution equation. This approach is based on the calculation of the partial fraction of both natural and tracer cadmium on isotope 111. The concentration is derived from a calibration line obtained with natural cadmium standards. $^{111}Cd$ is the major abundant tracer isotope (table 1). The cadmium isotope ratios versus $^{111}Cd$ isotope are given in table 2.

| isotope | natural cadmium[10] $A_n \pm U$ (%) | tracer cadmium[a] $A_t \pm U$ (%) |
|---|---|---|
| $^{106}Cd$ | 1.25 ± 0.06 | < 0.005 |
| $^{108}Cd$ | 0.89 ± 0.03 | < 0.005 |
| $^{110}Cd$ | 12.49 ± 0.18 | 0.425 ± 0.020 |
| $^{111}Cd$ | 12.80 ± 0.12 | 95.740 ± 0.021 |
| $^{112}Cd$ | 24.13 ± 0.21 | 2.0809 ± 0.0047 |
| $^{113}Cd$ | 12.22 ± 0.12 | 0.5570 ± 0.0027 |
| $^{114}Cd$ | 28.73 ± 0.42 | 1.0411 ± 0.0042 |
| $^{116}Cd$ | 7.49 ± 0.18 | 0.4560 ± 0.0021 |
| [a] Certified spike isotope reference material IRMM-621 | | |

Table 1: The relative abundances (± uncertainties) of isotopes for tracer and natural cadmium.

| isotope ratio versus $^{111}Cd$ | natural cadmium[10] $R_n \pm U$ | tracer cadmium[a] $R_t \pm U$ |
|---|---|---|
| $^{106}Cd$ / $^{111}Cd$ | 0.0977 ± 0.0048 | < 0.00005 |
| $^{108}Cd$ / $^{111}Cd$ | 0.0695 ± 0.0024 | < 0.00005 |
| $^{110}Cd$ / $^{111}Cd$ | 0.976 ± 0.017 | 0.00444 ± 0.00021 |
| $^{112}Cd$ / $^{111}Cd$ | 1.885 ± 0.024 | 0.02174 ± 0.00005 |
| $^{113}Cd$ / $^{111}Cd$ | 0.955 ± 0.013 | 0.005818 ± 0.000028 |
| $^{114}Cd$ / $^{111}Cd$ | 2.245 ± 0.039 | 0.010875 ± 0.000044 |
| $^{116}Cd$ / $^{111}Cd$ | 0.585 ± 0.026 | 0.001629 ± 0.000022 |
| [a] Certified spike isotope reference material IRMM-621 | | |

Table 2: Cadmium isotope ratios versus 111Cd (± uncertainties) for natural and tracer cadmium.

The calculation of the partial fraction natural cadmium on isotope 111 ($^{111}f_n$) is based on the assumption that the total amount of the measured signal on mass 111 originates from the sum of natural cadmium ($^{111}Cd_n$) and tracer cadmium ($^{111}Cd_t$). The same assumption can be made for the measured signal on mass 113. The ratio of the ICP-MS signals of mass 113 to 111 for the sample ($R_s$) is given by:

$$\begin{cases} R_s = \dfrac{\text{mol } {}^{113}Cd_n + \text{mol } {}^{113}Cd_t}{\text{mol } {}^{111}Cd_n + \text{mol } {}^{111}Cd_t} \\ \text{mol } {}^{111}Cd_n + \text{mol } {}^{111}Cd_t = \text{mol } {}^{111}Cd_s \end{cases} \quad (1)$$

The fraction of natural cadmium 111 isotope ($^{111}Cd_n$) in the total cadmium 111 isotope signal ($^{111}Cd_s$) is equal to:

$$^{111}f_n = \frac{\text{mol } {}^{111}Cd_n}{\text{mol } {}^{111}Cd_t + \text{mol } {}^{111}Cd_n} = \frac{\text{mol } {}^{111}Cd_n}{\text{mol } {}^{111}Cd_s} = \frac{R_t - R_s}{R_t - R_n} \quad (2)$$

where $R_t$ and $R_n$ are the ratios of the abundances of isotope 113 to 111 for, respectively, tracer and natural cadmium (see table 2). $R_s$ is the ratio of the signals of mass 113 to 111 for the sample measured with ICP-MS.

A calibration line on isotope 111 is set up with two natural cadmium calibration standards and the concentration of natural cadmium in the column effluents can be quantified by:

$$[Cd_n] = \left[\frac{^{111}f_n \cdot I_s - I_1}{I_2 - I_1}\right] \cdot ([Cd_2] - [Cd_1]) + [Cd_1] \quad (3)$$

where $I_s$, $I_1$ and $I_2$ are the ICP-MS signals on isotope 111 for, respectively, the sample, calibration standard 1 and calibration standard 2. $[Cd_1]$ and $[Cd_2]$ are the concentrations of the calibration standards. The concentration of tracer cadmium present in the column effluent can be deduced from:

$$[Cd_t] = \frac{^{111}A_n}{^{111}A_t} \cdot \frac{R_s - R_n}{R_t - R_n} \cdot [Cd] \quad (4)$$

$$^{111}C_t = \frac{^{111}A_n}{^{111}A_t} \cdot \frac{R_s - R_n}{R_t - R_n} \quad (5)$$

where $^{111}A_n$ and $^{111}A_t$ are the relative abundances of $^{111}Cd$ isotope for, respectively, natural and tracer cadmium (table 1). The concentration of tracer cadmium in the column effluents is given by:

$$[Cd_t] = \left[\frac{^{111}C_t \cdot I_s - I_1}{I_2 - I_1}\right] \cdot ([Cd_2] - [Cd_1]) + [Cd_1] \quad (6)$$

## Experimental

### Soil history and soil treatment

Undisturbed acrylic soil columns (diameter 5.6 cm; length 10 cm) were taken from different horizons in a sandy soil at a distance of about 3 km from a metallurgical plant. The experimental site is located in an old dune heath area with solitary pine trees. The soil was classified as a mesic typic Humod according to Soil Survey Staff (1996). The columns were capped and transferred to the laboratory.

The soil columns were placed on a glass filter (air entry pressure 2 kPa). At the bottom of the column a negative pressure was created using a vacuum device (KnF Verder vacuum controller). At the top of the column solute is applied using a peristaltic pump (minicartridge, Cole Parmer) at a flow rate of 60 $cm.day^{-1}$. A rotating lid and a thin gravel layer ensures a homogeneous distribution of solute over the soil surface, as shown by a dye tracing experiment with methylene blue. The effluent is cycled through a conductivity cell (Shott, 2ml) before being collected by a fraction collector (LKB-Bromma, 2211 Superrac). The conductivity cell is connected to a conductivity measurement device (KM 200, Sensortechnik Meinsberg) for a continuous registration of electrical conductivity on a computer.

**Standard solutions and reagents**

For the preparation of all solutions ultra-pure water with a resistivity of 18 $M\Omega\ cm^{-1}$ obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA) was used. $HNO_3$ solutions were prepared by diluting subboiled 65 % $HNO_3$ (*pro analysi*, Merck, Darmstadt, Germany). An 1 M $CaCl_2$ stock solution was prepared by dissolving 14.702 g $CaCl_2.2H_2O$ (*pro analysi* ,Merck) in 100 ml of water. All solutions were stored in polyethylene bottles.
For the determination of the mass bias a 25 ng $ml^{-1}$ Cd solution (2 % v/v $HNO_3$) was prepared from a Cd stock solution of 1000 µg $ml^{-1}$ (Merck). For the determination of the dead time a 200 ng $ml^{-1}$ Rh solution (2 % v/v $HNO_3$) was used (Perkin Elmer, Norwalk, CT).

Calibration standards were diluted from a Cd stock solution of 1000 µg $ml^{-1}$ (Merck). The concentration levels of the standards were 0.5 and 7.5 ng $ml^{-1}$ Cd and a calibration blank was used. The standards were prepared in a 1 mM $CaCl_2$ and 2 % v/v $HNO_3$ matrix.

The internal standard 100 ng $ml^{-1}$ Rh solution (2% v/v $HNO_3$) was prepared from a stock solution of 1000 µg $ml^{-1}$ Rh (Merck). The choice of the internal standard was based on the similarity between the masses of the analysed cadmium isotopes (111 and 113 amu) and the rhodium mono isotope mass (103 amu). For the preparation of the control standard solution of 1 ng $ml^{-1}$ Cd (2% v/v $HNO_3$, 1 mM $CaCl_2$) a stock solution of 10000 µg $ml^{-1}$ Cd (SPEX, New Jersey, USA) was used. The rinsing solution consisted of a 2 % v/v $HNO_3$ solution.

**Instrumentation**

Samples were analysed by ICP-MS with a Perkin-Elmer SCIEX (Thornhill, ON, Canada) Elan 6000 instrument using an on line packed reaction coil for addition of internal standard solution. A gem tipped cross-flow nebuliser (Perkin-Elmer) interfaced with a Perkin-Elmer (Ryton) Scott double pass spray chamber, using a 2.0 mm id alumina injector tube, comprised the sample introduction system. The on line addition of the internal standard causes a dilution of the sample by 20 %. A peristaltic pump controlled the sample liquid uptake rate (± 1.0 ml $min^{-1}$) with 0.75 mm id tubing for the sample and 0.19 mm id for the internal standard. The instrumental measurement settings were optimised and are shown in table 3.

| parameter | value |
|---|---|
| **instrument settings** | |
| **nebuliser gas flow** | 0.88 ±0.02 l/min |
| **ICP RF power** | 1050 V |
| **analog stage voltage** | -2137.5 V |
| **pulse stage voltage** | 1300 V |
| **lens voltage** | 7.25 ± 0.5 V |
| **measured peak width** | 0.7 amu |
| **oxide level (CeO)** | < 3 % |

| | |
|---|---|
| double charged level ($Ba^{2+}$) | < 3 % |
| dead time detector | 62 ns |
| | |
| measurement settings | |
| scan mode | peak hopping |
| dwell time | 25 ms |
| sweeps / reading | 350 |
| readings / replicate | 1 |
| replicates | 5 |
| | |
| sample introduction | |
| peristaltic pump | 24 rpm |
| ∅ sample tubing | 0.75 mm |
| | |
| on line addition internal standard | |
| ∅ internal standard tubing | 0.19 mm |
| packed reaction coil (Dionex) | 500 µl |
| 3-way liquid mixing tees, PEEK (Dionex) | 0.79 mm (I.D. 10/32) |

Table 3: Optimised instrumental measurement settings ICP-MS, Perkin Elmer, Sciex, Elan 6000.

Before analysis, the instrument was preconditioned by aspirating a 1 mM $CaCl_2$ solution (2 % v/v $HNO_3$) for at least 2 hours. To fulfil the instrument optimisation criteria a plasma set up solution (Perkin Elmer, Norwalk, CT) was used. For the determination of the optimum lens voltage a 25 ng $ml^{-1}$ Cd solution (2% v/v $HNO_3$, 1 mM $CaCl_2$) was prepared from a Cd stock solution of 1000 µg $ml^{-1}$ (Merck, Darmstadt, Germany).

**Sample treatment**

At the start of the column experiment a 1 mM $CaCl_2$ leachant solution replaces the original soil solution. Afterwards, 10 ml of a $^{111}Cd$ tracer solution of 500 ng $ml^{-1}$ Cd (IRMM, Geel, Belgium) is added on top of the soil column (figure 1). The leachant solution (1mM $CaCl_2$) is added on top of the soil column at a rate of 1,44 l $day^{-1}$. The fractions are collected over 4 hours (± 250 ml), acidified with 5 ml $HNO_3$ and stored in polyethylene bottles.

**Quantification of combined uncertainty on the analytical measurement**

The GUM Workbench© program was used for the quantification of combined uncertainty on the analytical measurement (Metrodata GmbH, Germany, http://home.t-online.de/home/metrodata/). The analysis and computations follow the rules of the 'ISO guide to the expression of uncertainty in measurement.[9] and the EAL-R2 document of the 'European cooperation for Accreditation of Laboratories'.[11]

The program supports a systematic procedure in building an uncertainty analysis as requested in the EAL document. Starting with the mathematical equation which models the physical relationship of quantities in the measurement, the data needed for the analysis, like the standard uncertainty or the distribution of values, is interactively requested. A fitting classification of the input values according to the available information controls the analysis process.

## Results and Discussions

### Combined uncertainty calculation on [$Cd_n$]

The described method for the calculation of the combined uncertainty on the quantitative determination of tracer and natural cadmium emphasises the practical, realistic approach of estimating uncertainties based on statistical assumptions. The uncertainty estimation can roughly be divided into four steps: specification (relation between the element of concern and the parameters), identification of uncertainty sources, quantifying the uncertainty components and calculating the combined uncertainty.

The ISO guide[9] states that the uncertainty on a component can be grouped into two categories according to the way in which their numerical value is estimated:

- type A : those which are evaluated by statistical methods;
- type B : those which are evaluated by other means.

The difficulty in the estimation of combined uncertainty lies in the realistic quantification of the type B uncertainty.

In the calculation of the combined uncertainty on the concentration of natural cadmium in soil column effluents the output quantity, denoted by Y (*e.g.* [$Cd_n$]), depends upon a number of input quantities $X_i$ (i = 1, 2, ...., N) (*e.g.*, equation 3) according to a functional relationship

$$Y = f(X_1, X_2, ...., X_N) \quad (7)$$

An estimate of the measurand Y, the output estimate denoted by y, is obtained using input estimates $x_i$ for the values of the input quantities $X_i$ :

$$y = f(x_1, x_2, ...., x_N) \quad (8)$$

For not correlated input quantities the square of the standard uncertainty associated with the output estimate y is given by

$$u^2(y) = \sum_{i=1}^{N} u_i^2(y) \quad (9)$$

The quantity $u_i$ (y) (i = 1,2, ..., N) is the contribution to the standard uncertainty associated with the output estimate y resulting from the standard uncertainty associated with the input estimate $x_i$

$$u_i(y) = c_i \cdot u(x_i) \quad (10)$$

where $c_i$ is the sensitivity coefficient associated with the input estimate $x_i$, *i.e.,* the partial derivative of the model function f with respect to $x_i$,

$$c_i = \frac{\partial f}{\partial x_i} = \frac{\partial f}{\partial X_i} \Big|_{X_{1i}=x_1 ....X_N=x_N} \quad (11)$$

The following experimental steps are involved in the calculation of the combined uncertainty on the concentration of natural cadmium in soil column effluents:

1. collection of soil column effluents and sample treatment
2. preparation of calibration cadmium standards
3. measurement of samples by ICP-MS
4. calculation of concentration

**step 1: sample treatment**

The soil column fractions are collected over 4 hours (± 250 ml), acidified with 5 ml $HNO_3$ (65% ) and stored at 277 K in polyethylene bottles. The samples are, due to the acidification, diluted by a factor of approximately 1.02. For each fraction the collected volume is weighed and 5 ml $HNO_3$ is added with a pipette. The calibration certificate of the balance establishes a reproducibility of 200 ± 0.0002 g (95% confidence). This quantity needs to be divided by 1.96 to give the component of uncertainty as a standard deviation. The quality control log shows a standard deviation of ± 0.0003 g for a check weighing of 200 g. The two components are then combined to give an uncertainty:

$$u_{balance} = \sqrt{\left(\frac{0.2}{1.96}\right)^2 + 0.3^2} = 0.32 \text{ mg}$$

The density of water at 293 K is 0.99821 g $ml^{-1}$. For the conversion of the weight of the sample to a volume a possible temperature variation of ± 3 K (with 95 % confidence) is taken into account. Taking the coefficient of volume expansion of water as 2.1 x $10^{-4}$ $K^{-1}$, this gives a 95% confidence interval for the calculation of a volume of ± 3 x 2.1 x $10^{-4}$. Dividing this by 1.96 to obtain the standard deviation gives a value of ± 3.6 x $10^{-4}$ for the uncertainty due to incomplete temperature control. The sample volume is calculated as follows:

$$V_{sample} = m_{sample} \cdot 1/\delta_{water}$$

The uncertainty on the weighing is combined with the uncertainty on the conversion to volume:

$$\frac{u_{V_{sample}}}{V_{sample}} = \sqrt{\left(\frac{0.32}{200000}\right)^2 + \left(\frac{0.00036}{0.99821}\right)^2} = 0.00036$$

resulting in an uncertainty on a volume of 250 ml of ± 250 x 0.00036 = ± 0.09 ml. The technical data of the 5 ml pipette states an accuracy of 0.14 % on a volume of 5 ml. The standard deviation on different repeated pipette operations is ± 0.018 ml, resulting in a combined uncertainty on the acid volume of

$$u_{V_{acid}} = \sqrt{\left(\frac{0.0014 \cdot 5}{\sqrt{3}}\right)^2 + (0.018)^2} = 0.018 \text{ ml}$$

For a 250 ml sample the dilution factor, d, is equal to (see also table 4)

$$d = \frac{(V_{samle} + V_{acid})}{V_{sample}} = 1.02000 \pm 0.00007$$

model equation :

$$d = \frac{(V_{samle} + V_{acid})}{V_{sample}}$$

$$V_{sample} = m_{sample} \cdot {}^{1}\!/\!_{\rho_{water}}$$

| quantity | value | standard uncertainty $u(x_i)$ | df | sensitivity coefficient $c_i$ | uncertainty contribution $u_i(y)$ | uncertainty contribution (%) |
|---|---|---|---|---|---|---|
| $V_{sample}$ | 250 ml | 0.0802 | | | | |
| $m_{sample}$ | 249.5525 g | 3 E-03 | 50 | -80.1 E-06 | -240 E-09 | 0.0 |
| $\rho_{water}$ | 0.998210 g/ml | 360 E-06 | 50 | 0.02 | 7.21 E-06 | 1.0 |
| $V_{acid}$ | 5.000 | 0.018 | 50 | 4.0 E-03 | 72.0 E-06 | 99 |

result :
dilution factor d = 1.02000 ± 0.00014, where the reported uncertainty is calculated using a coverage factor of 2 (95%).

Table 4: Combined uncertainty on step 1 'treatment of sample'.

For a correct calculation of natural cadmium, the model stated in equation 3 has to be multiplied by this factor

$$[Cd_n] = \left( \left[ \frac{{}^{111}f_n \cdot I_s - I_1}{I_2 - I_1} \right] \cdot ([Cd_2] - [Cd_1]) + [Cd_1] \right) \cdot d \quad (3\_a)$$

**step 2: preparation of the calibration standards**

Two calibration solutions, $[Cd_1]$ = 0.5 ng $ml^{-1}$ and $[Cd_2]$ = 7.5 ng $ml^{-1}$, were prepared from a commercial stock solution of cadmium. The concentration of cadmium in the commercial solution was stated to be 1004 ± 2 mg $l^{-1}$. The dilution scheme is shown in figure 2.

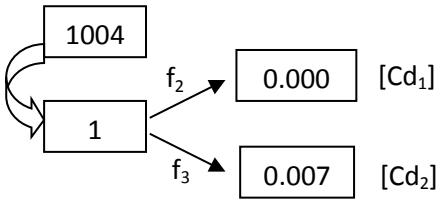


Figure 2: dilution scheme for the preparation of cadmium calibration standards (concentrations in ng $ml^{-1}$).

To calculate the uncertainties associated with each of the concentrations, it is necessary to determine the uncertainty on the stock solution, estimate the uncertainties in the dilution chain and combine the two sources of uncertainty. The 1:1000 dilution ($f_1$) was performed using a 100 µl pipette ($V_{0.1}$) and 100 ml volumetric flask ($V_{100}$). The 1:2000 dilution ($f_2$) was be performed using a 50 µl pipette ($V_{0.05}$) and 100 ml volumetric flask. The 1:133 dilution ($f_3$) was to be performed using a 750 µl pipette ($V_{0.75}$) and 100 ml volumetric flask. Contributions due to imperfect repeatability and variation within specification limits must be determined and combined for each type of pipette and glassware used. The uncertainty arising from imperfect repeatability is estimated from the standard deviation of a number of fill and weigh operations. The uncertainty arising from variation within

specification is obtained by dividing the manufacturers specification by $\sqrt{3}$ to convert from rectangular limits to standard deviation.[11] Table 5 summarises the data so obtained.

| | description | std dev (ml) | Spec./ $\sqrt{3}$ (ml) | $u_v$ (ml) | $u_v/V$ |
|---|---|---|---|---|---|
| $V_{0.1}$ | pipette of 0.100 ml | 0.00056 | 0.00006 | 0.00057 | 0.0057 |
| $V_{0.05}$ | pipette of 0.050 ml | 0.00040 | 0.00003 | 0.00040 | 0.0080 |
| $V_{0.75}$ | pipette of 0.750 ml | 0.0028 | 0.00043 | 0.0028 | 0.0038 |
| $V_{100}$ | flask of 100 ml | 0.051 | 0.06 | 0.08 | 0.0008 |

Table 5: Uncertainties on the different pipettes used for the preparation of the calibration standards.

