A review on sequential injection methods for water analysis

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A B S T R A C T

The development of fast, automatic and less expensive methods of analysis has always been the main aim of flow methodologies. The search for new procedures that still maintain the reliability and accuracy of the reference procedures is an ever growing challenge. New requirements are continually added to analytical methodologies, such as lower consumption of samples and reagents, miniaturisation and portability of the equipment, computer interfaces for full decision systems and so on. Therefore, the development of flow methodologies meeting the extra requirements of water analysis is a challenging work.

Sequential injection analysis (SIA) presents a set of characteristics that make it highly suitable for water analysis. With sequential injection analysis, most routine determinations in waters can be performed more quickly with much lower reagent consumption when compared to reference procedures. Additionally, SIA can be a valuable tool for analyte speciation and multiparametric analysis. This paper critically reviews the overall work in this area.

Introduction

Water is an essential resource that is being threatened by pollution; therefore, the monitoring of water quality has become an issue of vital importance. The European Union has created the Water Framework Directive (WFD) in order to improve, protect and

prevent further deterioration of water quality across Europe [1]. Accurate and frequent monitoring of water quality enables tighter control of the governmental regulations which is an important step in the reduction of the water pollution. It is estimated that, in European surface waters, the impact of pollution caused by industrial discharges of toxic substances has decreased 70% over the past 30 years [2]. This reduction has resulted from the implementation of stricter governmental regulations as much as the development of cleaner technologies.

The term "water" used in WFD includes most types of water, i.e. ground, surface and coastal waters. Several "water quality elements" are covered such as:

- Physicochemical properties – temperature, density, colour, turbidity, pH value, redox potential, conductivity, surface tension, suspended solids, total/dissolved organic carbon;
- Hydromorphological status – erosion and bench river characteristics;
- Biological – distribution and composition of the species and biological effects;
- Chemical monitoring – with particular emphasis on the contaminants in the list of priority pollutants.

Changes in water composition can be an indicator of pollution or contamination, so frequent water analysis is imperative. Some parameters are under strict regulation because of their risk to human health while others are not subject to enforceable regulation as they only cause visual or aesthetic effects [3]. More recently, the public concern for water safety has led to an increase on the use of disinfectants, which in turn has become a problem itself, if the carcinogenic by-products generated by the disinfectants are considered. Nevertheless, water disinfection is essential to ensure public health. Disinfectants prevent water contamination by bacteria but if in excess are harmful to human health, both directly and through by-products. In the last Analytical Chemistry biennial review on water analysis [4], the importance of disinfectants and their by-products as new contaminants was highlighted. These biennial reviews are focused on emerging contaminants and trends of analytical developments concerning water analysis.

The monitoring of water quality relies on effective routine water analysis, so this became a hot, sensitive and trendy issue. The range of methods, processes and tools available can be classified in different ways. A useful classification, revisited by Greenwood et al. [2], is based on the relationship between sample and analytical processes with three main categories: (i) *in situ*, (ii) on-line and (iii) off-line. Generally, the methods with no sampling, the methods with *in-situ* determination, use sensing devices such as probes inserted directly in the water body. Regarding on-line methods, the determination is carried out close to the water being monitored with direct feeding into the analytical system. In those cases, both discrete and continuous flow measurements can be performed.

Some major challenges in water quality monitoring include: a wide range of analyte concentration; variable salinity (wide range of ionic strength); colour or turbidity (mainly in waste waters); speciation; the need to mineralisation prior to quantifying the total amount. Analytes can be present in a high amount and so dilution may be necessary to fit the linear range, or they can be present in trace amounts and thus a preconcentration step is required. The variability in ionic strength may cause interferences in the chemistry itself or then influence the analytical signal, namely in spectrophotometric measurements. Water colour or turbidity may lead to high blank values which may adversely affect the limit of detection. The growing interest of environmental chemists in analyte speciation also poses an additional challenge, as some traditional methods only permit to quantify the total amount, namely when a reaction is used to quantify a certain analyte form may induce equilibrium shifts that unable to quantify the exact amount in that form. The interest of environmental chemists in analyte speciation relies on the tight relationship between speciation, bioavailability and toxicity. For example, aluminium is only bioaccumulated by organisms in the form of Al^{3+}. Organisms use nitrate as nitrogen source while the nitrite form is highly toxic. Furthermore, changes in the environment caused by pollution such as environmental acidification result in the release of the cationic form of several metals, their most bioavailable form. The impact to human health becomes a consequence of the environmental impact. With the sequential injection versatility, this issue of analyte speciation can be tackled.