To obtain the uncertainties for each dilution, each step is treated as a dilution factor made up from the initial and final volume.

$$f_1 = \frac{V_{100}}{V_{0.1}} \quad ; \quad f_2 = \frac{V_{100}}{V_{0.05}} \quad ; \quad f_3 = \frac{V_{100}}{V_{0.75}}$$

The calculation of the combined uncertainty on the lowest standard is summarised in table 6.

model equation :

$$[Cd_1] = \frac{[Cd_{stock}]}{f_1 \cdot f_2}$$

$$f_1 = \frac{V_{100}}{V_{0.1}} \quad ; \quad f_2 = \frac{V_{100}}{V_{0.05}}$$

| quantity | value | standard uncertainty $u(x_i)$ | df | sensitivity coefficient $c_i$ | uncertainty contribution $u_i(y)$ | uncertainty contribution (%) |
|---|---|---|---|---|---|---|
| $[Cd_{stock}]$ | 1004000 ng ml$^{-1}$ | 1160 | 50 | 500 E-09 | 578 E-06 | 1.3 |
| $f_1$ | 1000.0 | 9.7 | | | | |
| $f_2$ | 2000 | 22 | | | | |
| $V_{100}$ | 100.00 ml | 0.078 | 50 | -0.010 | -7.83 E-06 | 2.4 |
| $V_{0.1}$ | 0.1000 ml | 0.0006 | 50 | 5.02 | 2.86 E-03 | 32.3 |
| $V_{0.05}$ | 0.0500 ml | 0.0004 | 50 | 10.0 | 4.02 E-03 | 63.9 |

result :
$[Cd_1]$ = 0.502 ± 0.010 ng ml$^{-1}$, where the reported uncertainty is calculated using a coverage factor of 2 (95%).

Table 6: Combined uncertainty on step 2 'preparation of the calibration standard'.

The same model can be used for the calculation of the combined uncertainty on the upper calibration standard $[Cd_2]$ = 7.53 ± 0.11 ng ml$^{-1}$ (coverage factor 2, 95%). So far, the uncertainty arising from unknown constant temperature offset during the dilution has not been considered. The effect can readily be calculated from the known coefficient of expansion as in step 1. Any offset during the dilution process will affect $[Cd_1]$ and $[Cd_2]$ by the same factor. This factor, $f_K$, is incorporated in equation 3_a and applies directly to $[Cd_n]$ :

$$[Cd_n] = \left( \left[ \frac{^{111}f_n \cdot I_s - I_1}{I_2 - I_1} \right] \cdot ([Cd_2] - [Cd_1]) + [Cd_1] \right) \cdot d \cdot f_K \quad (3\_b)$$

**step 3: ICP-MS measurement**

**3.1 spectral and non-spectral interferences**

The analytical measurements with ICP-MS can be hampered by interference of different kinds (isobaric, oxides, poly-atomic, or doubly charged interferences). Study of the possible interference is necessary before starting the analysis. Because all the measured samples (soil column effluents) have more or less the same composition as the leachant, a solution consisting of 1 mM $CaCl_2$ (2 % v/v $HNO_3$) was analysed for a first evaluation of the interferences. From all the literature cited interferences in the cadmium mass range,[12-15] only the expected occurring poly-atomic interferences and all the isobaric interferences are listed in table 7.

| element | mass | interference | % abundance |
|---|---|---|---|
| **strontium** | | | |
| | 100 | $^{84}Sr^{16}O$ | 0.55 |
| | 101 | $^{84}Sr^{17}O$ | - |
| | 102 | $^{84}Sr^{18}O$, $^{86}Sr^{16}O$ | 9.84 |
| | 103 | $^{86}Sr^{17}O$, $^{87}Sr^{16}O$ | 6.99 |
| | 104 | $^{86}Sr^{18}O$, $^{87}Sr^{17}O$, $^{88}Sr^{16}O$ | 82.40 |
| | 105 | $^{87}Sr^{18}O$, $^{88}Sr^{17}O$ | 0.05 |
| | 106 | $^{88}Sr^{18}O$ | 0.17 |
| **lead** | | | |
| | 102 | $^{204}Pb^{++}$ | 1.4 |
| | 103 | $^{206}Pb^{++}$ | 24.1 |
| | 103,5 | $^{207}Pb^{++}$ | 22.1 |
| | 104 | $^{208}Pb^{++}$ | 52.4 |
| | | | **% relative abundance** |
| **tin** | | | |
| | 112 | $^{112}Sn$ | 0.97 |
| | 114 | $^{114}Sn$ | 0.65 |
| | 116 | $^{116}Sn$ | 14.53 |
| | | | |
| **indium** | | | |
| | 113 | $^{113}In$ | 4.3 |
| | | | |
| **palladium** | | | |
| | 106 | $^{106}Pd$ | 27.33 |
| | 108 | $^{108}Pd$ | 26.46 |
| | 110 | $^{110}Pd$ | 11.72 |

Table 7: Possible occurring interferences for the determination of cadmium in mass range 100 -116 u.

A mass scan of the matrix solution pointed out that approximately 0.2 ng $ml^{-1}$ Sn, 0.1 ng $ml^{-1}$ Pb, and 15 ng $ml^{-1}$ Sr are present in this solution. Since no evidence of the presence of indium was observed (and expected), the isobaric correction equation for indium on the cadmium isotope 113 was not used. The non spectral interferences were counteracted by the on line addition of internal standard (rhodium) as stated under Instrumentation.

### 3.2 uncertainty on ICP-MS signal, $u_I$

The uncertainties on all the parameters for the calculation of $f_n$, $[Cd_n]$ and $[Cd_t]$ are known with the exception of the measured ratio ($R_s$). The uncertainty on the measured isotope ratio is of course, to a certain extent, dependent on the concentration of the cadmium in the sample. According to Poisson statistics,[16] the noise or standard deviation of a signal measured using pulse counting can be estimated as the square root of the signal. This means precision should improve with increasing signal intensity. However, the aim of the uncertainty calculation, as described in this paper, is not a theoretical calculation of the dependence of the standard deviation on the instrument parameters and element concentration. Although those calculations are useful to understand the origin of the standard deviations,[17] the emphasis lies in the estimation of the magnitude of the uncertainty and the impact in the total uncertainty budget. In order to obtain a robust estimate of the uncertainty on an ICP-MS signal, the dependency of the signal versus its standard deviation was examined for all the cadmium measurements in the concentration range of 0 to 7.5 ng ml$^{-1}$ Cd (n = 425, figure 3).

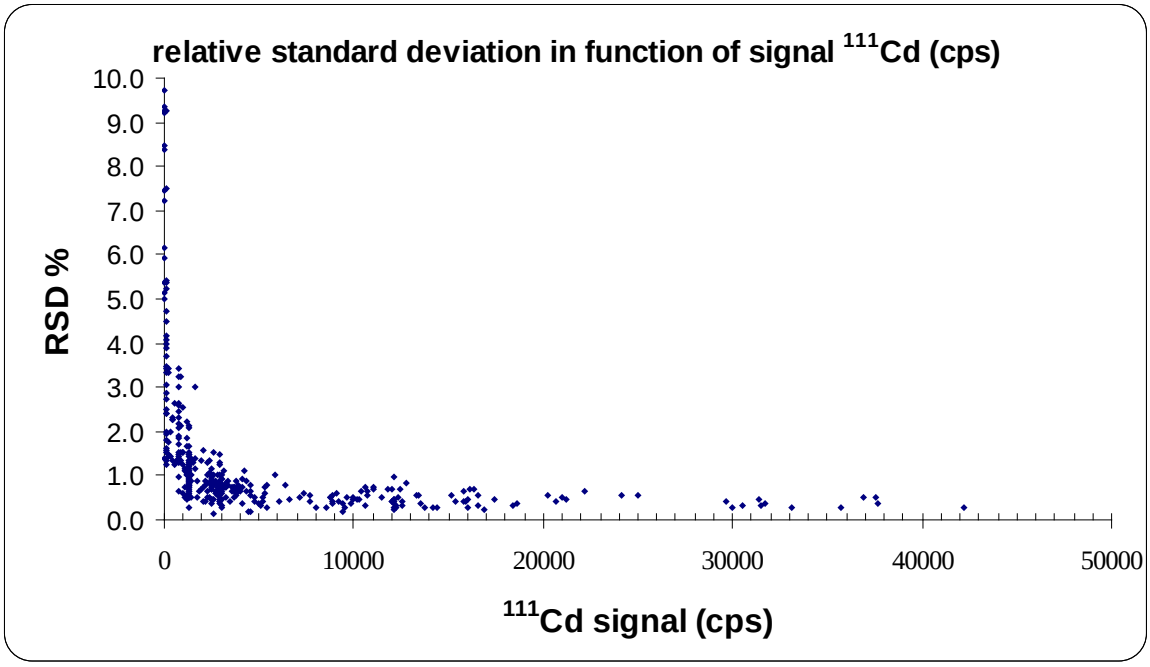


Figure 3: Relationship between relative standard deviation (%, 5 replicates) and signal intensity (cps) measured on $^{111}$Cd for different concentrations of cadmium in the sample.

The square root of the signals is proportional to the standard deviation ($s \sim \sqrt{I}$) up to approximately 10000 cps, with a factor of 0.4 (figure 4). Above this point a proportional relationship $s \sim I$ was observed, with a factor of 0.0047 (relative standard deviation of 0.47 %). Under the given ICP-MS conditions a signal of 1 ng ml$^{-1}$ Cd gives approximately 1000 cps on $^{111}$Cd.

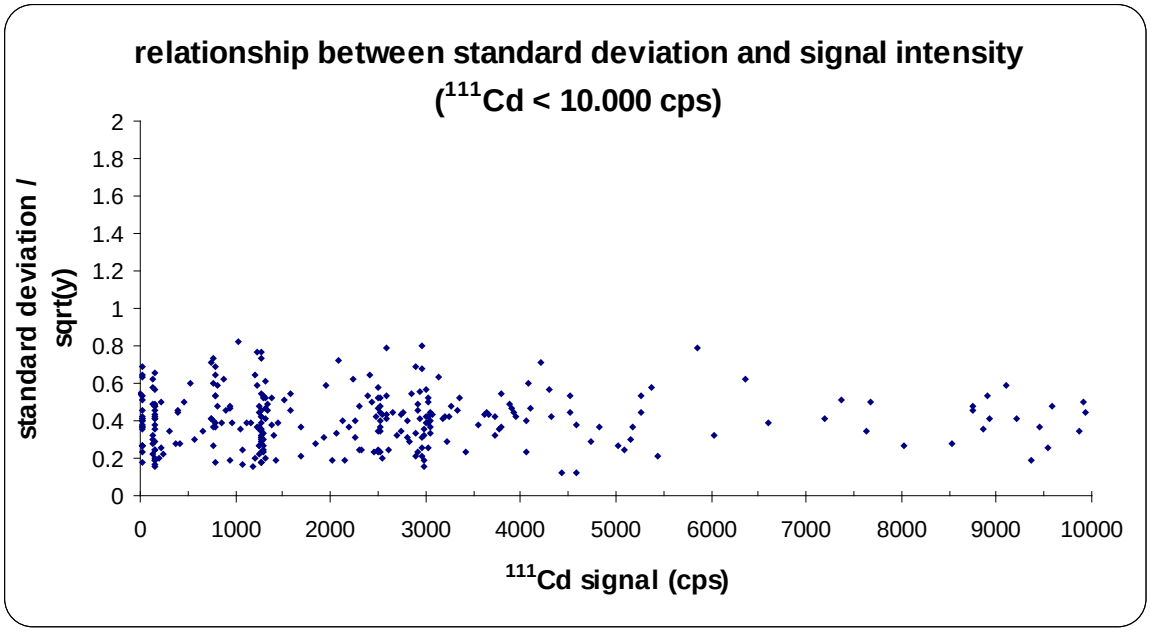


Figure 4: Relationship between square root of signal intensity (< 10.000 cps) and standard deviation (5 replicates) measured on $^{111}$Cd for different concentrations of cadmium. The proportional factor is equal to 0.408 ± 0.145 (standard deviation on 304 samples).



This approach was used to predict the uncertainty on the signal (standard deviation of the mean of 5 replicates) of the cadmium isotopes:

$$\text{I} < 10000 \text{ cps}, \quad u_I = 0.4 \cdot \frac{\sqrt{I}}{\sqrt{5}} \quad (12)$$

$$\text{I} > 10000 \text{ cps}, \quad u_I = 0.0047 \cdot \frac{I}{\sqrt{5}} \quad (13)$$

These results are in agreement with the results found by E. R. Denoyer *et al*.[16]

This uncertainty, $u_I$, reflects the repeatability of the signal during the measurement period but not the stability of the ICP-MS instrument during the analysis of the different samples. Because a calibration is performed every ten samples, the stability of the signal has to be quantified during that time period. The differences between the signal intensity (after correction with an internal standard, Rh) before and after the measurement of ten samples are compared for each individual calibration standard. The average value of the calculated differences in signal intensities for the standards (0.5 and 7.5 ng ml$^{-1}$ Cd) was 2.6 ± 1.2 % (eight measurement runs).

The clogging of the sampling cone by calcium salts present in the soil column effluents, causes a linear drift of the signal intensity resulting in a mean bias drift of 1.3% (2.6 %/2) across the measurement run. This bias is considered by multiplying the measured intensity of the sample, $I_s$, with a drift factor $I_{Rh}$ = 1 ± 0.013 in the model equation.

$$[Cd_n] = \left( \left[ \frac{^{111}f_n \cdot I_s \cdot I_{Rh} - I_1}{I_2 - I_1} \right] \cdot ([Cd_2] - [Cd_1]) + [Cd_1] \right) \cdot d \cdot f_K \quad (3\_c)$$

### 3.3 isotope ratio measurement

The observed isotope ratios deviates from the true values as a function of the difference in mass between the two isotopes.[18] The true ratio of isotopes A and B , $(A/B)_t$, can be related to the measured ratio, $(A/B)_m$, by :

$$\left(\frac{A}{B}\right)_m = \left(\frac{A}{B}\right)_t \cdot (1 + a \cdot n) \quad (14)$$

where *a* is the bias per mass unit, and n is the mass difference between isotopes A and B. Also, determination of the dead time is critical when ratios of isotopes with different relative abundances are calculated. Ten independent measurements of a 25 ng $ml^{-1}$ Cd (2 % v/v $HNO_3$) solution resulted in a mass bias per mass unit value of 0.0161 ± 0.0007 (standard deviation) based on cadmium isotope ratio 113 to 111.

For isotope dilution measurements, the error magnification factor has to be taken into account for the estimation of the added spike concentration.[19] For an optimum isotope dilution measurement (lowest uncertainty), the measured ratio has to be situated in the minimum of the error magnification factor curve. However, for column effluents the isotope ratios differ in each collected fraction and a compromise has to be found for the amount of tracer cadmium to be added.

### step 4: calculation of concentration natural cadmium

Owing to the restricted working area of the ICP-MS instrument (0.5 to 7.5 ng $ml^{-1}$), the linearity of the calibration line can be assumed. The combined uncertainty on the concentration natural cadmium in soil column effluent can be calculated from equation 3_c and for one collected soil column effluent the calculations are summarised in table 8.

model equation :

$$[Cd_n] = \left(\left[\frac{^{111}f_n \cdot I_s \cdot I_{Rh} - I_1}{I_2 - I_1}\right] \cdot ([Cd_2] - [Cd_1]) + [Cd_1]\right) \cdot d \cdot f_K$$

with

$$^{111}f_n = \frac{R_t - R_s}{R_t - R_n}$$

$$[Cd_1] = \frac{[Cd_{stock}]}{f_1 \cdot f_2}$$

$$[Cd_2] = \frac{[Cd_{stock}]}{f_1 \cdot f_3}$$

$$f_1 = \frac{V_{100}}{V_{0.1}} \quad ; \quad f_2 = \frac{V_{100}}{V_{0.05}} \quad ; \quad f_3 = \frac{V_{100}}{V_{0.75}}$$

$$d = \frac{(V_{samle} + V_{acid})}{V_{sample}}$$

$$V_{sample} = m_{sample} \cdot 1/\rho_{water}$$

| quantity | value | standard | df | type | sensitivity | uncertainty | uncertainty |
|---|---|---|---|---|---|---|---|

Scientific publication

| | | uncertainty $u(x_i)$ | | | coefficient $c_i$ | contribution $u_i(y)$ | contribution (%) |
|---|---|---|---|---|---|---|---|
| $^{111}f_n$ | 0.058401 | 887 E-06 | | | | | |
| $I_s$ | 17196.8 cps | 36.2 | 5 | A | -4.26 E-06 | -1.54 E-04 | 0.01 |
| $I_{Rh}$ | 1 | 0.013 | 16 | A | 0.698 | 9.08 E-03 | 34.8 |
| $I_1$ | 748.0 cps | 4.9 | 5 | A | -6.78 E-04 | -3.32 E-03 | 4.6 |
| $I_2$ | 11059.0 cps | 18.9 | 5 | A | -1.73 E-05 | -3.27 E-04 | 0.05 |
| $[Cd_1]$ | 7.530 ng $ml^{-1}$ | 0.053 | | | | | |
| $[Cd_2]$ | 0.502 ng $ml^{-1}$ | 0.005 | | | | | |
| d | 1.02 | 72.4 E-06 | | | | | |
| $f_K$ | 1.00 | 360 E-06 | 50 | B | 0.69 | 2.48 E-04 | 0.03 |
| $R_t$ | 5.818 E-03 | 28.2 E-06 | | | | | |
| $R_s$ | 0.061232 | 366 E-06 | | | | | |
| $R_n$ | 09547 | 0.0130 | | | | | |
| $^{113}A_t$ | 0.5570 | 2.70 E-03 | 50 | B | -0.124 | -3.35 E-04 | 0.05 |
| $^{111}A_t$ | 95.74 | 0.0210 | 50 | B | 7.21 E-04 | 1.51 E-05 | 0.00 |
| $^{113}A_n$ | 12.22 | 0.12 | 50 | B | -0.0575 | -6.90 E-03 | 20.1 |
| $^{111}A_n$ | 12.80 | 0.12 | 50 | B | 0.0549 | 6.59 E-03 | 18.3 |
| $[Cd_{stock}]$ | 1004000ng $ml^{-1}$ | 1150 | 50 | B | 6.87 E-07 | 7.91 E-04 | 0.26 |
| $^{113}I_s$ | 1086.9 cps | 5.9 | 5 | A | 7.10 E-04 | 4.19 E-03 | 7.4 |
| a | 0.0161 | 700 E-06 | 10 | A | -1.49 | -1.05 E-03 | 0.46 |
| n | 2.0 | | | | | | |
| $V_{sample}$ | 250.0000 ml | 0.0902 | | | | | |
| $V_{acid}$ | 5.0000 ml | 0.0180 | 50 | B | 2.71 E-03 | 4.87 E-05 | 0.00 |
| $m_{sample}$ | 249.55250 g | 3 E-03 | 50 | B | -5.42 E-05 | -1.63 E-07 | 0.00 |
| $\rho_{water}$ | .998210 g/ml | 0.154 | 50 | B | 0.0136 | 4.88 E-06 | 0.00 |
| $f_1$ | 1000.0 | 9.7 | | | | | |
| $f_2$ | 2000 | 22 | | | | | |
| $f_3$ | 133.333 | 0.509 | | | | | |
| $V_{100}$ | 100.00 ml | 0.078 | 50 | B | -0.0138 | -1.08 E-03 | 0.5 |
| $V_{0.75}$ | 0.7500 ml | 0.0028 | 50 | B | 0.255 | 7.13 E-04 | 0.21 |
| $V_{0.1}$ | 0.1000 ml | 0.0006 | 50 | B | 6.9 | 3.93 E-03 | 6.5 |
| $V_{0.05}$ | 0.0500 ml | 0.0004 | 50 | B | 9.99 | 3.99 E-03 | 6.7 |
| result : $[Cd_n]$ = 0.690 ± 0.031 ng $ml^{-1}$, where the reported uncertainty is calculated using a coverage factor of 2 (95%). | | | | | | | |

Table 8: Combined uncertainty on concentration natural cadmium in soil column effluents.

The leached concentrations of tracer and natural cadmium for one soil column experiment are shown in figure 5 and summarised in table 9, with the indication of the fraction that was used as an example for the uncertainty calculation in table 8.

| time (hours) | $[Cd_n] \pm U$ (ng $ml^{-1}$) | $[Cd_t] \pm U$ (ng $ml^{-1}$) |
|---|---|---|
| 20 | 6.078 ± 0.248 | 0.025 ± 0.027 |
| 24 | 4.100 ± 0.167 | 0.010 ± 0.021 |
| 28 | 4.913 ± 0.200 | 1.032 ± 0.038 |
| 32 | 2.090 ± 0.086 | 5.943 ± 0.218 |
| 36 | 1.772 ± 0.073 | 3.864 ± 0.142 |
| 40 | 1.478 ± 0.062 | 3.180 ± 0.117 |
| 44 | 0.998 ± 0.043 | 2.211 ± 0.081 |
| 48 | **0.690 ± 0.031** | **1.497 ± 0.054** |
| 49.2 | 0.519 ± 0.025 | 1.127 ± 0.042 |
| 65.25 | 0.348 ± 0.019 | 0.683 ± 0.027 |
| 69.25 | 0.268 ± 0.017 | 0.342 ± 0.017 |
| 73.25 | 0.212 ± 0.015 | 0.210 ± 0.014 |
| 77.25 | 0.238 ± 0.016 | 0.166 ± 0.014 |
| 81.25 | 0.217 ± 0.015 | 0.133 ± 0.013 |
| 85.25 | 0.183 ± 0.014 | 0.091 ± 0.013 |
| 89.25 | 0.188 ± 0.015 | 0.076 ± 0.013 |
| 93.25 | 0.163 ± 0.014 | 0.053 ± 0.013 |
| 94.05 | 0.174 ± 0.014 | 0.049 ± 0.013 |
| 98.05 | 0.162 ± 0.014 | 0.039 ± 0.013 |
| 102.05 | 0.161 ± 0.014 | 0.029 ± 0.013 |
| 106.05 | 0.143 ± 0.014 | 0.023 ± 0.013 |
| 110.05 | 0.139 ± 0.014 | 0.016 ± 0.013 |
| 112.45 | 0.138 ± 0.014 | 0.015 ± 0.013 |
| 116.45 | 0.124 ± 0.013 | 0.010 ± 0.013 |

Table 9: Concentrations of natural and tracer cadmium (± U, 95 % confidence intervals) in soil column effluents (figure 5). The fraction that was used for the example in tables 8 and 10 is indicated by bold type.

The calculation of the combined uncertainty on the concentration tracer cadmium is analogous to natural cadmium and for the same soil column effluent as above the budget was calculated in table 10.

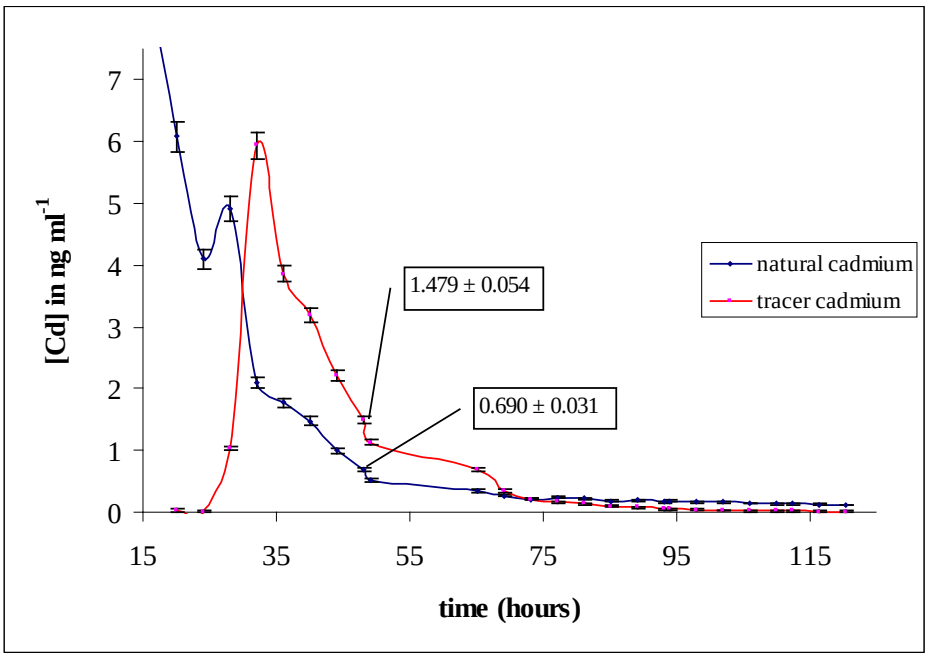


Figure 5: Example of tracer and natural cadmium in soil column effluents ($[Cd] \pm 2*u_{[Cd]}$, 95 % confidence intervals), the calculation of the uncertainties on the indicated points are summarised in table 8 and 10.

model equation :

$$[Cd_t] = \left( \left[ \frac{^{111}C_t \cdot I_s \cdot I_{Rh} - I_1}{I_2 - I_1} \right] \cdot ([Cd_2] - [Cd_1]) + [Cd_1] \right) \cdot d \cdot f_K$$

with

$$^{111}C_t = \frac{^{111}A_n}{^{111}A_t} \cdot \frac{R_s - R_n}{R_t - R_n}$$

other quantity equations see table 8.

| quantity | value | standard uncertainty $u(x_i)$ | df | type | sensitivity coefficient $c_i$ | uncertainty contribution $u_i(y)$ | uncertainty contribution (%) |
|---|---|---|---|---|---|---|---|
| $^{111}C_t$ | 0.12589 | 1.11 E-03 | | | | | |
| $I_s$ | 17196.8 cps | 36.2 | 5 | A | 9.35 E-05 | 3.38 E-03 | 1.65 |
| $I_{Rh}$ | 1 | 0.013 | 16 | A | 1.51 | 0.0196 | 55.48 |
| $I_1$ | 748.0 cps | 4.9 | 5 | A | -6.00 E-04 | -2.93 E-03 | 1.24 |
| $I_2$ | 11059.0 cps | 18.9 | 5 | A | -9.55 E-05 | -1.81 E-03 | 0.47 |
| $[Cd_1]$ | 7.530 ng $ml^{-1}$ | 0.053 | | | | | |
| $[Cd_2]$ | 0.502 ng $ml^{-1}$ | 0.005 | | | | | |
| d | 1.02 | 72.4 E-06 | | | | | |
| $f_K$ | 1.00 | 360 E-06 | 50 | B | 1.5 | 5.39 E-04 | 0.04 |
| $R_t$ | 5.818 E-03 | 28.2 E-06 | | | | | |
| $R_s$ | 0.061232 | 366 E-06 | | | | | |
| $R_n$ | 09547 | 0.0130 | | | | | |
| $^{113}A_t$ | 0.5570 | 2.70 E-03 | 50 | B | 0.0166 | 4.47 E-05 | 0.00 |
| $^{111}A_t$ | 95.74 | 0.0210 | 50 | B | -0.0158 | -3.32 E-04 | 0.02 |
| $^{113}A_n$ | 12.22 | 0.12 | 50 | B | 7.69 E-03 | 9.22 E-04 | 0.12 |
| $^{111}A_n$ | 12.80 | 0.12 | 50 | B | 0.11 | 0.0132 | 25.16 |
| $[Cd_{stock}]$ | 1004000ng $ml^{-1}$ | 1150 | 50 | B | 1.49 E-06 | 1.71 E-03 | 0.42 |
| $^{113}I_s$ | 1086.9 cps | 5.9 | 5 | A | -9.49 E-05 | -5.60 E-04 | 0.05 |
| a | 0.0161 | 700 E-06 | 10 | A | 0.2 | 1.40 E-04 | 0.00 |
| n | 2.0 | | | | | | |
| $V_{sample}$ | 250.0000 ml | 0.0902 | | | | | |
| $V_{acid}$ | 5.0000 ml | 0.0180 | 50 | B | 5.87 E-03 | 1.06 E-04 | 0.00 |
| $m_{sample}$ | 249.55250 g | 3 E-03 | 50 | B | -1.18 E-04 | -3.53 E-07 | 0.00 |
| $\rho_{water}$ | .998210 g/ml | 0.154 | 50 | B | 0.0294 | 1.06 E-05 | 0.00 |
| $f_1$ | 1000.0 | 9.7 | | | | | |
| $f_2$ | 2000 | 22 | | | | | |
| $f_3$ | 133.333 | 0.509 | | | | | |
| $V_{100}$ | 100.00 ml | 0.078 | 50 | B | -0.0299 | -2.34 E-03 | 0.79 |
| $V_{0.75}$ | 0.7500 ml | 0.0028 | 50 | B | 1.41 | 3.94 E-03 | 2.24 |
| $V_{0.1}$ | 0.1000 ml | 0.0006 | 50 | B | 15 | 8.53 E-03 | 10.51 |
| $V_{0.05}$ | 0.0500 ml | 0.0004 | 50 | B | 8.83 | 3.53 E-03 | 1.8 |

result :

$[Cd_t]$ = 1.497 ± 0.054 ng $ml^{-1}$, where the reported uncertainty is calculated using a coverage factor of 2.1 (95%).

Table 10: Combined uncertainty on concentration tracer cadmium in soil column effluents.

Each collected fraction is, as earlier stated, a unique combination of tracer and natural cadmium at a certain concentration level. In figure 6 the expanded uncertainty (U = 2*$u_{[Cd]}$, 95 % confidence intervals) on [$Cd_n$] and [$Cd_t$] for a total cadmium concentration level of 1 ng $ml^{-1}$ was calculated in function of the fraction natural cadmium 111 isotope ($^{111}f_n$).

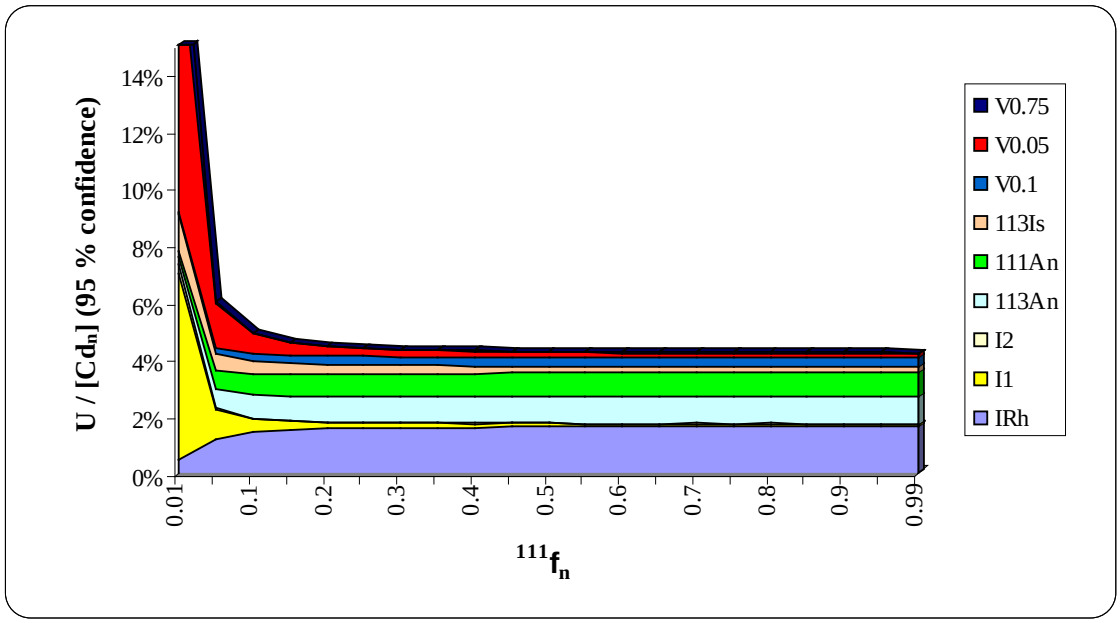


Figure 6: The major contributions to the expanded uncertainty (U) on the concentration of natural cadmium for a total cadmium concentration level of 1 ng $ml^{-1}$ in function of the fraction natural cadmium 111 isotope ($^{111}f_n$).

Only the major contributions (> 99%) to the uncertainty are shown. The same example is given for the expanded uncertainty on tracer cadmium in figure 7.

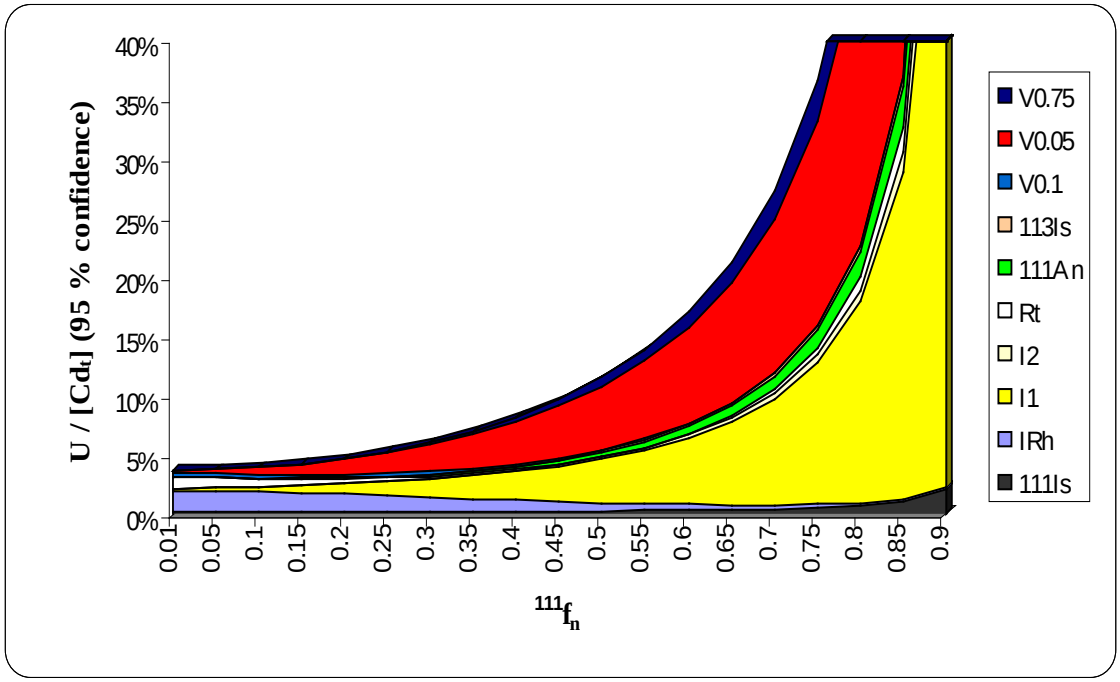


Figure 7: The major contributions to the expanded uncertainty (U) on the concentration of tracer cadmium for a total cadmium concentration level of 1 ng $ml^{-1}$ in function of the fraction natural cadmium 111 isotope ($^{111}f_n$).

For a $^{111}f_n$ value of about 0.2, which means that the fraction of natural cadmium on isotope 111 is 20 %, the expanded uncertainty on the concentration natural cadmium is approximately 4 %. At this point the concentration of natural cadmium is 0.650 ng $ml^{-1}$ (figure 8).

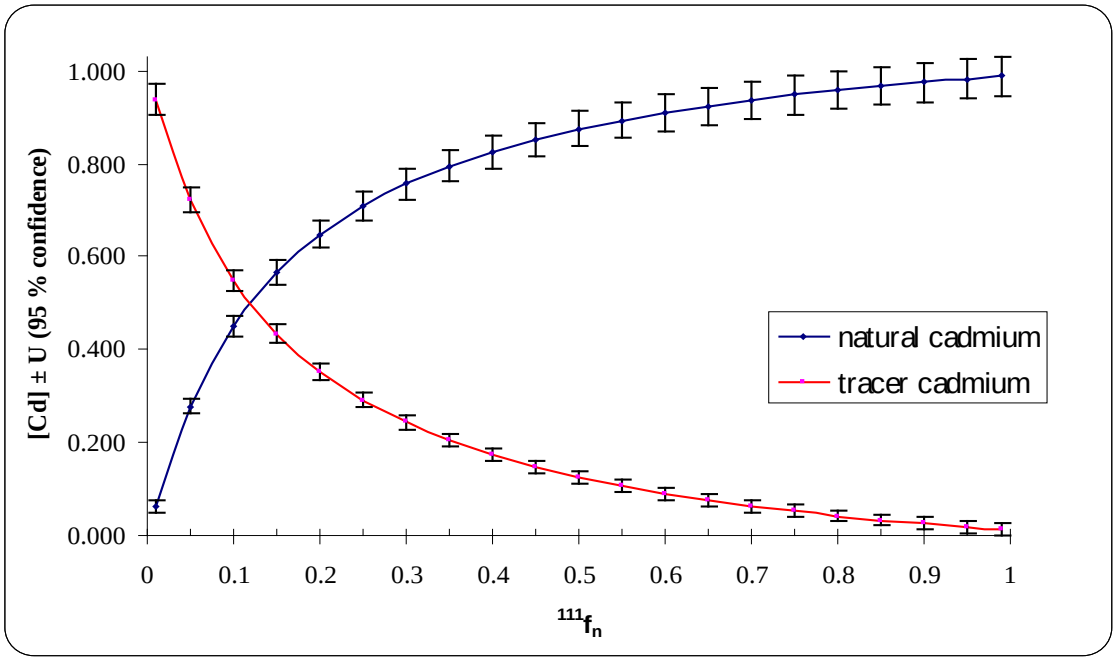


Figure 8: The concentration of tracer and natural cadmium (± U) for a total cadmium concentration level of 1 ng $ml^{-1}$ in function of the fraction natural cadmium 111 isotope ($^{111}f_n$).

The impact of the uncertainty on the analytical measurement on estimating transport parameters has been studied for the same example as presented in figure 5. The equilibrium convection-dispersion model was fitted to the experimental data in order to predict the retardation (r). The retardation determines the velocity at which an adsorbing component moves through a soil profile. This parameter could be considered as an indication for the time needed for the contaminant to reach the groundwater. The retardation of natural ($r_n$) and tracer cadmium ($r_t$) was obtained for three different sets of experimental data. The first set consisted of the mean analytical measurements ([Cd]), the second set included an alternate choice of the same analytical measurements increased or decreased by their expanded uncertainty ([Cd] +/- U). The third set was a combination of the mean analytical measurements ([Cd]), the same data increased ([Cd] + U) and decreased ([Cd] - U) by their expanded uncertainty. The results are briefly summarised in table 11 together with a 95 % confidence interval of the estimated retardation. The difference in the calculated retardation between the three different data sets is small compared to the extent of the 95 % confidence interval within one data set. Without going into detail on modelling aspects this uncertainty on the retardation is mainly due to fitting of the equilibrium convection-dispersion equation to the data.

| data set | $r_t$ ($Cd_t$) | 95 % confidence intervals | $r_n$ ($Cd_n$) | 95 % confidence intervals |
|---|---|---|---|---|
| [Cd] | 10.77 | 8.55 - 12.99 | 17.28 | 15.62 - 18.96 |
| alternate [Cd] +/- U | 10.75 | 8.47 - 13.03 | 16.94 | 15.44 - 18.43 |
| [Cd], [Cd] +U, [Cd] - U | 10.77 | 8.69 - 11.84 | 17.28 | 15.60 - 18.97 |

Table 11: Fitting of different experimental data sets with the equilibrium convection-dispersion model in order to predict the retardation.

## Conclusions

A calculation method for the simultaneous determination of tracer and natural cadmium with ICP-MS in soil column effluents is described. A full uncertainty calculation method and an overview of the uncertainty sources are given for the quantitative determination of tracer and natural cadmium with ICP-MS. Although each collected fraction of the column effluent is a unique combination of tracer and natural cadmium at a certain concentration level, the following general conclusions can be formulated. At low concentrations of cadmium (< 0.2 ng $ml^{-1}$ Cd), the uncertainty due to counting statistics is the major source of uncertainty. At higher concentrations the signal instability, partially due to the clogging of the sampling cone by calcium salts present in the leachant ($CaCl_2$), forms the largest contribution to the total uncertainty on the analytical measurement (4%, 95 % confidence intervals). The full uncertainty on the analytical measurement was negligible for the estimation of solute transport parameters.

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### 4.3. SOURCES OF NITRATE LEACHING

Fertiliser use is a major source of nitrate leaching into ground and surface water and constitutes an important problem in many European Union (EU) member states [157]. To reduce leaching, the EU Nitrate directive (91/676/EC) focuses on the pollution by nitrates from agriculture. Member states are obliged to identify waters in which the nitrate concentration is above, or at risk of exceeding the 50 mg/l $NO_3^-$ norm. Agricultural areas within the catchment area for these waters are then designated as a nitrate-vulnerable zone, in which member states are obliged to draw up an action programme and a code for good agricultural practise, involving, for example, fertilisation standards.

The Nitrate directive focuses primarily on the use of animal manure as fertiliser, because this practice is difficult to manage. In Flanders, difficulties in predicting the exact nutrient availability and uptake led to the imposition of a precautionary fertilisation standard for nitrate-vulnerable zones of 170 kg N $ha^{-1}$ $year^{-1}$. Although the Nitrate directive has been in force now for 20 years, many EU member states still experience difficulty in complying with its requirements and achieving environmentally beneficial outcomes. In some European catchment areas, the nitrate concentrations are still increasing.

The necessity for environmental management of surface and groundwater quality with respect to nitrate ($NO_3^-$) contamination is therefore well agreed upon nowadays [158]. The current most common approach to do so, is mainly based on monitoring $NO_3^-$ concentration in water and soils at various stations and times. Management programmes based on such a concentration approach can be very demanding. As an example, in Flanders, the on-going $NO_3^-$ management programme uses circa 800 monitoring stations for surface water and circa 2 100 for groundwater. Water samples from these locations are added to circa 28 000 soils samples from agricultural land to produce about 100 000 "classical" physical and chemical data points annually. Although this allows evaluating the water quality status, this monitoring strategy has not been successful at providing a clear understanding of the sources of $NO_3^-$ pollution. Indeed, there is ample evidence (*e.g.*, EC Implementation of Council Directive 91/676/) showing that despite a high density of monitoring stations, and associated high cost, N-species concentration data alone do not permit to establish adequately the nature and respective contribution of $NO_3^-$ sources responsible for water contamination. As a consequence, it is extremely difficult to design and adjust environmental management plans and to evaluate their effectiveness on the long run.

Due to a wide variety of potential sources, nitrogen (N) can enter the soil under several chemical forms: nitrate ($NO_3^-$), nitrite ($NO_2^-$), ammonium ($NH_4^+$), organic nitrogen compounds, *etc.* … N cannot be considered conservative because it is biologically modified through, for example, nitrification and denitrification reactions that cause isotope fractionation, and ultimately modifies the isotopic compositions of the dissolved N species. Since oxygen ($O_2$) is usually available in unsaturated soils, most of the N that reaches the groundwater has undergone nitrification and is present in its $NO_3^-$ oxidized form.

From the sole concentration measurements, it is generally hard to distinguish to what extent different sources (mineral fertilisers, animal's manure or sewage effluents) are contributing to the $NO_3^-$ level observed in water. It requires an extended dataset of spatially and temporally staggered concentration measurements, as well as detailed information on potential N sources in the surrounding area, hydrology, soil characteristics, … Even when abundant data is available, budgeting the different sources based on the sole concentration measurements remains difficult and highly uncertain. Moreover, such a characterisation of the observed $NO_3^-$ pollution might become very expensive and time-consuming in areas exposed to multiple possible N sources.