On the other hand, there are situations in which the quantification of the total amount is required and so drastic digestion conditions must be created. All these issues increase the complexity of water analysis.

In addition, the analysis of water should also try to comply with the objectives of so-called Green Chemistry [5], in order to reduce and/or eliminate the use and generation of hazardous substances. In fact, an ironic situation is created when the analytical methodologies employed to monitor pollutants generate chemical wastes that are highly polluting themselves [5]. In some cases, the chemicals used in the analysis are even more toxic than the analyte itself, which makes the search of new alternatives even more pertinent.

In this scenario, flow systems may provide answer to the above mentioned challenges, as virtually every unit operation can be implemented in-line, and offer several advantages for routine analysis namely, high sampling rate, miniaturisation, low sample and reagent consumption. The variety and capability of flow techniques and flow equipment has increased significantly over the last three decades. Scale of the equipment has gone from bench size equipment, handling volumes measured in liters, to coin size equipment with volumes in the order of microliters. This review focuses on the sequential injection analysis (SIA) approaches that meet some of these challenges, choosing sequential injection analysis [6] among the different automatic flow techniques (flow injection [7], multicommuted flow injection [8], multisyringe flow injection [9], multipumping flow [10]). This choice was determined by the robustness of the equipment along with the compact size, the possibility of multiparametric determinations and the low reagent consumption. In addition, the easy coupling of external devices such as gas diffusion or dialysis units, resin packed columns and so on, enables the application to a wide variety of waters. These features result from the versatility of the sequential injection valve which enables a direct connection to the various reagents and/or to external devices.

Sequential injection analysis

Fundamentals

Sequential injection was proposed as an evolution to flow injection analysis, to overcome some of its perceived disadvantages, the requirement for a separate manifold for the determination of each parameter and the continuous consumption of reagents. Other flow techniques such as multicommutation, multisyringe and multipumping overcome the continuous consumption of reagents but maintain, in many circumstances, the requirement of physical reconfiguration for different methodologies. Sequential injection has the ability of performing different determinations without system reconfiguration (placing different reagents on the ports of the selection valve) and there can be a reagent saving associated to non-continuous consumption. In a SIA manifold (Fig. 1(I)), sample and reagent solutions are sequentially aspirated into a holding coil, being the aspirated volumes determined by the time and aspiration

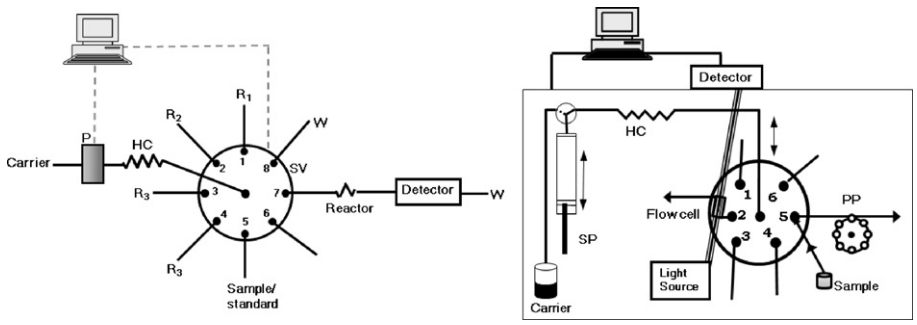

Fig. 1. Sequential injection manifolds: (I) conventional manifold of sequential injection: SV – selection valve, P – propulsion device, HC – holding coil, Ri – reagents, W – waste; (II) sequential injection lab-on-valve manifold: HC – holding coil, PP – peristaltic pump, SP – syringe pump.

rate; the mutual mixture is promoted by flow reversal, while sending the stacked zones towards the detection system. The computer control ensures the reproducibility of the process.

The basic components of sequential injection are schematically represented in Fig. 1(I). The key equipment is the multi-port selection valve as it enables the sequential selection of the various solutions and the subsequent redirection towards the detection system. Most of the characteristics attributed to sequential injection are due to the selection valve. In fact, the placement of different reagents on the ports permits different determinations with the same manifold and it is the structure of the selection valve itself that gives robustness to the sequential injection technique. The sequential aspiration of reagent and sample is made possible through the presence of the holding coil which prevents the contamination of the carrier. The propulsion system is usually a peristaltic pump or a piston pump and different detection systems can be used.