Given the complexity of the biogeochemical nitrogen cycle, both the nitrogen isotope composition ($\delta^{15}N$) and oxygen isotope composition ($\delta^{18}O$) of the $NO_3^-$ molecule have been widely used to i) trace its natural and anthropogenic sources, ii) identify transformation processes (*e.g.*, denitrification, nitrification and biological $N_2$ fixation) and iii) assess the N budget in water bodies. Mixing processes, which are generally controlling the input of $NO_3^-$ pollution in water, lead to a modification of the isotopic compositions (both $\delta^{15}N$ & $\delta^{18}O$) of the dissolved $NO_3^-$. This mixing effect can be amplified by the superimposition of transformation reactions such as natural denitrification. Therefore, discriminating multiple $NO_3^-$ sources based on the $\delta^{15}N$ and $\delta^{18}O$ isotope composition of $NO_3^-$ alone can sometimes become tricky, especially when secondary conversion processes occur.

Due to its ubiquitous nature, boron (B) commonly exists in groundwater as a minor constituent [159]. The large range of B isotope ratios observed in nature implies that significant contrasts between B sources in groundwater are possible. Previous studies on the B isotope ratio as tracer of human impact on water resources focused on the identification of waste water and sewage dominated by synthetic B products, as well as on the impact of fly ash leachate. Boron, also presents the great advantage of not being affected by $NO_3^-$ conversion processes (*i.e.,* natural denitrification does not modify the isotopic composition of B; $\delta^{11}B$). Therefore, the B isotope ratio can be used to improve the identification of sources of $NO_3^-$ when $NO_3^-$ transformation processes are involved.

Recent studies have shown that a multi-isotope approach, based on the combined use of $\delta^{15}N$ and $\delta^{18}O$ of $NO_3^-$ and $\delta^{11}B$ is more successful to trace the origin of $NO_3^-$ contamination compared to the sole monitoring of corresponding concentrations [159].

A European Life demonstration project was carried out for the Alsace aquifer, which is located in the Upper Rhine basin, between the German, French and Swiss borders. The aim of this ISONITRATE project (http://isonitrate.brgm.fr/, last accessed on 20/01/2013) was to demonstrate to policy makers and implementers that:

1. A water quality monitoring network, operated over years and integrating isotope data ($\delta^{15}N$, $\delta^{18}O$ & $\delta^{11}B$), inherently contains far more information than $NO_3^-$ concentrations alone (in terms of identifying pollution sources and assessing their respective contributions to the pollution pressure). It is technologically feasible, and generates environmental benefits.

2. Such an isotope ratio monitoring methodology greatly enhances the understanding of $NO_3^-$ pollution in water and leads to more effective planning and design of environmental management measures with respect to $NO_3^-$ pollution in river basins and water bodies defined by the Water Frame Directive (WFD).

The analytical part of the ISONITRATE project was carried out by the Bureau de Recherches Géologiques et Minières (BRGM, France), the Department of Applied Analytical and Physical Chemistry of Ghent University (ISOFYS, Belgium) and VITO. Based on both land use and field knowledge from local authorities, four sampling sites were chosen in the Alsace aquifer. Ground and surface water samples were taken 12 times between October 2007 and December 2008 and analysed for the $\delta^{15}N$ and $\delta^{18}O$ values of $NO_3^-$ and the $\delta^{11}B$ value (see paper: Boron isotope ratio ($\delta^{11}B$) measurements in WFD monitoring programs: comparison between double-focusing sector field ICP (ICP-SFMS) and thermal ionization mass spectrometry (TIMS), J. *Anal. At. Spectrom.*, 2010).

An International Workshop “Towards new methods to manage nitrate pollution within the Water Framework Directive” was organised in Paris (10-11/12/2009) to present and discuss new approaches to manage nitrate pollution.



Picture 12: International Workshop "Towards new methods to manage nitrate pollution within the Water Framework Directive" (Paris, UNESCO building, 10-11/12/2009).

The outcome of the workshop resulted in a guideline for policy makers to identify nitrate polluters and in which the use of compound-specific nitrogen ($\delta^{15}N$,), oxygen ($\delta^{18}O$), and bulk boron ($\delta^{11}B$) isotope ratios to identify sources of nitrate-contaminated waters was outlined [160].

# Boron isotope ratio ($\delta^{11}B$) measurements in WFD monitoring programs: comparison between double-focusing sector-field ICP (ICP-SFMS) and thermal ionization mass spectrometry (TIMS)

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(Reference list of this paper, see p. 217)

*Abstract*

*The aim of our research was to compare $\delta^{11}B$ measurements performed with thermal ionization mass spectrometry (TIMS) and sector-field inductively coupled plasma-mass spectrometry (ICP-SFMS) and evaluate the feasibility of implementing stable isotope methods in European water Framework directive (WFD) monitoring programs. The comparison was based on $\delta^{11}B$ measurements of 192 ground- and surface water samples and 15 leachates of nitrate pollution source materials (organic and mineral fertilisers). The precision of $\delta^{11}B$ measurements attainable with ICP-SFMS, $2\sigma = \pm$ 2.6 ‰; (n=192), is as expected lower than the precision achieved by TIMS, $2\sigma = \pm$ 0.3 ‰ (n=183). However the ease of use, rapidity and availability of ICP-SFMS on the one hand and the observed variability in $\delta^{11}B$ in ground- and surface water on the other (from -3.4 to +37 ‰), demonstrates that using ICP-SFMS as an isotopic screening method would promote the use of isotopic methodology for WFD monitoring.*
*Based on the results of the different case studies it is shown that retrieving precise information on the identification of pollution sources from $\delta^{11}B$ values requires reaching the best analytical precision and accuracy possible. Hence, the superior precision of TIMS advantages tracing of nitrate pollution sources. However for some cases, e.g., trying to decipher contributions between sources with really distinct $\delta^{11}B$ signatures (e.g., manure and sewage effluent), ICP-SFMS results lead to the same conclusions and can therefore be used as a first approachable screening method for the determination of $\delta^{11}B$ in WFD monitoring programs.*

## Introduction

With the increasing precision of state-of-art mass spectrometry instruments in determining isotope ratios, interest in isotopic fingerprinting techniques for a variety of elements is increasing. The natural observed variations in isotope ratios can be used, among others, in i) identification of archaeological artefacts, ii) food authentication, iii) provenance studies and tracing of sources of contamination.

There is a considerable interest in determining variations of boron isotope ratios ($^{11}B/^{10}B$) in geochemistry because of the wide natural range of $^{11}B/^{10}B$ ratios in rocks, sediments and waters. Boron isotopes have been successfully used for tracing sources of anthropogenic input into ground- and surface water,[1-5] rainwater and deposition,[6-8] freshwater lakes,[9] landfill percolates[10] and even anthropogenic emissions in the atmosphere.[11]

A variety of mass spectrometric techniques are used for isotope ratio measurements, depending on the demands of the specific application. The fundamentals and the use of plasma source mass spectrometry for isotope ratio measurements have been reviewed by several authors,[12-13] especially since the introduction of multi-collector ICP-MS.[14]

The classical method for measuring the boron isotopic composition, $\delta^{11}B$, is thermal ionization mass spectrometer (TIMS). It yields the highest degree of accuracy and precision (± 0.3‰). It is now well documented that various ICP-MS techniques are also widely used for measuring isotope ratios, with excellent results for multi-collector ICP-MS (MC-ICP-MS: $\delta^{11}B$ ± 0.2‰), satisfactory results for double-focusing sector-field ICP-MS (ICP-SFMS: $\delta^{11}B$ ± 2‰) and poor results using quadrupole-based ICP-MS (Q-ICP-MS: $\delta^{11}B$ ± 15‰).[15-24]

As boron isotope ratios are increasingly being applied in geochemistry, the comparison of isotopic measurements across different instrument types and techniques with respect to the demands of the application is of concern. Recently, an inter-laboratory comparison of boron isotope measurements was performed in order to address the correct reporting and comparison of isotopic measurements across different instrument types and techniques.[15] Kasemann *et al*. reported a comparison of isotopic measurements with respect to boron isotope composition of marine carbonates to reconstruct seawater pH values and atmospheric *p*CO2. [16]

To distinguish nitrate sources, trace them in water and quantify their respective contributions, research showed great added value of using a multi-isotopes approach including boron ($\delta^{15}N$-$NO_3$, $\delta^{18}O$-$NO_3$ and $\delta^{11}B$).4 Nitrate contamination in water is a worldwide environmental problem and is of special concern in the European Water Framework Directive.[25] Mean nitrate concentrations in groundwaters in Europe are above background levels but do not exceed the limit of 50 mg $L^{-1}$ as $NO_3$. On average, groundwaters in western Europe have the highest nitrate concentration, due to the most intensive agricultural practices, twice as high as in eastern Europe, where agriculture is less intense. In the EU, it is estimated that mineral fertilisers account for almost 50 % of nitrogen inputs into agricultural soils and manure for 40 %. The rate of percolation is often slow and excess nitrogen levels may be the effects of pollution on the surface up to 40 years ago, depending on the hydrogeological conditions. There are also other sources of nitrate, including treated sewage effluents, which may also contribute to nitrate pollution in some rivers.

However chemical data alone, currently used in the different types of monitoring programs defined in the Water Framework Directive, do not permit to establish unambiguously the type, location and contribution of different sources of nitrate in a river basin. In particular, differentiating urban and agricultural origin is difficult, even by increasing the number of monitoring stations or samples. This information is nevertheless critical in defining correct measures to reduce the nitrate contamination.
Within the frame of the European Life ISONITRATE project, the aim of our research was to compare $\delta^{11}B$ measurements via TIMS and ICP-SFMS for tracing nitrate sources and evaluate the feasibility of implementing stable isotope methods in European WFD monitoring programs.[26] Nitrate concentrations of more than 1000 groundwater monitoring stations across European countries are reported to the European Environment Agency.[25] However on a local scale, the frequency of quality monitoring of surface and groundwaters with respect to nutrients is much larger. In Flanders alone, more than 2000 groundwater and 4000 surface monitoring stations control on a regular basis the nitrate content.[27] Because of these high frequency monitoring requirements, the WFD implementation has triggered the use of screening methodologies in particular for the detection of accidental pollution or the control of water bodies at risk.[28]

For implementation and application of isotope techniques in WFD monitoring programs the ease and feasibility of measurement methods is of primary concern. The peculiar advantages of sector-field

based ICP-MS include high sample throughput, low analysis cost, instrument robustness, sensitivity and simple sample preparation. Moreover, these type of instruments are already available and implemented in WFD monitoring laboratories to analyse the content of different contaminants in ground- and surface water (Cd, Pb, ...). The more precise techniques (TIMS, MC-ICP-MS), on the other hand, often require labour-intensive sample preparation, such as chemical purification of the analyte and expensive equipment. The nitrate source tracking potential based on $\delta^{11}B$ measurements with TIMS and ICP-SFMS was evaluated in four different cases.

**Natural variations of $\delta^{11}B$**

A synthesis of boron isotope variations in nature has been reported amongst others by Barth.[29] The ratio between the two stable isotopes of boron, $^{11}B$ and $^{10}B$, is usually referred under the $\delta^{11}B$ notation, given by equation 1:

$$\delta^{11}B = \left[ \frac{\left(^{11}B/^{10}B\right)_{sample}}{\left(^{11}B/^{10}B\right)_{NIST\,951}} - 1 \right] \cdot 10^3 \quad \text{(equation 1)}$$

where NIST SRM 951 (boric acid) is the accepted international reference material, with $^{11}B/^{10}B$ = 4.04362 ± 0.00137. The relative large mass difference between the two stable isotopes of boron leads to a wide range of boron isotope variations in natural samples.[30] Natural waters, such as seawater, river water, rainwater, groundwater, brines, geothermal fluids and fumaroles' condensates encompass a range of $\delta^{11}B$ of nearly 76 ‰.[3] The lowest $\delta^{11}B$ values at -16 ‰ are reported for groundwater from the Artesian Basin in Australia, the most enriched reservoirs measured, to date, are saline groundwater in Israel and brines from the Dead Sea and Australian salt lakes with $\delta^{11}B$ values up to + 60 ‰.

The dominant boron species in aquatic systems are $B(OH)_3$ and $B(OH)_4^-$, which are in isotopic equilibrium as shown in equation 2:[2]

$$^{11}B(OH)_3 + {}^{10}B(OH)_4^- \Leftrightarrow {}^{10}B(OH)_3 + {}^{11}B(OH)_4^- \text{ (equation 2)}$$

The calculated equilibrium constant for this reaction is 0.981 at 25°C. This implies that $^{10}B$ is preferentially present in the tetrahedral species, while $^{11}B$ is enriched in the trigonal species. The $B(OH)_4^-$ species are preferably adsorbed by soil and minerals, leading to an enrichment of $^{10}B$ in the solid phase (fractionated by 30-40 ‰) when boron is incorporated from aquatic systems by heterogeneous exchange, and a concomitant enrichment of $^{11}B$ in the residual fluids. In contrast, leaching of clay minerals (*e.g.,* desorption) or extraction of fluid inclusions in crystalline rocks result in low $\delta^{11}B$ in the residual fluids. In aqueous solutions, the equilibrium between $B(OH)_3$ and $B(OH)_4^-$ is pH-dependent (equation 3):

$$B(OH)_3 + H_2O \Leftrightarrow B(OH)_4^- + H^+ \text{ (equation 3)}$$

At high pH values (pH > 11), $B(OH)_4^-$ dominates, while $B(OH)_3$ is the dominant form at pH < 7. An equilibrium isotope fractionation can, therefore, only be expected if the aquatic system has a pH between 7 and 11.

**Anthropogenic influence of $\delta^{11}B$ in ground and surface water**

With respect to nitrate groundwater contamination from intensive agriculture, the main sources to distinguish are mineral fertilizers, organic fertilizers (animal manure) and sewage. While Boron concentrations in natural groundwater and surface water are generally low (< 0.05 mg $L^{-1}$), the contaminant sources are enriched in boron (0.1 – 1.5 mg $L^{-1}$ in sewage effluent, > 1 mg $L^{-1}$ in liquid manure, up to 22 mg $L^{-1}$ in mineral fertilizer leachate).[31-32] Consequently the boron isotope composition is sensitive to mixing of pristine and contaminated waters. Moreover the isotopic composition of boron, as a nitrate co-migrant, is not affected by denitrification and can therefore be used as a conservative tracer of mixing processes. [31-32] Figure 1 summarizes the boron isotope composition ranges for the main anthropogenic sources. A synthesis of using coupled nitrogen and boron (measured with TIMS) isotopes for tracing the sources of nitrate in groundwater has been reported by Widory *et al.*.[4] A recent review of stable isotope methods for nitrate source identification ($\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$) was presented by Xue *et al.*.[33] In this paper it is shown that especially in the case of differentiation between manure and sewage the $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ approach alone does not allow clear differentiation of the sources.

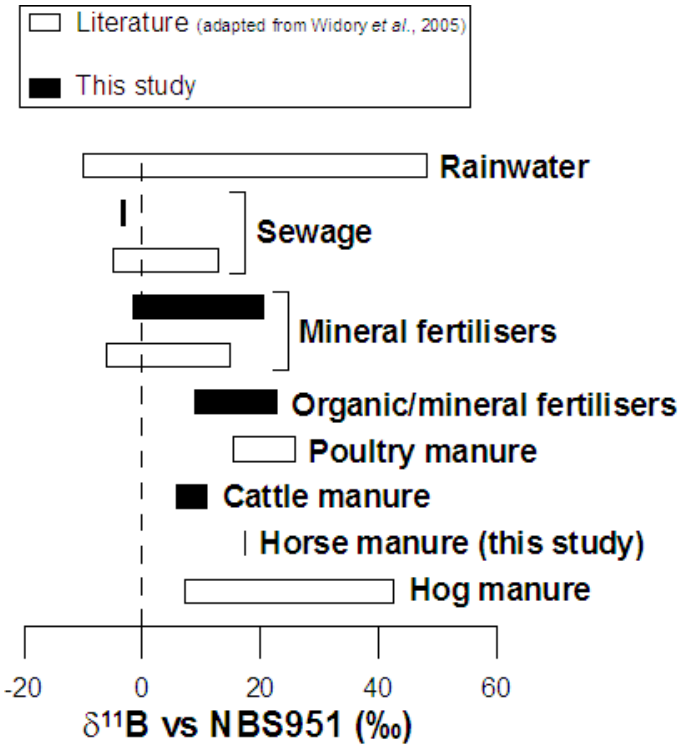



Figure 1: Literature overview of $\delta^{11}B$ values of main $NO_3$ pollution sources in combination with data from the ISONITRATE project [4].

A summary of boron isotope ratios and concentration data for the main nitrate contaminant sources are given below.

*Sewage water*

The first studies of B isotopes as tracers of human impact on water resources have focussed on the identification of wastewater and sewage dominated by synthetic B products. Sodium perborate (either monohydrate $NaBO_3 \cdot H_2O$ or tetrahydrate $NaBO_3 \cdot 4H_2O$) is widely used as a bleaching agent in a variety of domestic and industrial cleaning products. The raw materials are mainly from large non-marine evaporate deposits in the USA (*e.g.*, Boron, Searles Lake) and western

Turkey (*e.g.*, Kirka) which account for almost 90 % of world production of sodium perborate. During end use of perborate-enriched detergents and cleaning products, the anthropogenic water soluble boron compounds are discharged with domestic aqueous effluents into sewage treatment plants, where little or no boron is removed during conventional processing of the wastewater. Hence the anthropogenic boron load is almost entirely released into the aqueous environment by entering a receiving surface water system where further dilution occurs. Boron concentrations in secondary effluents typically range from 0.1 to 1.5 mg $L^{-1}$. Co-variations observed between B concentrations of freshwaters and P concentrations or anionic detergent structures support the fact that sodium perborate is to be considered as the major anthropogenic source of boron. In natural borate minerals, $\delta^{11}B$ ranges from -5.4 to 10.2 ‰ for Na-borates, from -16 to -1.1 ‰ for Na/Ca borates and from -21.9 to -4.9 ‰ for Ca-borates. The rather narrow range in $\delta^{11}B$ of Na-borate minerals allows an isotope approach to distinguish a specific anthropogenic source of boron (mainly from industrial perborate, the dominant use of mined boron) in a given natural aquatic system, characterized by a distinct local background $\delta^{11}B$. The boron isotopic signature for a series of industrial sodium perborate monohydrate and tetrahydrate products manufactured in Europe (Germany) were reported by Barth.[16] Sodium perborate monohydrate and tetrahydrate samples were characterized by $\delta^{11}B$ values ranging from -3.9 to +0.9 ‰ and -4.8 to +0.5‰, respectively. The total range in $\delta^{11}B$ values (-4.8 to +0.9‰) overlaps with the ranges of $\delta^{11}B$ reported for non-marine Na-borate minerals and commercial borax from the USA (-1.3 to +10.2 ‰) and Turkey (-5.4 to -1.7 ‰).

*Fertilizers*

Boron isotope signatures of inputs related to agriculture (*e.g.,* hog manure, cattle feedlot runoff, synthetic fertilizers) and the combination of N and B isotopes were first used in 1997 to distinguish $NO_3^-$ anthropogenic inputs to both ground- and surface water.[31] For B to fulfil this role, however, manure and fertilizers must contain detectable B with distinctive isotopic compositions.
Komer *et al.* reported averaged boron concentrations in liquid hog manure of 2.9 mg $L^{-1}$ (n=7), [31] for cattle manure and poultry manure concentrations of respectively 1.8 and 13.4 mg $kg^{-1}$ were reported.[32] In this study it was also shown that boron concentrations moderately correlated with potassium, a soluble element that occurs mostly in urine, but not with phosphor, an element that is mostly in faeces. These correlations are consistent with boron residing mainly in the urine component of manure. Boron concentrations in fertilizers (on a dry weight basis) ranged from below detection limit for some brands of ammonium nitrate and urea up to 382 mg $kg^{-1}$ in magnesium sulphate.[31]

However, the amounts of boron added to cultivated fields with fertilizers depend on the application rates of the specific fertilizer and its boron contents. As an example, it was calculated by Komer *et al.* that for typical liquid manure application rates a 0.28-0.42 kg B $ha^{-1}$ is added, while for N mineral fertilizers 0.05 kg B $ha^{-1}$ and in case of some brands of urea or ammonium nitrate no detectable boron was added.

In conclusion, boron isotopes can be used as tracers for discerning distinct solute sources in natural waters since (i) boron is highly soluble in aqueous solutions, and therefore an ubiquitous minor or trace constituent in nearly all water types, (ii) the boron isotopic composition is controlled by several known parameters among which the solute source compositions and isotope fractionation processes related to adsorption/desorption, mineral precipitation and dissolution, and volatilization are the most relevant and (iii) the relative large mass difference between the two stable isotopes of boron leads to a wide range of variations of boron isotope compositions in the nature.

However considering the concentration ratio of nitrate and boron in the different nitrate sources, boron isotopes are mainly useful for tracing or discerning organic fertilizer (manure) and sewage

effluent (washing detergents). This is especially relevant considering the impossibility to clearly differentiate between these two sources with the $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ approach alone.