Micro SIA (SI-LOV) and bead injection (BI)

A step forward in miniaturisation and compaction of the sequential injection concept was recently achieved with micro sequential injection lab-on-valve (SI-LOV) equipment [11]. The SI-LOV concept was described as a universal micro-flow analyser based on the sequential injection concept. It resulted from the incorporation of the detection system in the selection valve which was made possible due to the use of fibre optics technology. With this significant down scale of sequential injection, there is an even lower consumption of reagents and samples. The micro sequential injection lab-on-valve concept is considered the third generation of flow analysis.

All the equipment, i.e. selection valve, propulsion device and detector, are assembled in the same box (Fig. 1(II)) resulting in the most compact of all the flow methodologies. As mentioned above, the volumes used are extremely small and the flow cell is positioned on the valve, which makes the analytical path rather short. The advantages in reagent and sample consumption minimisation are obvious and make SI-LOV a perfect tool for enzymatic and the so-called bead injection assays. The bead injection technique can be considered a "hyphenated" technique as it is commonly coupled with some other fluidic handling technique [12], where beads replace the reagent solution and the assay is carried on in the beads surface. This technique is especially suitable for immunoassays, coating the beads with antibodies.

Evolution of the SIA application

The features of simplicity and versatility allied with robustness have created an exponential growth of SIA applications. This growth in publications since SIA was first described in 1990, results not only from the relatively simple implementation but also the wide applicability of sequential injection techniques. From 1990, the cumulative number of papers increased to 286 in 2000, reaching 1204 papers last year (calculated using ISI Web of Knowledge – Web of Science, keyword "sequential injection", 19/01/2009). The increase in SIA publications numbers is not, however comparable to flow injection and one of the reasons for that could be the requirement of computer control. This requirement implies some knowledge in computing for writing the programs as well as interfacing of the equipment used, which may be complex. Another reason could be the parallel development of other flow techniques (mentioned above) that have emerged from the original main concept of flow injection.

Along with all this increase in the diversity of flow manipulation, the possibilities in detection systems have also evolved extraordinarily. This evolution was not only in diversity but also in size, while fluid volumes have been reduced from mililiters to microliters and spectrophotometers have decreased in size about 80 fold. Therefore, the combination of flow handling techniques and detection systems has led to a countless number of possibilities. This may be the reason why there has also been an increase in the range of applications. Nowadays, flow systems have been developed for nearly all types of samples ranging from pharmaceutical preparations to complex solid samples such as soil and food. Based on the previously ISI Web of Knowledge – Web of Science search (Fig. 2) of sequential injection publications, a cross linked search with possible samples or types of sample enabled some conclusions to be drawn regarding the application of the described sequential injection systems.

First the types of sample were broadly categorized on environmental, food, pharmaceuticals or biological. Then, more specific classifications were used: wine, milk, water, plant extracts, soils and slurry. It is quite obvious that some overlap occurred as for example wine and milk are included in "food", and water and soil are included in "environmental", but the idea was to be as thorough as possible. "Biological samples" is the term commonly

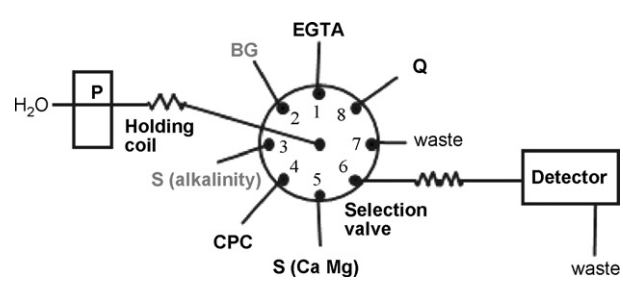

Fig. 2. Schematic representation of a SIA manifold for the multiparametric determination of calcium, magnesium and alkalinity in natural waters (adapted from [78]): P – peristaltic pump, BG – bromocresol green reagent for alkalinity determination, Q – hydroxiquinoline as masking agent for magnesium in calcium determination, EGTA – masking agent for calcium in magnesium determination, CPC – cresolphtalein complexone colour reagent for calcium and magnesium determination, S (alkalinity)/S (Ca, Mg) – sample for alkalinity or calcium and magnesium determination, respectively.

used for samples as urine, blood and serum. In the end, almost half of all the described publications were not included in any category. Nevertheless, water samples are one of the three most common applications of the sequential injection technique along with pharmaceutical preparations and biological samples. It is a quite significant percentage which illustrates the concern for automation of water monitoring, especially when the other two main applications are health related, to pharmaceuticals and biological samples.

Water analysis using SIA

Introduction

As far as we know, no previous review was dedicated solely to sequential injection for water analysis. A review by Cerdà et al. [13] was dedicated to sequential injection applied to environmental samples, which include water, plants and soils. The papers [9,14–16] describe different flow methods for analysing waters and [17,18] are dedicated to the application of flow injection to the same matrix.

In some reviews [19–21], the focus was on the evolution of flow methodologies, in which sequential injection was mentioned as a versatile and robust flow technique to couple with devices for in-line treatments. Other reviews have focused on new developments in detection systems coupled with flow techniques [22–25], namely sequential injection. Some reviews of specific detection methods such as vibrational spectroscopy [22], FTIR [23], electrothermal atomic absorption spectroscopy [24] and electronic tongues [25] emphasised the versatility of flow techniques, including sequential injection.

It is also worth mentioning reviews on the determination of specific parameters/analytes (nutrients in aquatic systems [26], phosphorus determination [27]), or a specific type of sample (sea water analysis [28]).

The applications of the sequential injection concept to water analysis are presented in Table 1. Molecular absorption spectrometry is by far the most commonly used detection method. This may be due to characteristics such as the robustness of the equipment, the possibility of miniaturisation, the versatility of application and the overall cost. Furthermore, it is a quite simple technique, not requiring any specific training. Other spectrophotometric detection systems such as flame emission atomic spectrometry (FEAS), flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma mass spectrometry (ICP-MS) are generally more sensitive and selective, allowing trace elements analysis, but present a high maintenance costs and are not easily miniaturised. In addition, a more specific training is normally required. In the case of fluorescence and luminescence, the miniaturisation and cost are no longer a problem but the applicability is highly restricted. As for detection systems based in electroanalytical techniques such as potentiometry, amperometry and voltammetry, the portability and the *in-situ* determination are the main advantages. The problem with these techniques might be robustness and in some cases the limits of quantification.

One of the most common drawbacks attributed to sequential injection methods is the lower determination rate, especially when compared to flow injection. Nevertheless, that depends entirely on the method itself as it can be observed in Table 1.

There is an extremely wide range of determination rates; from 3 determinations per hour in a methodology including separation and preconcentration [118] to 189 determinations per hour in a multiparametric determination [83]. The easy implementation of multiparametric determinations and diverse in-line sample treatments is a key attribute of sequential injection systems.

Water samples

More than 45% of the methods listed in Table 1 were applied to more than one type of water and 12% were applied to more than two types. This emphasises the versatility of sequential injection which can be applied to different types of water samples, by minor modifications in the flow programming, without any physical change of the manifold. Actually, some observations can be pointed out: (i) the significant percentage (over 6%) of papers that did not specify the sample used; (ii) the percentage of papers that classified the sample as “natural water”, close to 11%, which include several types of water (sea, rain, river, lake, ground, mineral and tap water); and (iii) the percentage of papers that classified the sample as “surface water”, close to 5%, which also includes several types of water (sea, mineral river and lake). Tap water and waste water were the most analysed types with about 15% each of the listed papers. Rain [118] and mine [136] waters were the least analysed, with only one methodology applied to each one.

Multiparametric determinations

One of the main advantages of sequential injection analysis is its potential to perform multiparametric analyses. This means that by using the same manifold but placing different reagents on the selection valve ports, and changing the operational parameters, more than one analyte can be determined. From the listed papers, over 40% involved the determination of more than one analyte [34–36,39,40,45,49–53,55,59–61,72,74,78,83–85, 94,96,101–104,106,107,114,116,117,119,120,132,135,138,140,141,145, 148,149,153,155], with close to 18% describing the determination of more than two analytes [34–36,40,45,49–51,53,74,83,78,102,101, 116,140]. Some more detailed examples of bi-parametric determinations will be detailed in Section 3.4.2, as they usually involve quantifying two oxidation states. When more than two analytes are considered, it usually implies the coupling to multi-analyte detection systems like ICP, HPLC or an array of sensors. This multiparametric capacity minimises the disadvantage of a low sample throughput that is often attributed to SIA. An example of a multiparametric SIA system with a determination rate of 40 h^{-1} for two parameters (calcium and magnesium) and 65 h^{-1} for a third one (alkalinity) is illustrated in Fig. 2.