## Experimental

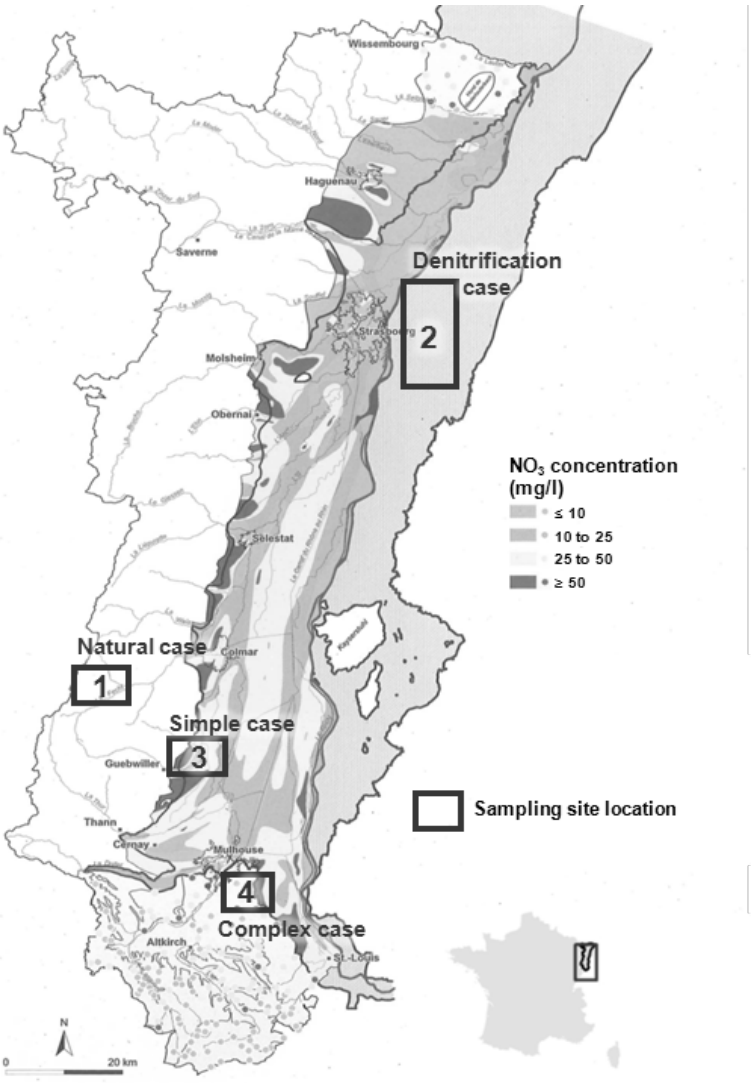
### Instrumentation

Two distinct types of mass spectrometers were used to measure and compare $\delta^{11}B$ values:

1. a single-collector double-focusing ICP-SFMS (ELEMENT II, ThermoFisher, Germany)
2. a single-collector thermal ionization mass spectrometer TIMS (MAT261, Finnigan®, Germany)

### Water Samples

The ISONITRATE demonstration project relied upon a survey of 12 sampling campaigns over a 15 months period (October 2007 – December 2008).[26] The pilot site is located in the Alsace region (France), it is part of the Upper Rhine basin between the German-French-Swiss border near Basel in the south and the mouth of the river Nahe near Bingen in the north. The site is flanked by the low mountain ranges of the Vosges and the Pfälzerwald in the west as well as of the Black forest and the Odenwald in the east.




Picture 13: Locations of the four sampling sites on the trans-boundary Alsace aquifer [158].

Because of an intensive agricultural land use, viniculture and the presence of industries and mining activities in the Upper Rhine Valley, water on this pilot site is strongly impacted by anthropogenic inputs. The average nitrate concentration of the groundwater in the Upper Rhine Valley is just under 30 mg $L^{-1}$ nitrate and herewith indicates a substantial pollution of the groundwater.
Within the Alsace aquifer four distinct scenarios were selected:

i) Natural case (B1-2, boron corresponding to the local, natural recharge);
ii) Simple case (A1-4, the source of anthropogenic boron is unique);
iii) Complex case (C1-5, multiple distinct sources of boron involved);
iv) Denitrification case (D1-5,nitrate is reduced but should not affect the boron isotopic budget).

Picture 14: Survey of 12 sampling campaigns over a 15 months period (October 2007 – December 2008).

The description of the collected water samples is given in table 1. All samples for $\delta^{11}B$ measurement were collected in polyethylene (PE) bottles and stored at about 5°C in a refrigerator until they were analysed. Other parameters that were monitored are pH, Eh, EC, $O_2$, T°, $NO_3$, $NH_4$, P, TOC, Ca, Mg, Cl, Zn, B, and alkalinity.

| | code | type |
|---|---|---|
| Single source of $NO_3$ | A1 | Surface water |
| | A2 | Surface water |
| | A3 | Groundwater |
| | A4 | Groundwater |
| Unpolluted water | B1 | Surface water |
| | B2 | Groundwater |
| Multiple sources of $NO_3$ | C1 | Surface water |
| | C2 | Surface water |
| | C3 | Groundwater |
| | C4 | Groundwater |
| | C5 | Groundwater |
| Natural Denitrification | D1 | Groundwater |
| | D2 | Groundwater |
| | D3 | Groundwater |
| | D4 | Groundwater |
| | D5 | Groundwater |

Table 1: Description of ground - and surface water samples. Four different environmental contexts: i) single source of $NO_3$, ii) "unpolluted" water, iii) multiple sources of $NO_3$, iv) natural denitrification.

**Source material samples**

After identification, local sources of anthropogenic inputs were sampled from farms or farming cooperative and sewage stations. For the natural case, no pollution sources were sampled as this site represents the natural/uncontaminated reference. For the simple case, which was supposed to be impacted by a single pollution source consisting of mineral fertilizers used for viticulture, the sampling of the main fertilizers was done in a local agricultural marketing cooperative (Pfaffenheim, France). The fertilizers sampled are representative for usage in this specific basin. It thus appears that even if mineral fertilizers are the dominant products, there is also a non negligible use of organic fertilizers.

The complex case is located in the eastern part of the Sundgau in an area dominated by farming (cows, horses), agriculture (maize, wheat, sugar beet, rape), direct waste water inputs to surface water were also identified from detached houses which are not connected to a water treatment plant. Most of the waste water of this area are collected and treated in the waste water treatment plant of Sierentz located a few km south-east from the basin. The effluents of this waste water treatment plant were sampled in February 2008. The solid residues of the water treatment are dried in the Sierentz station to be used as fertilizers (dried mud) and were also sampled in February 2008. The main livestock farming consist of cows and horses. Three samples of manures were sampled directly from farms of this basin (April 2008) as well as a dunghill liquid effluent. Sampling of the main fertilizers was done in a local agricultural marketing cooperative (Sierentz). The sampled fertilizers are representative of the products used in this specific basin. The denitrification case is located in the German part of the Alsace plain, the site mainly consists of vineyards. The main mineral fertilizers used in this region were sampled in a local agricultural marketing cooperative (2 samples). A dunghill located nearby the D5 piezometer was also sampled. The source materials were extracted with milli-Q water (L/S = 10) and the $\delta^{11}B$ measurements were performed on the filtrated leachates.

**Reagents and standard solutions**

Boron standard solutions were prepared form a 10 g $L^{-1}$ commercially available standard (Spex CertiPrep Inc., Metuchen, NJ). De-ionised water was purified by a Millipore Milli-Q system. The $\delta^{11}B$ vales were calculated based on standard reference material NIST 951a Boric acid. All solutions were gravimetrically prepared in polypropylene bottles.

**Optimisation ICP-SFMS**

Many factors may affect precision and accuracy of isotope ratio determination by ICP-SFMS, among which sensitivity, spectroscopic interferences, mass discrimination and dead time correction.

*Sensitivity*
Using the instrument settings given in table 2, a sensitivity of 100,000 counts per second (cps) per µg B $L^{-1}$ for $^{11}B$ was obtained using Ni cones. In order to achieve better precision on the isotope ratio, samples containing boron concentrations > 25 µg $L^{-1}$ were diluted so that both isotopes were measured in counting mode. The instrument is equipped with a perfluoroalkoxy copolymer resin (PFA) nebulizer and spray chamber in order to reduce background level. For pure water, a reading of ~ 10,000 cps on $^{11}B$ was obtained (~ 0.1 µg B $L^{-1}$). Washing periods of 1 h are insufficient to reduce the memory effect below 1%, even when using a range of different solvents (mannitol, ammonia).[23] In our study, after 4 min rinsing with pure water, the signal intensity on $^{11}B$ typically dropped to < 2 % of the analyte signal intensity typical for the natural surface and groundwater samples. The blank can, thus, be considered as negligible.

| | |
|---|---|
| **Nebulizer type** | PFA micro flow |
| **Spray chamber** | PFA Scott type |
| **RF power (W)** | 1050 |
| **Cooling gas flow rate (L $min^{-1}$)** | 15 |
| **Auxiliary gas flow rate (L $min^{-1}$)** | 1 |
| **Nebulizer gas flow rate (L $min^{-1}$)** | 0.95 |
| **Solution uptake rate (ml $min^{-1}$)** | 0.7 |
| **Ion extraction lens (V)** | -2000 |
| **Focus lens (V)** | -1140 |
| **Mass resolution (m/Δm)** | 300 (low) |
| **Uptake time** | 4 min |
| **Analysis time** | 4 min 15 sec |
| **Rinsing time** | 4 min |
| **Scan type** | E-scan |
| **Detection mode** | Counting |
| **Mass range** | 10.012-10.013 ($^{10}B$) |
| | 11.008-11.010 ($^{11}B$) |
| **Mass window (%)** | 5 |
| **Settling time (s)** | 0.001 |
| **Sample time (s)** | 0.02 ($^{10}B$) |
| | 0.005 ($^{11}B$) |
| **Samples per peak** | 100 |
| **Runs** | 10 |
| **Passes** | 200 |
| **Integration type** | Average |
| **Dead time (ns)** | 10 |

Table 2: Optimised instrument settings for measurement of $\delta^{11}B$ with ICP-SFMS.

*Spectroscopic interferences*

In order to reduce the spectroscopic interference of $^{40}Ar^{4+}$ on the $^{10}B^{+}$ peak, the ratio frequency power setting was reduced and the auxiliary and nebuliser gas flow optimised.[1] The use of a magnetic sector ICP-MS at a low resolution mode yields flat topped peaks. Higher signal intensity coupled to the flat tops of the peaks at lower resolution is used for precise isotope ratio measurements.[34] In the low resolution mode, the peak width (located at 5 % peak height) for $^{10}B$ is 0.033 amu (9.979–10.046 amu), and the instrument is set to divide this peak into 100 measurement samples. The mass window for precise isotope ratio measurement is set to a narrow range of 5%, meaning that the scanning range of the instrument around the boron peak represents ± 2.5% peak width of the accurate mass and is centred in the flat top region 10.012-10.013.

*Mass discrimination*

The space charge effect is assumed to have the strongest influence on the total mass discrimination in an ICP-MS.[13] After the positively charged ion beam leaves the skimmer cone, the mutual repulsion of ion limits the total number of ions which are transmitted by the optics. If an ion beam consists of light and heavy ions, the light ions are deflected more extensively than the heavy ions, whereas the heavy ions preferably remain in the central ion beam. The total mass bias can be experimentally determined by the mass discrimination factor $f_{MD}$:

$$f_{MD} = R_{true}/R_{measured} \qquad \text{(equation 4)}$$

where R is the isotope ratio of the light over the heavy isotope. Due to the large percentage mass difference between the two stable boron isotopes and the relatively low degree of ionization of boron in the argon plasma of an ICP-MS instrument, the mass discrimination is significant. Based on the alternate NIST SRM 951 measurements during the measurement run, the range of mass discrimination per mass unit, MD, ranged between 7.5 an 10.5 %. Correction for mass discrimination is performed by bracketing samples with NIST SRM 951, the average $^{11}B/^{10}B$ ratio of NIST SRM 951 measured before and after each sample is used to calculate the $\delta^{11}B$ value of the bracketed sample, which is the recommended routine procedure for $\delta^{11}B$ analysis.[15] The correction for matrix-induced mass discrimination was also investigated by Gäbler *et al.* by analyzing seawater. They found, with instrumental settings similar to ours, comparable results for $\delta^{11}B$ measurements by both ICP-SFMS and NTIMS.[1]

*Dead time*

Boron isotope ratios were calculated from dead-time corrected intensities. Because of the 4 fold difference in natural abundance of B isotopes, a dead time correction in counting mode is necessary to obtain concentration-independent and accurate values of $\delta^{11}B$. The dead time is iteratively deduced from the measurement of the $^{235}U/^{238}U$ isotope ratio in 0.4, 0.6, 0.8 and 1 µg U $L^{-1}$ standard solutions according to the manufacturer instructions. The optimized dead time obtained was 10 ns.

In conclusion, using the typical optimized instrumental settings as summarized in table 2, single $\delta^{11}B$ measurement with ICP-SFMS can be performed without sample pre-treatment within 12 minutes (before starting a series of boron measurements, rinsing the ICP-SFMS instrument with Milli-Q water is recommended). For the routine measurement of $\delta^{11}B$ with ICP-SFMS, the following procedure was used on a set of 16 samples per campaign.

The instrument is tuned to maximum sensitivity for boron (NIST SRM 951 solution of 25 µg $L^{-1}$), by tuning ion lenses and adjusting the nebulizer gas flow rate. Subsequently, in order to reduce the

spectroscopic interference of $^{40}Ar^{4+}$ on the $^{10}B^{+}$ peak, the auxiliary and nebuliser gas flow are further optimised.

Samples are analysed by bracketing with NIST SRM 951 standards, the average $^{11}B/^{10}B$ ratio of NIST SRM 951 measured before and after each sample is used to calculate the $\delta^{11}B$ value of the bracketed sample, which is the recommended routine procedure for $\delta^{11}B$ analysis.[15]

*Boron concentration measurements*

When using ICP-SFMS an advantage, compared to TIMS, is that in one single analysis both boron concentrations and its isotope composition can be obtained simultaneously. For the determination of the boron concentration in the water samples, an external calibration line where Be was added on-line as internal standard was used. In the frame of this project it was evaluated if the ICP-SFMS method optimised for isotopic analysis can be used for the quantification of the concentration. In this case, the average of the $^{11}B$ signal (cps) of NIST SRM 951 before and after the measurement of the $^{11}B$ signal (cps) of the sample was used to calculate the B concentration of the sample. The concentration of Boron in the prepared NIST SRM 951 standard amounted 27.5 µg $L^{-1}$.

**Optimisation TIMS**

For Boron isotope compositions ($\delta^{11}B$) in water, sample volume is determined to ultimately yield a quantity of 6 to 10 µg of boron. Samples then undergo a two-steps chemical purification using Amberlite IRA-743 selective resin (method adapted from Gaillardet *et al.*).[35] First, the sample (pH ~7) is loaded on a Teflon PFA® column filled with 1ml resin, previously cleaned with ultrapure water and 2N ultrapure NaOH. After cleaning again the resin with water and NaOH, the purified boron is collected with 15 ml of sub-boiled HCl 2N. After neutralisation of the HCl by Superpur $NH_4OH$ (20%), the purified boron is loaded again on a small 100µl resin Teflon PFA® column. Boron is collected with 2ml of HCl 2N. An aliquot corresponding to 2µg of boron is then evaporated below 70°C with mannitol in order to avoid boron loss during evaporation.[36] The dry sample is loaded onto a tantalum (Ta) single filament with graphite (C), mannitol ($C_6H_8(OH)_6$) and cesium (Cs). $\delta^{11}B$ are then determined by measuring the $Cs_2BO_2^+$ ion.[37,38] The analysis is run in dynamic mode by switching between masses 308 and 309. Each analysis corresponds to 10 blocks of 10 ratios. Samples are always run twice. Total boron blank is less than 10 ng corresponding to a maximum contribution of 0.2%, which is negligible. Seawater (IAEA-B1) is purified regularly in the same way in order to check for a possible chemical fractionation due to an uncompleted recovery of boron, and to evaluate the accuracy and reproducibility of the overall procedure.[39-41] Reproducibility was obtained by repeated measurements of the NBS951, accuracy and reproducibility are controlled with the analysis of the IAEA-B1 seawater standard.

**Statistical evaluation**

The Bland-Altman technique was used to assess agreement between two measurement methods. This technique was conducted in this study to compare results obtained via the TIMS and ICP-SFMS for the determination of $\delta^{11}B$. The average ( $\bar{d}$ ) and standard deviation ( $s_d$ ) of the difference (d) between the measurement results of two methods on the samples were computed. If the differences are normally distributed, and 95% of the differences lie between $\bar{d} - 1.96\, s_d$ and $\bar{d} + 1.96\, s_d$ (termed “95% limits of agreement”), the two analytical methods can be used interchangeably.

## Results and discussion

The implementation of $\delta^{11}B$ and boron concentration measurements in large scale WFD monitoring programs requires high sample throughput. The discussion on the nitrate source tracking potential is therefore focussed on the attainable analytical performances of $\delta^{11}B$ measurement with a ICP-SFMS instrument operating without additional sample pretreatment on the one hand versus a TIMS instrument including labour intensive matrix separation on the other. The interpretation on the use of the multi-isotopes approach ($\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$ and $\delta^{11}B$) to distinguish nitrate sources will be presented elsewhere.[26]

The average results of the characterisation of the water samples during the monitoring campaign (12 sampling campaigns over a 15 months period) are summarised in the tables below.

| | T (°C) | pH | $E_h$ (mV) | $E_h$ (mV NHE) | Cond (µs/cm) à T°C | Cond (µs/cm) à 25°C | $O_2$ (% saturation) |
|---|---|---|---|---|---|---|---|
| **A1** | 10.4 | 8.0 | 89 | 317 | 542 | 778 | 85 |
| **A2** | 10.4 | 8.0 | 143 | 352 | 394 | 567 | 89 |
| **A3** | 13.1 | 7.0 | 143 | 352 | 463 | 624 | 66 |
| **A4** | 13.2 | 7.4 | 204 | 423 | 464 | 611 | 60 |
| **B1** | 8.2 | 7.4 | 157 | 368 | 37 | 62 | 91 |
| **B2** | 8.1 | 6.9 | 194 | 405 | 24 | 38 | 84 |
| **C1** | 8.9 | 8.0 | 194 | 403 | 578 | 804 | 79 |
| **C2** | 8.9 | 8.2 | 179 | 389 | 576 | 827 | 83 |
| **C3** | 11.7 | 7.1 | 125 | 343 | 634 | 898 | 51 |
| **C4** | 11.8 | 7.1 | 148 | 364 | 588 | 838 | 72 |
| **C5** | 11.9 | 7.4 | 126 | 336 | 508 | 720 | 44 |
| **D1** | 8.1 | 5.0 | 265 | 481 | 28 | 43 | 87 |
| **D2** | 12.0 | 6.1 | 207 | 425 | 344 | 481 | 75 |
| **D3** | 13.5 | 7.0 | 96 | 307 | 594 | 780 | 55 |
| **D4** | 10.9 | 6.2 | 104 | 316 | 132 | 177 | 18 |
| **D5** | 12.5 | 7.1 | 146 | 361 | 503 | 691 | 7 |

| | Ca mg/l | Mg mg/l | Na mg/l | K mg/l | $NO_3^-$ mg N/l | Total N mg N/l | $Cl^-$ mg/l | $SO_4^{2-}$ mg/l | DOC mg/l | DIC mg/l | Dry cont. mg/l | Ash Cont. mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **A1** | 114 | 34 | 10 | 1.9 | 1.5 | 1.7 | 20 | 70 | 2.6 | 76 | 485 | 349 |
| **A2** | 81 | 22 | 7.9 | 2.8 | 1.5 | 2.2 | 14 | 47 | 1.9 | 58 | 362 | 267 |
| **A3** | 81 | 15 | 15 | 18 | 10 | 12 | 29 | 53 | 0.8 | 49 | 422 | 292 |
| **A4** | 100 | 16 | 8.3 | 1.6 | 20 | 23 | 39 | 36 | 0.7 | 44 | 474 | 258 |
| **B1** | 4.9 | 1.2 | 2.5 | 0.8 | 0.6 | 0.9 | 3.6 | 3.4 | 1.6 | 3.4 | 48 | 29 |
| **B2** | 4.3 | 1.1 | 1.5 | 0.3 | 0.7 | 1.0 | 1.2 | 3.2 | 0.9 | 3.1 | 35 | 16 |
| **C1** | 130 | 23 | 9.0 | 2.3 | 7.8 | 8.1 | 35 | 32 | 3.1 | 79 | 568 | 403 |
| **C2** | 131 | 24 | 12 | 3 | 8.0 | 8.6 | 41 | 39 | 3 | 77 | 560 | 389 |
| **C3** | 147 | 22 | 12 | 3.2 | 18 | 20 | 37 | 34 | 2.5 | 81 | 597 | 395 |
| **C4** | 139 | 22 | 12 | 3.7 | 13 | 15 | 29 | 39 | 2.3 | 81 | 541 | 378 |
| **C5** | 112 | 20 | 11 | 3.7 | 3.9 | 4.0 | 38 | 33 | 1.2 | 71 | 461 | 333 |
| **D1** | 2.4 | 0.6 | 1 | 1.7 | 1.8 | 2.0 | 1.7 | 5.4 | 0.9 | 1.5 | 29 | 16 |
| **D2** | 59 | 8.8 | 13 | 3.2 | 17 | 20 | 23 | 100 | 0.8 | 11 | 382 | 229 |
| **D3** | 120 | 18 | 15 | 1.4 | 9.0 | 9.8 | 24 | 45 | 1.7 | 76 | 491 | 363 |
| **D4** | 25 | 3.5 | 2.0 | 0.8 | 0.7 | 1.1 | 1.3 | 7.5 | 6.7 | 21 | 134 | 93 |
| **D5** | 126 | 10 | 7.0 | 1.0 | 7.9 | 7.0 | 29 | 37 | 0.9 | 66 | 467 | 329 |

Table 3a: Average results of of the characterisation of the water samples during the monitoring campaign .