In-line treatments

Another mentioned advantage of sequential injection is the ease coupling of separation devices to the valve, without overall manifold reconfiguration. This feature is due to the use of a selection valve, enabling the direct connection to the separation device. In fact, about 45% of all the listed papers described an in-line treatment of the sample. Within these papers, different types of in-line treatment are considered, some aiming for the separation and/or preconcentration of the analyte (≈70%) and others aiming for the change of the oxidation state of the analyte (≈30%).

Separation and/or preconcentration

Most of the works that include preconcentration and/or separation of the analyte refer to coupling SI methodology with ICP [50,51,58,102] and AAS [38,39,41,47,48,56,72,73,90,99,100, 113,114,126,129,143]. The combination of SIA with ICP or AAS associates the advantages of SIA such as versatility, robustness and automation (useful for handling reagent and sample preparation) with selectivity and sensitivity of those detection methods. The problems that normally arise from using a complex matrix were avoided by appropriate sample preparation, namely the inclusion of a preconcentration step; additionally, limits of detection of 1 pg L^{-1} were obtained [50].

Table 1
Sequential injection systems for water analysis.

Year	Analyte	Sample	Detection system	Determination conditions	Dynamic range	LOD	RSD	Determination rate	Ref.
2008	Methyl parathion	Surface water	Voltammetry	SI for in-line sample conditioning and standard addition	0.010–0.50 mg L^{-1}	0.002 mg L^{-1}	<4.5%	25–61 h^{-1}	[29
2008	Linear alkylbenzene sulfonates	Natural water	Spectrophotometry/ chromatography	Lab-on-valve approach used for application of two detection methods	0.07–10 μg L^{-1}	21 ng L^{-1}, 15 μg L^{-1}	<10.2%	36–29 h^{-1}	[30]
2008	Nitrite	Seawater	Spectrophotometry	Griess reaction with solid phase enrichment of the coloured product prior to detection	0.71–42.9 nM and 35.7–429 nM	0.1 nM	1.44%	4 h^{-1}	[31]
2008	Fluoride	Natural water	Potentiometry	Comparison between a SI system and a flow injection system for the application of a tubular electrode	0.5–6.0 mg L^{-1}	0.1 mg L^{-1}	4%	30 h^{-1}	[32]
2008	Phosphorus	Sea water	Spectrophotometry	Solid phase extraction with a hydrophilic–lipophilic balance used to enrich phosphomolybdenium blue	3.4–1132 nmol L^{-1}	1.4 nmol L^{-1}	2.5%	6–10 h^{-1}	[33]
2008	Na, K and chloride	Mineral water	Potentiometry	SI system with integrated multisensor chip as base for “electronic tongue”	0.05 mM–0.01 M	–	<8%	–	[34]
2008	Mg, Ca, Na and K	Synthetic water	Potentiometry	SI for automate the training of the “electronic tongue” employing the pulse transient response	–	–	–	–	[35]
2008	Na, K and chloride	Mineral water	Potentiometry	SI system based on a multisensory ISFET array monolithically integrated in one chip	–	–	–	–	[36]
2008	Al	Natural and waste water	Spectrophotometry	A direct and kinetic determination based in the reaction with chrome azurol S	0.040–0.500 mg L^{-1} 0.05–0.300 mg L^{-1}	0.002 mg L^{-1}, 0.012 mg L^{-1}	<5%, <9%	57 h^{-1} 31 h^{-1}	[37]
2008	Cr(III) and Cr(VI)	Certified river water and cave water	Electrothermal atomic absorption spectrometry	Chromium speciation by bio-sorption of Cr(VI) on egg-shell membrane, Cr(III) obtained by subtraction (after conversion to Cr(VI)	0.05–1.25 μg L^{-1} Cr(VI)	0.01 μg L^{-1} Cr(VI)	3.2%	15 h^{-1}	[38]
2008	Cr(VI) and Cr(III)	River and tap water	Electrothermal atomic absorption spectrometry	Preconcentration and speciation of chromium using two mini-columns	0.1–0.25 μg L^{-1} Cr(III), 0.12–2.0 μg L^{-1} Cr(VI)	0.02 Cr(III), 0.03 Cr(VI) (μg L^{-1})	1.9% Cr(III), 2.5% Cr(VI)	10 h^{-1}	[39]
2008	Pb, Cd and Zn	Certified river water	Voltammetry	Anodic stripping voltammetry with a bismuth film screen-printed carbon electrode	0–70 μg L^{-1} Pb e Cd, 0.075–0.200 μg L^{-1} Zn	0.89 μg Pb L^{-1}, 0.69 μg Cd L^{-1}	<8.8%	–	[40]
2008	Pb(II)	Natural water	Flame atomic absorption spectrometry	Liquid–liquid micro-extraction for preconcentration and/or separation	3.0–250.0 μg L^{-1}	1.4 μg L^{-1}	2.9%	25 h^{-1}	[41]
2007	Alkylphenol polyethoxylates	River water	Chemiluminescence	Immunoassay with microbeads	0–1000 μg L^{-1}	10 μg L^{-1}	–	4 h^{-1}	[42]
2007	Picloram	River and tap water	Squarewave voltammetry	Mercury drop electrode	0.1–2.5 mg L^{-1}	36 μg L^{-1}	10.0%	37 h^{-1}	[43]
2007	Chlorine	Surface and tap water	Spectrophotometry	Direct determination with as a new application of tetramethylbenzidine	0.09–1.3 mg L^{-1}	80 μg L^{-1}	–	60 h^{-1}	[44]

Table 1 (*Continued*)

Year	Analyte	Sample	Detection system	Determination conditions	Dynamic range	LOD	RSD	Determination rate	Ref.
2007	Mg, Ca, Ba	Mineral water	Potentiometry	Electronic tongue, PVC-membrane potentiometric sensor array and multivariate calibration	0–120 mg Ca L^{-1}	–	–	–	[45]
2007	Hg	Certified river water and sea water	Atomic fluorescence spectrometry	Lab-on-valve approach with a micro-scale vapor generation chamber	0.06–10 μg L^{-1}	0.02 μg L^{-1}	4.4%	90 h^{-1}	[46]
2007	Cd	Lake water and certified river water	Electrothermal atomic absorption spectrometry	Use of cell-sorption for separation/preconcentration	0.005–0.2 μg L^{-1}	1.0 ng L^{-1}	2.3%	20 h^{-1}	[47]
2007	Cu	Coastal seawater and certified seawater	Electrothermal atomic absorption spectrometry	Sequential injection used for sample pre-treatment and concentration	0.05–1.00 μg L^{-1}	0.015 μg L^{-1}	1.8%	26 h^{-1}	[48]
2007	Co, Ni, Cu, Fe	Drinking waters	HPLC/spectrophotometry	SI for automated handling of sample/reagents, on-line pre-column derivatization and propulsion to HPLC	From 5–75 μg L^{-1} to 7–1000 μg L^{-1}	From 1 μg L^{-1} to 2 μg L^{-1}	6.0%	4 h^{-1}	[49]
2007	Be, Cd, Cr, Cu Pb and other metals	Certified river water and tap water	ICP-MS or ICP-AES	SI for sample preparation and pre-treatment	From 0.001–10 ng L^{-1} to 0.1–10 ng L^{-1}	From 0.001 ng L^{-1} to 018 ng L^{-1}	9.6%	11 h^{-1}	[50]
2007	Ag, Be, Cd, Co, Cu, Ni, Pb, U, V	River water	ICP-MS	Preconcentration of trace elements	From 0.005–5 μg L^{-1} to 1–5 μg L^{-1}	From 0.001 μg L^{-1} to 0.93 μg L^{-1}	From 0.2% to 1.2%	–	[51]
2006	Ammonia phosphate	River and marine water	Fluorimetry	Free reactive phosphate detected by suppression of rhodamine fluorescence by phosphomolybdate and ammonia with phthaldehyde	0.02–20 μM 0.04–4 μM	0.02 μM 0.04 μM	–	120 h^{-1}	[52]
2006	Chloride, nitrate, hydrogencarbonate	Well, spring and tap water	Potentiometry	Array of potentiometric sensors and artificial neural network, “electronic tongue”	–	–	<7%	–	[53]
2006	Pharmaceutical compounds	Surface water and raw and treated waste waters	HPLC/spectrophotometry	Lab-on-valve as a front end to HPLC with on-line solid phase extraction	–	0.05 μg L^{-1}	–	–	[54]
2006	As(III) and As(V)	Tap water and groundwater	Chemiluminescence	SI for fluidic handling for measure waterborne arsenic	0–50 μg L^{-1}	0.05 μg L^{-1}	–	15 h^{-1}	[55]
2006	Ni	Tap and seawater	Electrothermal atomic absorption spectrometry	Bead injection for separation/preconcentration	0.2–2 μg L^{-1}	0.05 μg L^{-1}	4.8%	10 h^{-1}	[56]
2006	Se	River, lake and tap water	AAS-Hybrid	SI for handling sample/reagent	0.10–8.0 μg L^{-1}	0.03 μg L^{-1}	2.8%	24 h^{-1}	[57]
2006	Pb	Reference river water & river samples	ICP-MS	Preconcentration resin Vs = 5 Preconcentration resin Vs = 10	0.1–5 ng mL^{-1}	70 pg mL^{-1} 30 pg mL^{-1}	0.5%	12 h^{-1}	[58]
2006	Cu(II) Fe	Standard solution and industrial waste water	Spectrophotometry	LOV, use of reducing agent for determination of iron(II)	0.1–2 mg L^{-1} 0.1–5 mg L^{-1}	50 μg L^{-1} 25 μg L^{-1}	2.0% 1.8%	18 h^{-1}	[59]
2006	Cr(VI) Cr(III)	Simulated water samples	Spectrophotometry–diode array	Chemometric tools-multivariate curve resolution alternative least squares (MCR-ALS)	0.02–0.5 mg L^{-1} –	2.4 μg L^{-1} –	3.7% 4.9%	54 h^{-1}	[60]
2006	Cr(VI) Cr(III)	Simulated water samples	Renewable surface reflection spectrophotometry	Reaction with Cr(IV) in beads and oxidation of Cr(III) to Cr(IV)	0.02–0.5 mg L^{-1} –	2.4 μg L^{-1} –	1.3% 2.5%	53 h^{-1}	[61]
2005	3,5,6-trichloro-2-pyridinol	Tap water and river water	Electrochemical immunoassay	Magnetic beads coated with antibody in a permanent magnet reaction zone	0.01–2 μg L^{-1}	6 ng L^{-1}	<3.9%	-	[62]
2005	Cationic surfactants	Well and tap water	Spectrophotometry	Reaction of cationic surfactants as zephiramine among others with bromophenol blue	7–50 μg L^{-1}	0.22 μg L^{-1}	1.8%	28 h^{-1}	[63]