**Boron concentration levels**

An overview of the measured concentrations of boron and nitrate over the different locations is given in figure 2 and table 3b. The Nitrate Directive (91/676/EEC) aims to control nitrogen pollution and requires member states to identify groundwaters that contain more than 50 mg $L^{-1}$ nitrate or could contain more than 50 mg $L^{-1}$ nitrate if preventative measures are not taken.

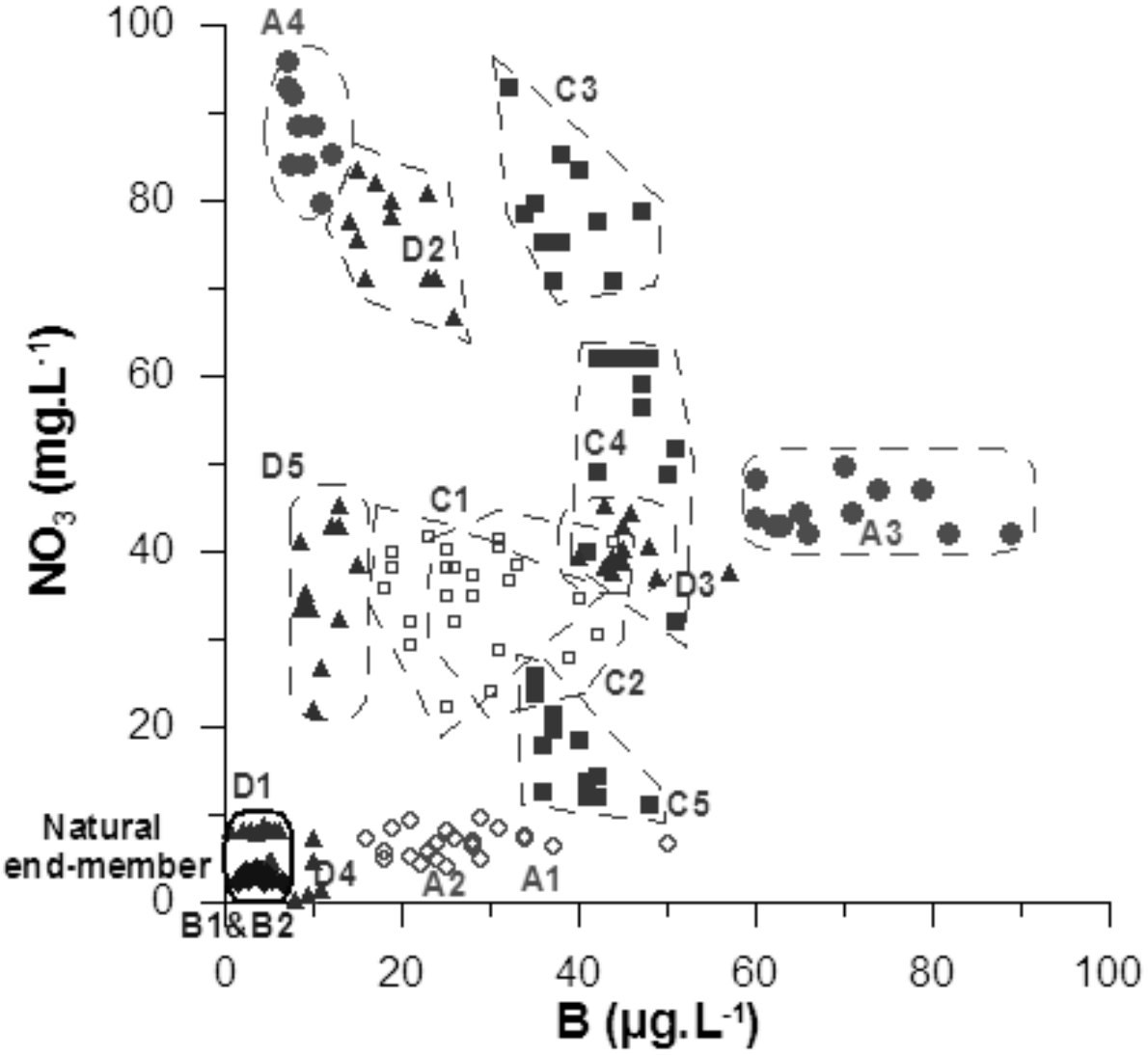



Figure 2: General overview of the coupled variations of nitrate and boron concentrations for the different case studies. Empty symbols represent surface water samples.

Ground waters A4, D2 and C3 are well above the current limit of nitrate, A3, C4, D3 and 5 are around the limit and C5, D1 and B1 are below the limit.

| | [B] µg $L^{-1}$ | 2σ | min | max | [$NO_3$] mg N $L^{-1}$ | 2σ | min | max | $NO_3$/B |
|---|---|---|---|---|---|---|---|---|---|
| **A1** | 30 | 15 | 22 | 50 | 1.5 | 0.5 | 0.9 | 1.8 | 50 |
| **A2** | 23 | 10 | 16 | 31 | 1.5 | 0.9 | 0.9 | 2.2 | 70 |
| **A3** | 70 | 19 | 60 | 89 | 10.1 | 1.2 | 9.5 | 11.2 | 140 |
| **A4** | 8.7 | 3.2 | 7 | 12 | 20.0 | 2.2 | 18.0 | 21.6 | 2300 |
| **B1** | 4.4 | 2.0 | 3 | 7 | 0.65 | 0.2 | 0.49 | 0.86 | 150 |
| **B2** | 3.3 | 2.2 | 2 | 5 | 0.70 | 0.2 | 0.50 | 0.86 | 210 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C1 | 25 | 12 | 18 | 40 | 7.8 | 2.5 | 5.0 | 9.4 | 320 |
| C2 | 32 | 13 | 25 | 44 | 8.0 | 2.6 | 5.4 | 9.3 | 250 |
| C3 | 43 | 32 | 32 | 92 | 17.3 | 4.4 | 12.0 | 21.0 | 400 |
| C4 | 46 | 7 | 41 | 51 | 12.2 | 4.5 | 7.2 | 14.0 | 260 |
| C5 | 39 | 8 | 35 | 48 | 3.8 | 2.3 | 2.5 | 5.8 | 100 |
| D1 | 3.7 | 3.4 | 1 | 6 | 1.8 | 0.2 | 1.6 | 1.9 | 480 |
| D2 | 19 | 8 | 14 | 26 | 17.0 | 2.4 | 15.0 | 18.8 | 900 |
| D3 | 46 | 8 | 40 | 57 | 9.0 | 1.2 | 8.3 | 10.1 | 200 |
| D4 | 8.2 | 4.8 | 5 | 11 | 0.7 | 0.9 | 0.1 | 1.6 | 80 |
| D5 | 11 | 4 | 9 | 15 | 8.0 | 3.1 | 4.9 | 10.1 | 720 |

Table 3b: Average boron (B) and nitrate ($NO_3$) concentrations.

The average B concentration for the 16 sites ranged from 3 to 70 µg $L^{-1}$ (table 4). The variability during the 15 months sampling campaign per location ranged from ± 2 (B1) to ± 32 (C3) µg B $L^{-1}$ (2σ, n=12). For the natural case, the average concentration was 3.8 ± 1 µg B $L^{-1}$ (2σ, n=12).

| | Time of sampling (month/year) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [B] µg $L^{-1}$ | 10/07 | 11/07 | 12/07 | 01/08 | 02/08 | 03/08 | 04/08 | 06/08 | 08/08 | 10/08 | 11/08 | 12/08 | mean µg $L^{-1}$ | 2*σ |
| A1 | 22 | 26 | 28 | 28 | 24 | 29 | 25 | 37 | 28 | 50 | 34 | 34 | **30** | **15** |
| A2 | 23 | 21 | 21 | 19 | 18 | 18 | 16 | 28 | 24 | 25 | 31 | 29 | **23** | **10** |
| A3 | 70 | 71 | 63 | 66 | 60 | 62 | 60 | 65 | 79 | 82 | 74 | 89 | **70** | **19** |
| A4 | 7.7 | 8.3 | 7.5 | 9 | 7.2 | 7 | 7.1 | 8.6 | 12 | 9.9 | 8.5 | 11 | **8.7** | **3.2** |
| B1 | 5.2 | 4.2 | 4.6 | 4.5 | 4.4 | 4.6 | 2.7 | 4.8 | 4.3 | 6.5 | 3.2 | 3.5 | **4.4** | **2.0** |
| B2 | 3.7 | 5 | 4.3 | 3.7 | 3.4 | 3.8 | 1.5 | 2.4 | 2.1 | 4.7 | 2.5 | 2.3 | **3.3** | **2.2** |
| C1 | 19 | 25 | 25 | 21 | 18 | 21 | 19 | 23 | 26 | 31 | 28 | 40 | **25** | **12** |
| C2 | 31 | 42 | 30 | 26 | 25 | 28 | 25 | 31 | 44 | 39 | 33 | 32 | **32** | **13** |
| C3 | 34 | 35 | 32 | 37 | 36 | 38 | 38 | 40 | 42 | 44 | 47 | 92 | **43** | **32** |
| C4 | 42 | 44 | 42 | 46 | 45 | 48 | 47 | 41 | 51 | 50 | 47 | 51 | **46** | **7** |
| C5 | 37 | 41 | 36 | 41 | 42 | 42 | 40 | 35 | 35 | 37 | 36 | 48 | **39** | **8** |
| D1 | 4.5 | | 6.2 | 5.7 | 5.1 | 4.7 | 0.6 | 2.6 | 2.1 | 3.6 | 3.1 | 2.9 | **3.7** | **3.4** |
| D2 | 15 | 23 | 26 | 16 | 15 | 16 | 14 | 19 | 17 | 19 | 23 | 24 | **19** | **8** |
| D3 | 43 | 45 | 40 | 44 | 44 | 45 | 43 | 45 | 48 | 49 | 46 | 57 | **46** | **8** |
| D4 | 9.4 | 8.1 | 5.3 | 10 | 5.2 | 5.1 | 5 | 9.4 | 11 | 11 | 9.5 | 9.9 | **8.2** | **4.8** |
| D5 | 11 | 10 | 9.2 | 8.5 | 9.6 | 9.3 | 8.7 | 12 | 13 | 13 | 13 | 15 | **11** | **4** |

Table 4: Boron concentrations measured by ICP-SFMS.

A comparison between the B concentration in 72 water samples measured with ICP-SFMS using an external calibration line on the one hand and the bracketed NIST SRM 951 on the other hand showed a correlation coefficient of 0.99 (y = 1.02 x + 0.12). The average measurement difference of boron concentration was 0.4 µg $L^{-1}$ and the 95 % limits of agreement according to the Bland-Altman technique amounted –3.4 and 4.3 µg $L^{-1}$.

The large variation in boron concentration levels observed between the different collected samples in combination with (in most cases) low variability per sample makes it possible to use the data for interpretation. However, there is no general correlation between the boron and nitrate concentrations, *e.g.,* the most contaminated nitrate groundwater A4 has a concentration in boron similar to the natural background. This is in line with the remarks by Komer *et al.* that the amounts of

boron added to cultivated fields with fertilizers depend on the application rates of the specific fertilizer and its boron contents.[31]

When using boron as a co-migrant tracer of nitrate, it is important to consider the extracted $N_{total}$/B concentration ratio from the different pollution sources. In general the following order in the $N_{total}$/B ratio can be derived (table 5): mineral fertilizer (ammonium nitrate, urea): $1/10^6$; mineral fertilizer (NPK): $1/10^3$; organic fertilizer: $1/10^2$; sewage effluent: 1/10. In the case of A4, high nitrate concentration in combination with low boron concentration could indicate the use of mineral fertilizers.

| | | | $NH_4$ | $NO_3$ | $NO_2$ | $N_{tot}$ | B | $N_{tot}$/B |
|---|---|---|---|---|---|---|---|---|
| **Name** | **Source Type** | **Sampling location** | **mg N $L^{-1}$** | **mg N $L^{-1}$** | **mg N $L^{-1}$** | **mg N $L^{-1}$** | **µg $L^{-1}$** | |
| NPK 14-7-17 | Mineral fertilizer | Single source of $NO_3$ | 7600 | 5800 | <0.15 | 13000 | 13900 | 940 |
| NPK 15-5-20 | Mineral fertilizer | | 10000 | 6300 | <0.15 | 15000 | 14400 | 1040 |
| Fumeterre | Organic/mineral fertilizer | | 20 | 45 | 0.8 | 160 | 380 | 420 |
| Orgaveg | Organic/mineral fertilizer | | 270 | 0.005 | - | 630 | 1300 | 490 |
| Ammonium nitrate 27% | Mineral fertilizer | Multiple sources of $NO_3$ | 14000 | 5300 | <0.15 | 24000 | 20 | 1200000 |
| NPK 13-13-21 | Mineral fertilizer | | - | - | - | - | - | - |
| NPK 18-46 | Mineral fertilizer | | - | - | - | - | - | - |
| Urea 46% | Mineral fertilizer | | 220 | 3.9 | - | 43000 | 70 | 614000 |
| Cow manure | Organic fertilizer | | 12 | 1.5 | 0.8 | 44 | 150 | 300 |
| Cow manure | Organic fertilizer | | 16 | 1.3 | 74 | 120 | 290 | 410 |
| Cow manure - liquid | Organic fertilizer | | 0.5 | 2.5 | <0.15 | 11 | 130 | 80 |
| Horse manure | Organic fertilizer | | 0.5 | 0.23 | <0.15 | 30 | 220 | 140 |
| WWTP - dry mud | WWTP - dry mud | | 5.4 | 230 | <0.15 | 810 | 220 | 3700 |
| WWTP effluent | WWTP-effluent | | 0.9 | 1.4 | <0.15 | 1.5 | 130 | 12 |
| Ammonium nitrate 27% | Mineral fertilizer | Natural Denitrification | 17000 | 13000 | <0.15 | 27000 | 30 | 900000 |
| NPK 14-8-13 | Mineral fertilizer | | 9800 | 3500 | - | 13000 | 2700 | 4800 |
| Cow manure | Organic fertilizer | | 1.1 | 2.5 | 0.2 | 60 | 410 | 150 |

Table 5: Chemical characterisation of the extracts of collected nitrate pollution sources (L/S = 10, the WWTP effluent was measured directly).

**Comparison of $\delta^{11}$B measurement by ICP-SFMS and TIMS on water samples**

The average $\delta^{11}$B values varied over the 16 sampling sites from -3.4 (C5) to 37‰ (D2) (table 7). The $\delta^{11}$B variability during the 15 months sampling campaign per location ranged from ± 1.0 to ± 15 ‰ (2σ, n=12). These data show that single sampling and analysis will not lead in all cases to a correct interpretation of the isotope ratios and this has to be considered when implementing in monitoring programs. On the other hand, the observed large variation in $\delta^{11}$B values allows clear discernible distinction between samples.

An estimate of the analytical performance characteristics of the $\delta^{11}$B measurement by ICP-SFMS was derived based on the measurements of the bracketed NIST SRM 951 samples. In a typical measurement run the 16 samples of the sampling campaign were bracketed in between the measurement of 17 NIST SRM 951 samples. Per measurement run 15 $\delta^{11}$B values of NIST SRM 951 were derived, *e.g.*, $\delta^{11}$B of NIST SRM 951 (3$^{rd}$ position) was calculated using the average $^{11}B/^{10}B$ ratio from NIST SRM 951 (2$^{nd}$ position) and NIST SRM 951 (4$^{th}$ position). The average of the in such a way calculated $\delta^{11}$B values of NIST SRM 951 (theoretical value = 0) in the course of the project amounted -0.096 ± 2.6 ‰ (2σ, n=192). The analytical performance is in agreement with previous reported precision values of $\delta^{11}$B measured by ICP-SFMS.[1,15]

For TIMS measurement, reproducibility was obtained by repeated measurements of the NBS951 and the accuracy was controlled with the analysis of the IAEA-B1 seawater standard ($\delta^{11}B$ = 38.6 ± 1.7‰). The $^{11}B/^{10}B$ ratio of replicate analyses of the NBS951 boric acid standard (after oxygen correction) was 4.05045±0.00130 (2σ, n = 183). The reproducibility of the $\delta^{11}B$ determination was ±0.32‰ (2σ). The mean value obtained on $\delta^{11}B$ of seawater was = 39.21 ± 0.31 ‰ (2σ) (n = 20).

The individual $\delta^{11}B$ values measured with ICP-SFMS and TIMS on the water samples are summarized in respectively table 6 and table 7.

| $\delta^{11}B$ | 10/07 | 11/07 | 12/07 | 01/08 | 02/08 | 03/08 | 04/08 | 06/08 | 08/08 | 10/08 | 11/08 | 12/08 | mean | 2*σ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 6.6 | 5.4 | 5 | 4.3 | 3.9 | 3.3 | 4.5 | 0.8 | 6.4 | 0.6 | 4.8 | 4.4 | **4.2** | **3.8** |
| A2 | 4.4 | 4.4 | 8.3 | 7.9 | 7.7 | 5.4 | 7.9 | 3.4 | 2.6 | 2.5 | 8.6 | 6.4 | **5.8** | **4.6** |
| A3 | 14.8 | 14.7 | 16 | 18.1 | 16.9 | 16.3 | 19.3 | 18.5 | 19 | 14 | 15.6 | 17.3 | **17** | **3.5** |
| A4 | 8.5 | 7.9 | 10.7 | 6.5 | 7.3 | 8.3 | 8.4 | 9.6 | 9 | 8.2 | 9 | 9.5 | **8.6** | **2.2** |
| B1 | 12.7 | 15.3 | 17 | 16.1 | 16.6 | 19.3 | 16 | 14.3 | 12.8 | 16.1 | 17.8 | 18 | **16** | **4.0** |
| B2 | 22.7 | 24.9 | 27.6 | 26.9 | 27 | 24.9 | 25 | 30.8 | 31 | 27.9 | 28.2 | 25.1 | **27** | **5.0** |
| C1 | -1.2 | 4.3 | 4.4 | 4.9 | 1 | 2.8 | -2.2 | -0.9 | 1.3 | 3.7 | 4.5 | 3 | **2.1** | **5.0** |
| C2 | 3.9 | 5.4 | 5.5 | 7.1 | 4.5 | 3.9 | 8.9 | 4.2 | 5.1 | 2.4 | 5.3 | 6.7 | **5.2** | **3.4** |
| C3 | 4.1 | 7 | 4.1 | 5.3 | 5.5 | 4.9 | 10.2 | 5.9 | 8.1 | 6.1 | 9.9 | 10.6 | **6.8** | **4.7** |
| C4 | 3 | 2.3 | -0.6 | 0.3 | 0.5 | -1.9 | -0.6 | 3.6 | 2.7 | -0.5 | 2.5 | 0.7 | **1.0** | **3.5** |
| C5 | -0.3 | -1.1 | -2.3 | -1.8 | -2 | -3.9 | -1.3 | -3.9 | 2 | -3.4 | -0.5 | 0.9 | **-1.5** | **3.7** |
| D1 | 27.2 | - | 25.3 | 26 | 25.7 | 27.3 | 27.9 | 29.4 | 29.5 | 26.9 | 27.3 | 31.7 | **28** | **3.8** |
| D2 | 41.5 | 28.3 | 23.8 | 38.9 | 37.2 | 35.2 | 40.2 | 45.4 | 42.8 | 43.4 | 35 | 39.7 | **38** | **12.6** |
| D3 | 12.1 | 14.9 | 13.9 | 15 | 14.6 | 13.7 | 14 | 14.8 | 17 | 13.8 | 14 | 14.4 | **14** | **2.3** |
| D4 | 6.9 | 8.5 | 13.6 | 14.2 | 13.4 | 9.5 | 12.9 | 10.2 | 8.1 | 9.4 | 11.8 | 12.9 | **11** | **4.9** |
| D5 | 8.6 | 4.5 | 6.8 | 6.7 | 6.1 | 6.8 | 9.3 | 8.3 | 8.4 | 5.8 | 6.4 | 9.4 | **7.3** | **3.0** |

Table 6: $\delta^{11}B$ values (in ‰ vs. NBS951) measured with ICP-SFMS during ISONITRATE sampling campaign.

| $\delta^{11}B$ | 10/07 | 11/07 | 12/07 | 01/08 | 02/08 | 03/08 | 04/08 | 06/08 | 08/08 | 10/08 | 11/08 | mean | 2*σ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 3.9 | 3.3 | 3.3 | 3.8 | 3.1 | 3.1 | 1.6 | 2.3 | 3.1 | 4.0 | 3.9 | **3.2** | **1.4** |
| A2 | 3.4 | 4.3 | 6.4 | 6.3 | 6.1 | 6.1 | 5.2 | 3.9 | 3.4 | 5.3 | 6.1 | **5.1** | **2.4** |
| A3 | 16.7 | 16.4 | 16.3 | 17.7 | 17.2 | 17.2 | 17.7 | 17.4 | 15.6 | 17.7 | 16.9 | **17** | **1.3** |
| A4 | 9.0 | 8.8 | 8.0 | 8.8 | 9.2 | 9.8 | 8.9 | 10.1 | 7.1 | 10.1 | 10.6 | **9.1** | **2.0** |
| B1 | 12.4 | 18.2 | 18.6 | 18.8 | 19.3 | 21.5 | 17.2 | 16.0 | 11.9 | 21.7 | 22.3 | **18** | **6.9** |
| B2 | 28.6 | 30.9 | 31.7 | 28.3 | 31.0 | 29.7 | 31.1 | 34.3 | 31.9 | 34.1 | 34.6 | **32** | **4.3** |
| C1 | -0.4 | 3.3 | 2.9 | 3.2 | 1.1 | 1.9 | 1.0 | 1.9 | 1.1 | 4.7 | 3.6 | **2.2** | **2.9** |
| C2 | 4.1 | 4.6 | 3.7 | 3.4 | 2.6 | 3.8 | 3.4 | 2.6 | 4.5 | 4.3 | 3.0 | **3.6** | **1.4** |
| C3 | 4.2 | 3.8 | 4.0 | 4.2 | 4.5 | 4.1 | 4.1 | 4.2 | 4.7 | 6.0 | 6.4 | **4.6** | **1.7** |
| C4 | -1.3 | -1.6 | -1.5 | -1.7 | -1.4 | -2.1 | -2.0 | -0.4 | -1.4 | 0.1 | 0.2 | **-1.2** | **1.6** |
| C5 | -2.8 | -3.4 | -3.7 | -4.1 | -4.2 | -5.3 | -5.3 | -3.9 | -3.0 | -1.0 | -1.1 | **-3.4** | **2.9** |
| D1 | - | - | 27.5 | 26.7 | 29.8 | 30.2 | 25.4 | 30.6 | 30.9 | 31.2 | 32.4 | **29** | **4.7** |
| D2 | 42.0 | 27.4 | 20.8 | 38.9 | 40.4 | 36.1 | 39.4 | 44.1 | 44.1 | 44.5 | 33.1 | **37** | **15.1** |
| D3 | 13.3 | 13.2 | 13.5 | 13.3 | 13.0 | 13.5 | 13.5 | 13.8 | 14.0 | 14.7 | 14.9 | **14** | **1.2** |
| D4 | - | 11.2 | 14.7 | 12.6 | 11.2 | 11.7 | 11.6 | 10.4 | 9.9 | 12.8 | 14.1 | **12** | **3.1** |
| D5 | 6.5 | 6.5 | 6.4 | 7.1 | 7.1 | 6.6 | 7.2 | 7.7 | 7.3 | 7.8 | 7.5 | **7.1** | **1.0** |

Table 7: $\delta^{11}B$ values (in ‰ vs. NBS951) measured with TIMS during ISONITRATE sampling campaign.

There is a positive linear relation between the $\delta^{11}B$ values measured by the two methods (figure 3, y = 0.90x + 0.86) with a high correlation coefficient ($r$ = 0.98).

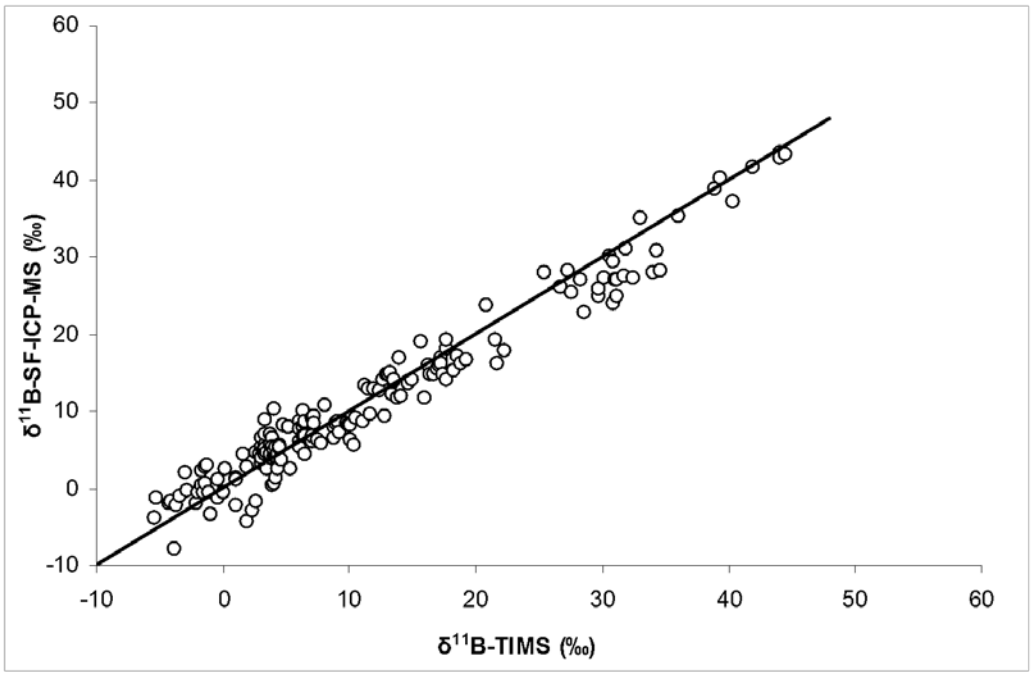



Figure 3: Relation between $\delta^{11}B$ determined by both TIMS and ICP-SFMS for all water samples. The solid line represents the 1:1 line (y=x), calculated linear regression equation is y=0.90x+0.86 (r=0.98, n=176).

The average difference in $\delta^{11}B$ values measured by TIMS and ICP-SFMS is -0.3‰ (figure 4) and there is no tendency for the difference to vary with variation of isotope ratios. The Kolmogorov-Smirnov normality test showed that differences of the $\delta^{11}B$ as determined by TIMS and ICP-SFMS (p = 0.23) were normally distributed. The limits of agreement within which 95% of the differences are expected are calculated according to the Bland-Altman technique as -5.4 and +4.8‰.

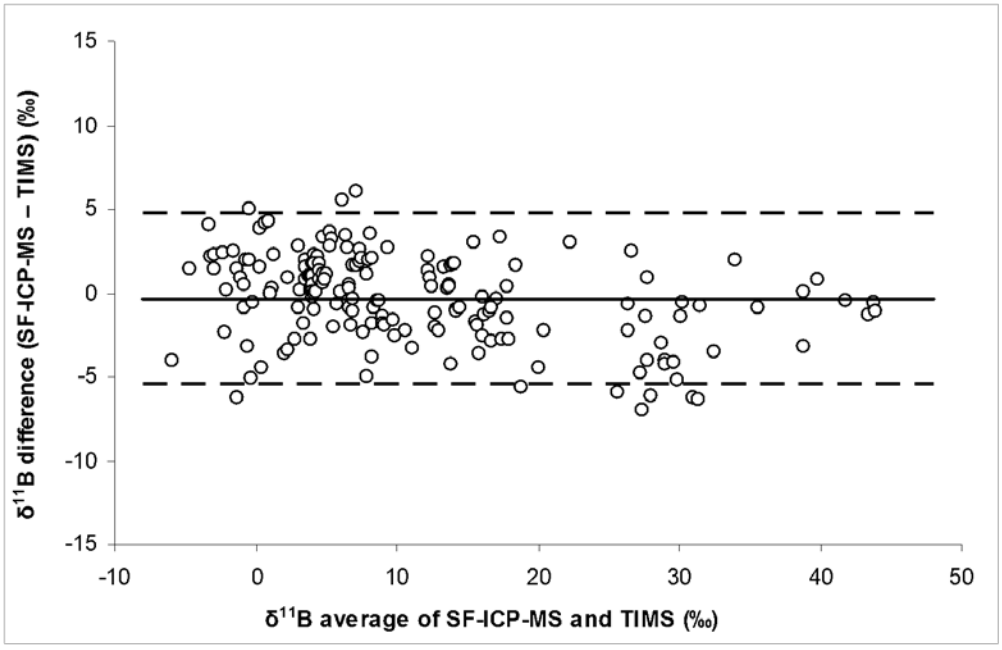



Figure 4: Bland-Altman comparison of the TIMS and ICP-SFMS $\delta^{11}B$ determinations of water samples collected during the ISONITRATE project. The solid line represents the average difference between both methods, while the dashed lines represent the 95% limits of agreement.

However, for the 3 locations with a boron concentration less than 5 µg $L^{-1}$ (B1, B2 and D1), the difference in $\delta^{11}B$ values measured by TIMS and ICP-SFMS are significantly larger (see tables 6 and 7),

which indicates that there is a tendency for the difference to vary with (low) boron concentration. Further study of the $\delta^{11}B$ value measured by ICP-SFMS is needed to attribute these observed differences to the influence of the matrix and/or the boron concentration level.

The consequences of the difference in analytical precision of $\delta^{11}B$ measurements with TIMS and ICP-SFMS with respect to the interpretation to distinguish nitrate sources, is discussed for the complex case (C1-C5) and the denitrification case (D1-D5).

*Complex case*

In figure 5 (left), the $\delta^{11}B$ values measured with TIMS versus 1/B for the water samples collected at the complex case are compared to the ranges measured for local nitrate pollution sources.

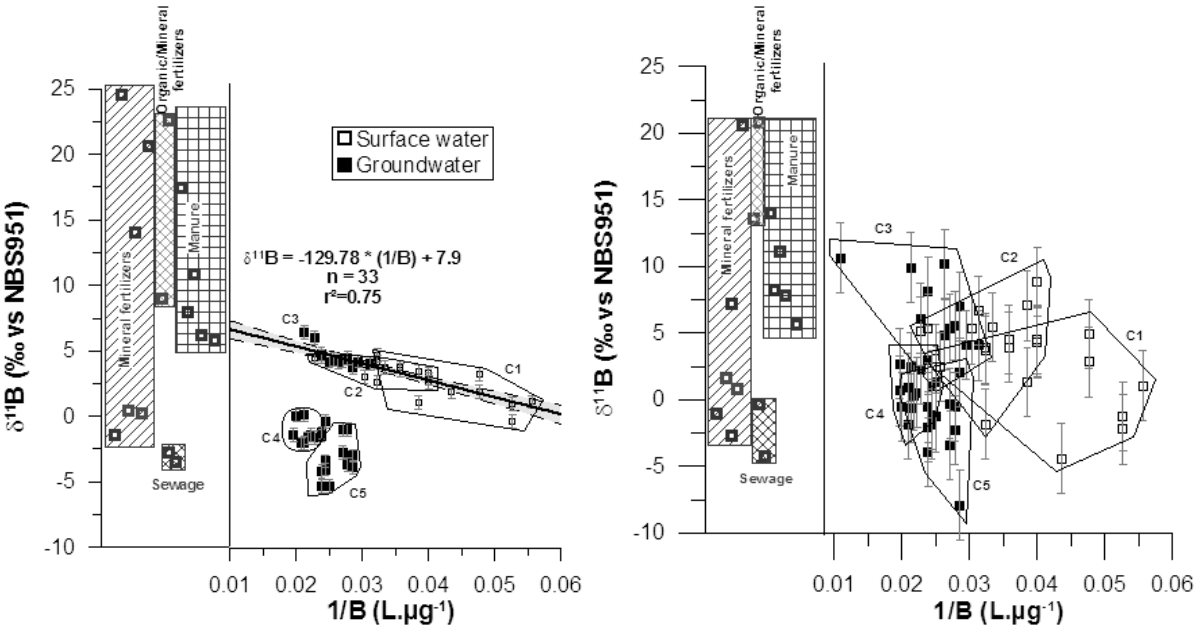



Figure 5: Comparison of the identification of sources of nitrate pollution by coupling the reciprocal of B content and $\delta^{11}B$ values of the water samples from the multiple sources case study. The boxes on the left represent the range of the measured $\delta^{11}B$ values of the different nitrate pollution sources. $\delta^{11}B$ vales are determined by TIMS (left) and ICP-SFMS (right) (error bars represent the 95 % confidence limits).

Based on the TIMS results, surface waters (C1 and C2) together with groundwater C3 yield similar $\delta^{11}B$ values, slightly positive ($\delta^{11}B$ = 2 to 6‰), whereas both C4 and C5 (groundwaters) were depleted in $\delta^{11}B$. When plotting $\delta^{11}B$ versus 1/B, three different scenarios appear: (i) samples C1, C2 and C3 define a negative trend according to $\delta^{11}B = -129.8 * (1/B) + 7.9$ (n = 33, $R^2$=0.75).

This trend characterises potentially the input of an organic fertilizer (with a $\delta^{11}B$ around 8 ‰), in agreement with the local measured manures and the $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ data;[26] (ii) C4 samples present a very homogeneous signature over the hydrological cycle.

This sampling site is affected by mineral fertilizer/wastewater, with wastewater being probably more realistic considering the depleted $\delta^{11}B$ of the pollution source ($\delta^{11}B$~ -6 ‰) and the characterization of the local sources (table 8); (iii) C5 samples present the most negative $\delta^{11}B$ signatures, in agreement with the signatures of the WWTP effluents (locally identified).[4]

| | | | B | $\delta^{11}B$ (TIMS) | $\delta^{11}B$ (ICP-SFMS) |
|---|---|---|---|---|---|
| **Name** | **Type** | **Sampling location** | **µg $L^{-1}$** | **‰** | **‰** |
| NPK 14-7-17 | Mineral fertilizer | Single source of $NO_3$ | 13900 | 0.2 | 0.8 |
| NPK 15-5-20 | Mineral fertilizer | | 14400 | 0.4 | 1.6 |
| Fumeterre | Organic/mineral fertilizer | | 380 | 9 | 13.6 |
| Orgaveg | Organic/mineral fertilizer | | 1300 | 22.6 | 20.8 |
| Ammonium nitrate 27% | Mineral fertilizer | Multiple sources of $NO_3$ | 20 | -1.4 | -1 |
| NPK 13-13-21 | Mineral fertilizer | | - | 24.6 | - |
| NPK 18-46 | Mineral fertilizer | | - | 14.1 | - |
| Urea 46% | Mineral fertilizer | | 70 | 20.6 | 20.6 |
| Cow manure | Organic fertilizer | | 150 | 10.9 | 11.1 |
| Cow manure | Organic fertilizer | | 290 | 6.2 | 7.8 |
| Cow manure - liquid | Organic fertilizer | | 130 | 5.8 | 5.7 |
| Horse manure | Organic fertilizer | | 220 | 17.4 | 14 |
| WWTP - dry mud | WWTP - dry mud | | 220 | -3.5 | -4.2 |
| WWTP effluent | WWTP-effluent | | 130 | -2.8 | -0.3 |
| Ammonium nitrate 27% | Mineral fertilizer | Natural Denitrification | 30 | - | -2.7 |
| NPK 14-8-13 | Mineral fertilizer | | 2700 | - | 7.2 |
| Cow manure | Organic fertilizer | | 410 | 8 | 8.2 |

Table 8: Comparison of $\delta^{11}B$ (in ‰ vs. NBS951) values measured by both TIMS and ICP-SFMS on leachates from $NO_3$ sources.

Based on the ICP-SFMS measurements as shown in figure 5 (right) a negative trend according to $\delta^{11}B = -195.8 * (1/B) + 10.8$ (n = 33) with a worse correlation ($R^2 = 0.34$) is found. The results are visually more scattered and there is overlap between the C3, C4 and C5 measurement areas. In contrast to the TIMS data, no trend to a distinct potential nitrate pollution source can be characterized.

These findings illustrate that end-users have to keep in mind that retrieving precise information on the identification of pollution sources from $\delta^{11}B$ values requires reaching the best precision and accuracy possible.

*Denitrification case*

On the other hand, as presented in figure 6 for the denitrification case, both analytical methods come to a same conclusion when trying to decipher contributions between sources with really distinct $\delta^{11}B$ signatures: (i) the signature of D1 values centred around 30‰, close to the value expected for boron from natural rainwater origin; (ii) D2 (*i.e.*, the samples with the highest $NO_3$ concentrations, presumed to represent the closest agreement with the input of pollution source), displays large $\delta^{11}B$ variations (from 20 to more than 40‰) together with large variation of boron concentrations (14 to 27 µg $L^{-1}$). D2 reaches values that are higher (> 40‰) than all the measured pollution sources. In the light of the available results it is not possible to conclude if other nitrate sources are present or other processes occur (*i.e.*, interactions with clay minerals); (iii) D3 to D5 display intermediate boron isotopic compositions ($5<\delta^{11}B<15$‰) that may correspond to the mixing of different pollutions sources including mineral fertilizer, manure and sewage.

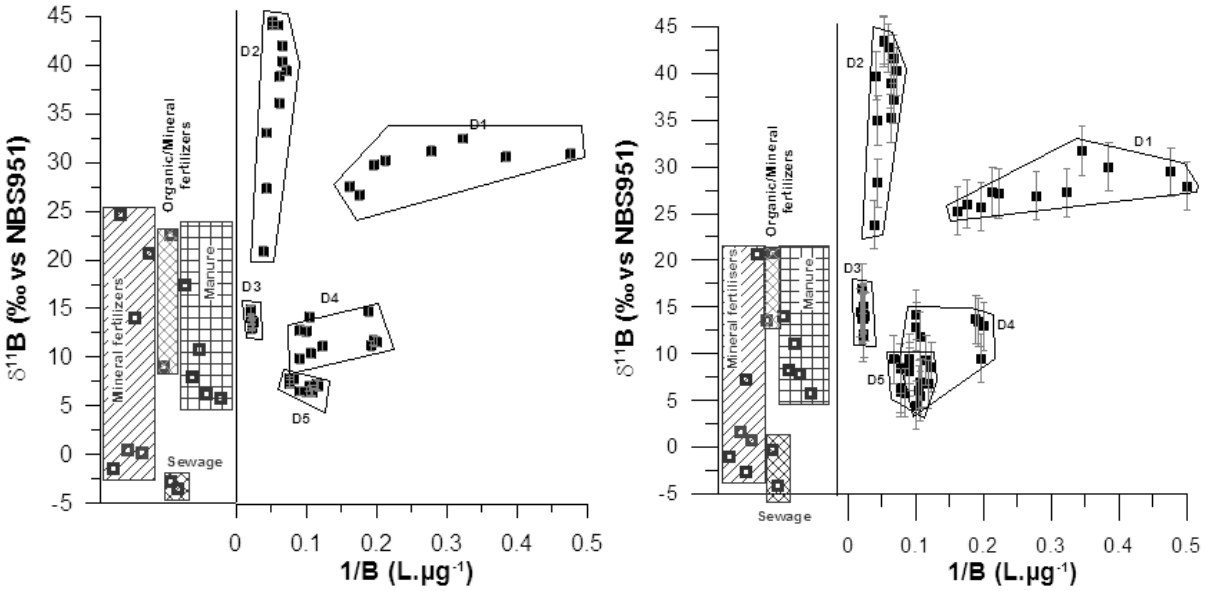



Figure 6: Comparison of the identification of sources of nitrate pollution by coupling the reciprocal of B content and $\delta^{11}B$ values of the water samples from the natural denitrification case study. The boxes on the left represent the range of the measured $\delta^{11}B$ values of the different nitrate pollution sources. $\delta^{11}B$ vales are determined by TIMS (left) and ICP-SFMS (right) (error bars represent the 95 % confidence limits).



**Comparison $\delta^{11}B$ measurement ICP-SFMS and TIMS on source material**

Table 8 shows comparable results between $\delta^{11}B$ values measured with TIMS and ICP-SFMS on the leachates of the different pollution sources (correlation coefficient of 0.96, y = 0.88 x + 1.10; due to limited results (n = 13) no further Bland-Altman statistics were performed). The extracted boron and nitrate contents (table 5) are in line with previous reported results on manure and mineral fertilizers.[31,32] These results show the method robustness and the ease of using one single ICP-SFMS method for $\delta^{11}B$ measurements of both water samples and leachates of the source materials.

An overview of literature data of $\delta^{11}B$ in combination with the data of source materials collected during the ISONITRATE project are summarised in figure 1. The measured $\delta^{11}B$ values are in agreement with previous published data, but it should be stressed that for interpretation of the multi-isotopic approach accurate and precise $\delta^{11}B$ data of local source materials need to be included in the monitoring program. As an example the mineral fertiliser NPK 13-13-21, collected in the multiple sources of nitrate case, showed based on literature unexpected high $\delta^{11}B$ value (NPK 13-13-21 : $\delta^{11}B$ = + 24.6; table 8). This may indicate that the origin of boron in this specific mineral fertiliser material is different than previously measured mineral fertilisers.

## Conclusions

During the last decade, the number of isotope systems currently being explored in new investigations and (routine) application fields has exploded. As both the number of techniques being developed and the number of laboratories making these measurements increase, it is important to evaluate the fit-for-purpose of measurement techniques for (routine) application.

An evaluation of boron isotope compositions measured in parallel by both ICP-SFMS and TIMS was performed in the ISONITRATE project. Based on the results of the different case studies it is shown that end-users have to keep in mind that retrieving precise information on the identification of pollution

sources from $\delta^{11}B$ values requires reaching the best analytical precision and accuracy possible. However for some cases, *e.g.,* trying to decipher contributions between sources with really distinct $\delta^{11}B$ signatures, ICP-SFMS has shown to come to the same conclusions. The ease of use, rapidity and availability of ICP-SFMS on the one hand and the observed variability in $\delta^{11}B$ in ground- and surface water on the other demonstrates that using ICP-SFMS as isotopic screening method would promote the use of isotopic methodology in WFD monitoring programs.

**Acknowledgements**
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## 4.4. SUMMARY AND CONCLUSION

The versatility of ICP-MS instruments in investigative environmental monitoring was demonstrated in this chapter, in which the possibility to determine isotope ratios in different environment-related application fields is discussed. Isotope ratio measurement, especially in the case of isotope dilution used as a primary method for the determination of trace element concentrations, has always strongly been linked to measurement uncertainty and metrology.

In the context of this dissertation, single-collector ICP-mass spectrometers were used for isotope ratio measurements. With the attainable precision of a quadrupole-based ICP-MS instrument, tracer studies have been successfully performed to study the cadmium transport from the soil surface through the unsaturated zone into the groundwater. Also a full uncertainty calculation was performed according to the principles of the *ISO Guide to the Expression of Uncertainty in Measurement,* giving an overview of the uncertainty sources in the quantitative determination of tracer and natural cadmium by ICP-MS. The significant contribution of the signal instability, caused by the clogging of the sampling cone by calcium salts, to the total uncertainty can be reduced nowadays. Recently, some instrument manufacturers offer not one type, but a series of sampling cones, more dedicated to the type of analysis, *e.g.*, highest sensitivity versus higher matrix tolerance.