2005	Cationic surfactants	Surface and waste waters	Spectrophotometry	Different colour reagents for each determination	8.10^{-6} to 1.10^{-4} M, 1.10^{-4} to 5.10^{-4} M	$2.20.10^{-6}$ M, $2.96.10^{-4}$ M	4.57%, 4.93%	29 h^{-1}, 28 h^{-1}	[64]
2005	Anionic surfactant	Drainage water sample	Spectrophotometry	Liquid–liquid extraction, lab at valve approach	1–10 mg L^{-1}	0.48 mg L^{-1}	5.0%	5 h^{-1}	[65]
2005	*p*-Arsenilic acid (*p*-ASA)	Surface water from swine farm	Spectrophotometry	Sequential injection-long path length absorbance spectrometry (SI-LPAS)	0.1–1.0 mg L^{-1}	0.0212 mg L^{-1}	2.8%	7.5 h^{-1}	[66]
2005	Nitrite	Waste water treatment plant	Spectrophotometry	Adaptative system for 2 ranges, automatically programmable	0.0–3.0 mg L^{-1} 0.0–20.0 mg L^{-1}	0.048 mg L^{-1} 0.4 mg L^{-1}	–	12 h^{-1}	[67]
2005	Atrazine	Waste and fresh water	Square wave voltammetry	SI for conditioning and standard addition	1.2×10^{-7} M to 2.3×10^{-6} M	2.1×10^{-6} M	5.2%	37 h^{-1}	[68]
2005	Chlorine	Tap water, waste water and bleaches	Spectrophotometry	Gas diffusion unit for separation of free chloride, colorimetric detection	0.6–4.8 mg L^{-1} 0.047–0.188 g L^{-1}	0.5 mg L^{-1} 5 mg L^{-1}	2.0% 2.0%	15 h^{-1} 30 h^{-1}	[69]
2005	Chloride	Mineral drinking water and surface water	Potentiometry	Lab-at-valve approach with the electrodes attached to the multiposition valve	0.10–120 mM	–	1.3%	50 h^{-1}	[70]
2005	Fe(III)	Not specified water samples	Spectrophotometry	Home-made SIA, Fe–thiocyanate complex	1.0–7.0 mg L^{-1}	0.34 mg L^{-1}	1.1%	–	[71]
2005	Cr(VI) Cr(III)	River, lake and tap water	Electrothermal atomic absorption spectrometry	Bead injection for separation/preconcentration	0.035–0.4 μg L^{-1} 0.02–0.25 μg L^{-1}	0.02 μg L^{-1} 0.01 μg L^{-1}	2.2% 2.4%	8 h^{-1} 12 h^{-1}	[72]
2005	Cr(VI)	Seawater, tap water and certified natural water	Electrothermal atomic absorption spectrometry	Bead injection with renewable reverse phase for separation/preconcentration	0.12–1.5 μg L^{-1}	0.03 μg L^{-1}	3.8%	15 h^{-1}	[73]
2005	Cu, Fe, Mn, Zn	Natural, waste and spiked water samples	Spectrophotometry	Different colour reagents for each determination	0–5 mg L^{-1}, 0–10 mg L^{-1}, 0–4 mg L^{-1}, 0–5 mg L^{-1}	0.048 mg L^{-1}, 0.012 mg L^{-1}, 0.24 mg L^{-1}, 0.013 mg L^{-1}	2.4%, 2.8%, 2.1%, 2%	–	[74]
2004	Bromate	Not specified water samples	Spectrophotometry	Reaction between bromate and PADAP with thiocyanate	0.18–3.00 mg L^{-1}	0.15 mg L^{-1}	0.8%	45 h^{-1}	[75]