In the context of environmental forensics and to enhance the understanding of $NO_3^-$ pollution in groundwater, a single-collector sector-field ICP-MS instrument was used for the determination of $\delta^{11}B$, considered as a co-migrant of nitrate, in ground and surface water. In Flanders, more than 2000 groundwater and 4000 surface monitoring stations control the nitrate content on a regular basis. Because of these high frequency monitoring requirements, the Water Framework Directive implementation has triggered the use of screening methodologies in particular for the detection of accidental pollution or the control of water bodies at risk. The observed variability in $\delta^{11}B$ in ground- and surface water ($\delta^{11}B$ values ranging from – 3 to + 32 ‰ vs. NBS951), demonstrates that using ICP-SFMS as an isotopic screening method could promote the use of isotopic methodology in WFD monitoring programs. When interpreting isotopic data and supplementary to the measurement uncertainty, a degree of uncertainty exists due to (temporal) variability of nitrate sources, variation in water flow regimes, mixing of nitrate sources and denitrification. Still, the introduction of a more holistic approach in the current $NO_3^-$ monitoring by using isotopic methodology, could be beneficial and complementary in investigative monitoring of water bodies at risk.

During the past decade, multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) has replaced TIMS to a large extent for accurate and high-precision determination of isotope ratios and the technique is now deployed in various contexts [161]. The success of MC-ICP-MS is not only a result of its higher sample throughput (compared to TIMS), but also its slightly higher matrix tolerance and its capability to analyze elements with a high ionization energy (*e.g.*, B (8.3 eV)). However, MC-ICP-MS suffers from an important disadvantage, *i.e.,* instrumental mass discrimination, indicating that the heavier of any two isotopes is transported more efficiently than the lighter one. Preferably, “matrix-free” solutions of the target element are deployed. For samples, the target element is typically isolated from the concomitant matrix via chromatography. Current purification protocols require manually feeding separation columns, a process that can be time-consuming. However, also here automated, low-pressure ion exchange chromatography systems that can process samples in unattended operation are commercially available (*i.e.*, prepFAST-MC™).

# CHAPTER 5 SUMMARY AND CONCLUSIONS

The analytical methods described in this dissertation endorse that ICP-MS units are nowadays reliable, robust and high-throughput instrumentation, ideally suited for the determination, speciation and isotopic analysis of metals and oxy-anions in an environmental context.

The versatility of ICP-MS units as (i) environmental regulatory monitoring tool for the determination of major and trace elements, (ii) elemental-specific detector in the context of hyphenation with different separation techniques and (iii) mass spectrometer for the determination of isotope ratios are summarised below.

## → ICP-MS applications in environmental regulatory monitoring

A clean, healthy and diverse environment is a prerequisite for prosperity and well-being for everyone and this can only be achieved through a common framework. This common framework is needed in order to assure that environmental pollution, no matter where it comes from, is assessed in the same way across national or even regional borders. At a European level, major legal acts include the Water Framework Directive, the Waste Framework Directive, the Air Quality Directive and the upcoming Soil Framework Directive and all of these include monitoring programs to report on the state of our environment. However, the best legal provisions will not be successful if they are not implemented and this is the prime responsibility of the member states.

Since 1980, the management of the environment became a task for the regions (Flemish, Walloon and Brussels Capital Region) in Belgium. The last 30 years, different Flemish regulations for the protection of our environment have been implemented. The last years, this legislation was amended many times, mostly under the influence of new European environmental legislation. Currently, a shift from “environmental protection” to “environmental sustainability” is being introduced. Implementing a more sustainable approach to the consumption and production of chemicals would not only benefit Europe's environment but also reduce the detrimental effects arising in other parts of the world (*e.g.*, caused by electronic waste).

As 1980 is also the official birth year of ICP-MS, the link between the emergence of environmental legislation dedicated to *heavy metals* and the emergence of ICP-MS in environmental analysis is discussed in the first chapter of this dissertation.

Along with the implementation of regulatory monitoring requirements in the different European member states, the use of analytical methods developed by the European Committee for Standardization (CEN) was recommended. With common analytical European standards (EN) in all these countries and every conflicting national standard withdrawn, comparison between analytical results should become more feasible.

A beneficial side-effect, taking into account that since 1980 the management of the environment in Belgium became a task for the regions, is that the European environmental regulatory monitoring requirements not only triggered a harmonisation in the different European member states but also led to a “rapprochement” in the internal Belgian situation. With a witticism, one could say that the Belgian regions were forced by the different EU directives to unify the decision-making process in

environmental issues. Still, structural consultation between the regions in this respect would be desirable.

The introduction of ICP-MS under impulse of standards developed by the European Committee for Standardization (CEN) is in environmental regulatory monitoring of elements undoubtedly the most important advance of the last decade. Because of the availability of ICP-MS instruments nowadays, it can be argued that the main hindrance to the implementation of the European monitoring requirements is not the technical feasibility of analysis at these concentration levels, but rather potential contamination during sampling, sample storage, sample handling and analysis. Two additional comments with respect to a harmonised implementation of the European monitoring requirements may be formulated at this point. First, as for most monitoring techniques, results obtained are operationally-defined. The protocol, *e.g.,* acid digestion, 0.45 µm filtration*, ...* defines the answer, and while this may facilitate comparability of results acquired across Europe, data generated may have little relevance to bioavailable metal concentration. Second, more harmonization in communication and reporting of our chemical environmental status between member states is needed to compare regulatory monitoring data on a European scale, *e.g*., choice of sampling locations (rural versus industrial) and type of sample (biota versus water column).

As a case study and for the first time, ranges of background concentration of *heavy metals* were summarised for all environmental compartments in Flanders based on European Standards on the one hand and on a selection of (non-polluted) background locations on the other. The focus in chapter 2 of the dissertation is on the analysis (of acid digests) of environmental samples by ICP-MS, used for multi-elemental determination of elements. The range of background concentrations, derived from existing Flemish regulatory monitoring databases, illustrate *a match made in heaven* with the sensitivity of ICP-MS instruments.

The range of background concentrations of elements, derived and compiled in this PhD dissertation, can be considered as an indicator of the current “natural” chemical status of the Flemish environment and can be used to assess future anthropogenic influences within an EU regulatory monitoring context. However, as *heavy metals* do not disappear, but rather disperse from one environmental compartment to another, the chemical nature and quantity of the relevant element species in a matrix, its physical and chemical association, rather than the (pseudo) total element concentration is governing the mobility, bioavailability and, finally, the ecotoxicological or toxicological impact of that element. Therefore, only knowledge on speciation provides sufficient information for environmental risk assessment and this represents the subject of the analytical research papers described in chapter 3.

### → Determination of oxy-anions in water and solid samples

In this dissertation, speciation applications have been designed to determine chromate in solid materials, selenate and selenite in waste water and bromate in drinking water. All of the applications were driven by European legislation, *i.e.,* the restriction of hexavalent chromium in electrical and electronic equipment brought onto the European market, removal of oxy-anions from wastewater to ensure compliance with European environmental quality parameters and the control of the maximum level of carcinogenic disinfection by-products in European drinking water monitoring programs.

The efforts to set up an HPLC/ICP-MS system in the year 2000 for the speciation of selenium were mainly devoted to the automation and a proper communication interface between the sample injection system, the HPLC pump and the ICP-MS instrument. Ten years later and with the availability of a low pressure LC system, speciation analysis can be implemented easily on any ICP-MS

instrument and this was demonstrated for the determination of bromate in drinking water. Nowadays, LC/ICP-MS can truly be considered widespread sensitive and versatile speciation instrumentation.

Speciation is also increasingly being involved in multi-disciplinary approaches using so-called *orthogonal speciation schemes (e.g.,* ESI-MS and HPLC/ICP-MS) for (complex) species identification and/or quantification (*e.g.*, metallomics, pharmaceutical substances). Recent advances in this field, includes front-end modifications (*e.g*., micro nebulizers) to adapt the ICP-MS instrument to the low flow rates (~ µl $min^{-1}$) and/or high organic content solutions delivered by the LC system and the use of reaction cells to chemically resolve polyatomic interferences from the element of interest (e.g., $SeO^{+}$).

Quality control and quality assurance programs carried out along these speciation research projects are of utmost importance, *e.g*., control of the level of oxidation of Cr(III). Correction for the species interconversion observed remains ambiguous when the chemical form of the species present in the sample (*e.g*., $FeCr_2O_4$) is different from the added spike (*e.g*., $Cr(NO_3)_3.9H_2O$). On the other hand, knowledge of the method-induced interconversion is particularly relevant for the determination of Cr(VI) in ambient particulate matter ($PM_{10}$) as the level of observed Cr(III) oxidation is within the range of the level of monitored Cr(VI) and could lead to false positives exceeding of the air quality guideline value. It is conceivable that XANES spectroscopy can serve as a benchmark for improvements or modifications to wet chemistry extraction methods.

While the relevance of elemental speciation in regulatory monitoring is not at stake, why is elemental speciation not done routinely with LC/ICP-MS in analytical laboratories? First, European Directives and legislation about elemental speciation are to a great extent still missing with the exception of those for a few species (*e.g.,* Cr(VI), organotin compounds, methylmercury) and therefore, routine laboratories lack the incentive to invest in the technologies. Second, for the determination of some species, *e.g.,* bromate, alternative cheap methods (as compared to LC/ICP-MS) are available for monitoring at the concentration level of the regulatory limit value. Third, the assumption of monitoring in a regulatory context is that only one or a few constituents of a sample - usually the analytes of interest - play a role in the measurement that is obtained. When applying standardized procedures in routine, users tend to have as little concern as possible about what other species in the sample might yield a false response or whether the method is applicable to all samples in the measurement run. However, and especially for solid samples, elemental speciation analysis is not considered as a course of actions to always be followed and interpreted in the same way. These restrictions have often led to the current pragmatic approach in elemental speciation in regulatory context, *i.e.,* only in case the total concentration is above the limit value, an elemental speciation analysis is performed.

### → Tracer experiments with stable isotopes in environmental studies and use of natural isotopic variation as a proxy

The versatility of ICP-MS instruments in investigative environmental monitoring is further demonstrated in chapter 4, in which the possibility to determine isotope ratios in different environment-related application fields is discussed. Isotope ratio measurement, especially in the case of isotope dilution used as a primary method for the determination of trace element concentrations, has always strongly been linked to measurement uncertainty and metrology. Nowadays, the level of required precision and accuracy will guide to the technique to be used (quadrupole based ICP-MS, ICP-SFMS or MC-ICP-MS) or conversely the available instrumentation will tell which environmental applications are within reach. During the past decade, MC-ICP-MS has replaced TIMS to a large extent for accurate and high-precision determination of isotope ratios and the technique is now

deployed in various contexts (*e.g.*, geochronology, study of a large variety of geochemical phenomena and provenance determination).

In the context of this dissertation, single-collector ICP-mass spectrometers were used for isotope ratio measurements. With the attainable precision of a quadrupole-based ICP-MS instrument, tracer studies have been successfully performed to study the cadmium transport from the soil surface through the unsaturated zone into the groundwater. Also a full uncertainty calculation was performed according to the principles of the *ISO Guide to the Expression of Uncertainty in Measurement,* giving an overview of the uncertainty sources in the quantitative determination of tracer and natural cadmium by ICP-MS.

While metrology has always been an asset to analytical chemistry, end-users of analytical data still have ambiguous relations to the concept of measurement uncertainty and how to deal with it. Often, so-called *significantly* higher levels have been reported in (bio-)monitoring studies, without considering the issue of uncertainty. Reporting estimates of measurement uncertainty is the prime responsibility of the analyst and should trigger the end-user to use and interpret this information properly. Also, the translation and interpretation of probabilistic data (analytical data) into boolean data (yes/no) is still a main challenge in an environmental regulatory context.

In the context of environmental forensics and to enhance the understanding of $NO_3^-$ pollution in groundwater, a single-collector sector-field ICP-MS instrument was used for the determination of $\delta^{11}B$, considered as a co-migrant of nitrate, in ground and surface water. In Flanders, more than 2000 groundwater and 4000 surface monitoring stations control the nitrate content on a regular basis. Because of these high frequency monitoring requirements, the Water Framework Directive implementation has triggered the use of screening methodologies in particular for the detection of accidental pollution or the control of water bodies at risk. The observed variability in $\delta^{11}B$ in ground- and surface water ($\delta^{11}B$ values ranging from – 3 to + 32 ‰ vs. NBS951), demonstrates that using ICP-SFMS as an isotopic screening method could promote the use of isotopic methodology in WFD monitoring programs. When interpreting isotopic data and supplementary to the measurement uncertainty, a degree of uncertainty exists due to (temporal) variability of nitrate sources, variation in water flow regimes, mixing of nitrate sources and denitrification. Still, the introduction of a more holistic approach in the current $NO_3^-$ monitoring by using isotopic methodology, could be beneficial and complementary in investigative monitoring of water bodies at risk.

### → Recommendations for future research

Since its introduction in 1980, ICP-MS evolved from a lab-built instrument to a family of commercially available analytical techniques, ranging from single collector quadrupole mass filter units (ICP-QMS) to single-collector and multi-collector sector-field based ICP-MS instruments with high mass resolution capabilities. The introduction of ICP-MS not only triggered new research opportunities in the field of environmental, geochemical and life sciences, but also initiated further improvements in the analytical workflow and front-end modifications. The following recommendations are delineated for future research and activities linked to ICP-MS in an environmental context:

- The **panoramic analysis capabilities** of ICP-MS are not yet fully exploited with respect to its linear dynamic range and multi-element capabilities. The determination of *heavy metals* in environmental monitoring has traditionally focused on a relative small number of elements (*e.g.*, As, Cd, Pb, Hg), but it is to be expected that future regulatory monitoring will include more elements (holistic approach) and that the panoramic analysis capabilities of ICP-MS will be further exploited. This is also being stimulated in sustainable material management, for which knowledge on the presence of (economically) critical elements (*e.g.*, rare earth and platina-group elements) in (contaminated) solid materials are of potential interest.

- New or innovative approaches in the **(on-line)-automation** of the labor-intensive steps of sample digestion, preparation of calibration standards, dilution of samples and the addition of internal standards. Further improvements in the analytical workflow (*e.g.*, contamination), front-end modifications (*e.g.,* on-line sample preparation automation) and sample introduction systems are needed. Automation is not only considered as a *time-saving* operation (cost price), but also as a *time-gaining* opportunity for the analyst to process (expert judgement) the raw data (quality).
- ICP-MS is increasingly being involved in **multi-disciplinary approaches** for (complex) species identification and/or quantification. Further research in the field of speciation includes front-end modifications (*e.g.*, micro and capillary nebulizers) to adapt the ICP-MS instrument to the low flow rates and/or high organic content solutions delivered by LC systems. With respect to possible species interconversion, multi-disciplinary approaches, *e.g.*, using XANES are needed to evaluate the performance of wet chemistry extraction methods for the determination of species in solid samples. To separate, detect and quantitate engineered nanoparticles (ENPs) – emerging contaminants – in environmental matrices, field-flow fractionation, a size-separation technique, shows a great deal of promise when coupled to ICP-MS.
- Further instrumental innovation, with focus on **reliable and robust ICP-MS instrumentation,** in combination with *blue economy principles* by*, e.g.*, reducing/eliminating combustible gas usage, power consumption (create solutions that are both environmentally beneficial and which have financial benefits). Additionally, innovation in ultra-fast electronics can provide advantages in the collection of more data per unit of time (*e.g.*, single-particle inductively coupled plasma–mass spectrometry).
- New developments in (cheap) clean room facilities and workflows (including sampling), combined with higher purity demands for reagents and recipients are needed to fully exploit the instrumental **detection limits** attainable by ICP-MS.
- Optimising the balance between **analytical management and analytical quality** in a high-throughput laboratory. An inverse relationship is being created in high-throughput environmental laboratories between standardization and accreditation on the one hand and understanding and knowledge of the analytical measurement within the context of the sample on the other. *Where is the wisdom we have lost in knowledge? Where is the knowledge we have lost in information?* is changing to *Where is the time to acknowledge the information ?*
- **Communication** and **knowledge exchange** among laboratories/scientists and policy-makers on the translation of the analytical regulatory needs and the scientific capabilities/boundaries. Especially in the case of **passive samplers** to become a standard inventory in the toolbox for regulatory monitoring, the remaining obstacles to a more widespread adoption lay in communicating the knowledge produced by the scientific community to the intended audience of policy makers, managers and operational staff, who administrate and execute regulatory monitoring programs.

The (inorganic) analytical team at Vito anno 2000.

The analytical team at Vito anno 2013.

The biennial meetings at the European Winter Conference with Martin Resano and Frank Vanhaecke (Zaragoza, Spain, 2011).

# References

For the scientific papers, the reference lists are provided separately at the end of each paper:

- p. 84, Characterization of inorganic selenium species by ion chromatography with ICP-MS detection in microbial-treated industrial waste water.
- p. 106, Determination of hexavalent chromium by species-specific isotope dilution mass spectrometry and ion chromatography-1,5-diphenylcarbazide spectrophotometry.
- p. 127, Validation of a European Standard for the determination of hexavalent chromium in solid waste material.
- p. 148, Determination of hexavalent chromium in ambient air: a story of method-induced Cr(III) oxidation?
- p. 165, Determination of bromate in drinking waters using low pressure liquid chromatography / ICP-MS.
- p. 193, Full uncertainty calculation on quantitative determination of tracer and natural cadmium in soil column effluents with ICP-MS.
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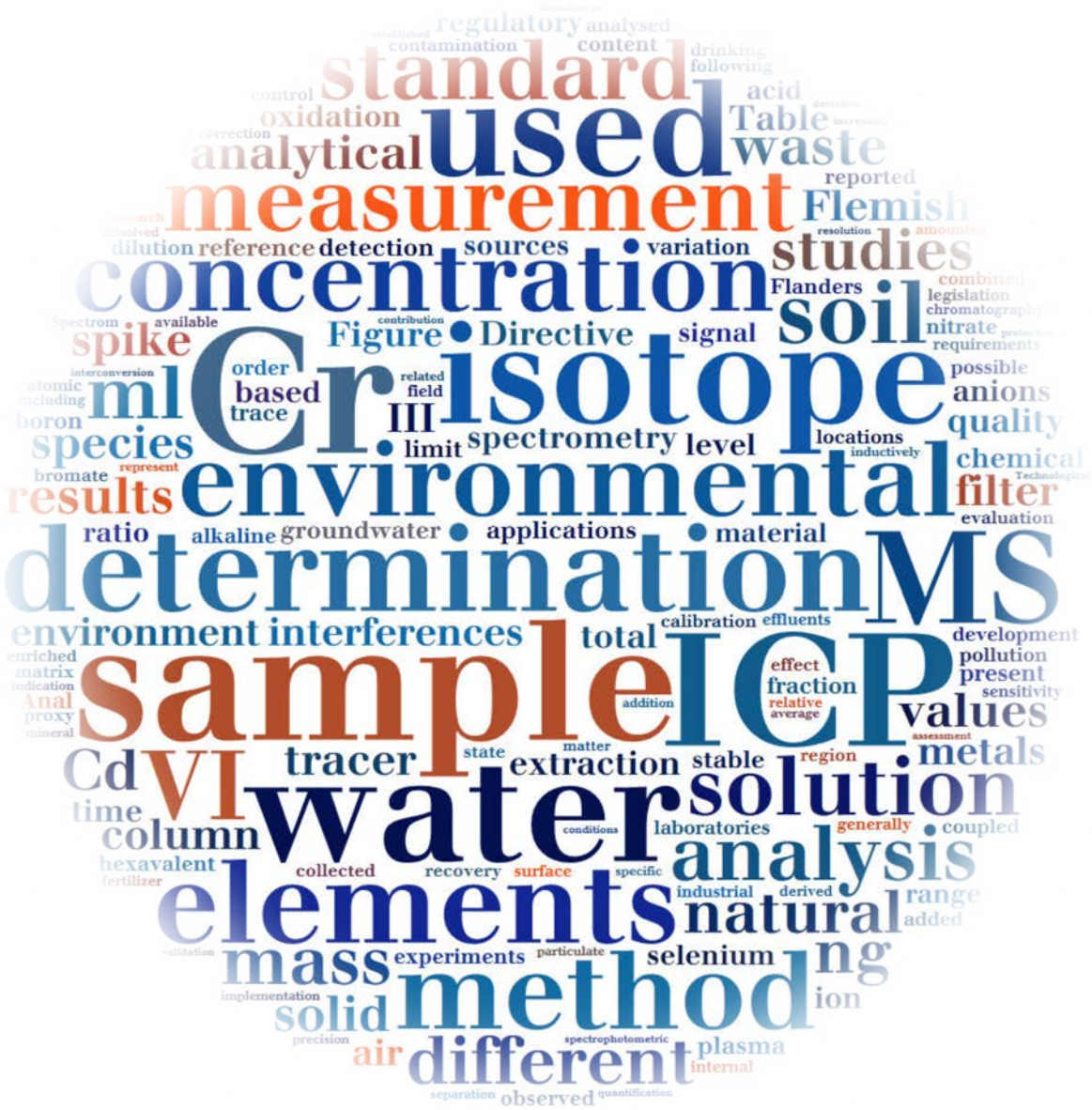


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