2004	Boron	Natural waters and pharmaceuticals	Fluorimetry	Calibration curve based in boric acid and related to boron	8–350 mg L^{-1}	0.003 mg L^{-1}	2.7%	49 h^{-1}	[76]
2004	Orthophosphate	Waste water treatment plant	Spectrophotometry	On-line electrochemical generation of molybdenum blue	0.3–20 mg L^{-1} P	0.100 mg L^{-1} P	2.4%	18 h^{-1}	[77]
2004	Ca, Mg Alkalinity	Drinking, surface, tap water and reference water	Spectrophotometry	Same reagent for Ca and Mg (cresolftaleine) with masking agents, alkalinity with bromocresol green	0.5–5 mg Ca L^{-1}, 0.5–10 mg Mg L^{-1} 10–100 mg L^{-1} HCO_3^-	0.32 mg Ca L^{-1}, 0.03 mg Mg L^{-1} 5.1 mg L^{-1} HCO_3^-	2.0% Ca, 2.1% Mg 0.4%	40 + 40 h^{-1} 65 h^{-1}	[78]
2004	Al	Drinking water during and after flocculation/coagulation	Fluorimetry	Separation of Al from matrix with XAD-4 (chelating resin) reaction with hydroxyquinoline	0.2–500 mg L^{-1}	0.2 mg L^{-1} (mL^{-1} sample)	–	–	[79]
2004	Hg	River and sea water	Cold-vapour atomic absorption spectrometry	Inclusion of a new integrated gas–liquid separator operating in parallel as a reactor	0.05–5 μg L^{-1}	0.02 μg L^{-1}	2.6%	25 h^{-1}	[80]
2004	Pb	Natural and waste water	Spectrophotometry	Preconcentration of Pb in Chelex and interferences removal in AG1X8 (resins)	0.05–0.30 mg L^{-1} 0.30–1.0 mg L^{-1}	25 μg L^{-1} 165 μg L^{-1}	3.6% 1.0%	17 h^{-1} 24 h^{-1}	[81]
2004	Pb	Drinking water samples	Spectrophotometry	Catalytic effect on reaction with reazurin	0–0.100 mg	–	3.0%	–	[82]
2004	Pb, Zn, Co, Cd, Cu, Fe(III), Hg	Soils, tap waters, urine and certified samples	Spectrophotometry–diode array	Thin-film SI extraction with multivariate calibration and multiwavelength detection	1–20 Co, Cu, Pb, 1–10 Hg, 1–20 Zn, 1–20 Cd (mg L^{-1})	–	2.0%	27 h^{-1} (189 dt h^{-1})	[83]

Table 1 (*Continued*)

Year	Analyte	Sample	Detection system	Determination conditions	Dynamic range	LOD	RSD	Determination rate	Ref.
2003	Carbonate and hydrogencarbonate	Not specified water samples	Spectrophotometry	Titration using phenolphthalein and methyl orange	0.8–10 mM CO_3^{2-}, 1–10 mM HCO_3^-	–	2% CO_3^{2-}, 1.5% HCO_3^-	12 h^{-1}	[84]
2003	Bromine Bromide	Spiked water samples and effluents streams	Spectrophotometry	Determination of bromine and total bromine, oxidation, (bromide by the difference)	1–10 mg L^{-1} Br_2 0.8–15 mg L^{-1} total Br_2	0.6 mg L^{-1} Br_2 0.4 mg L^{-1} total Br_2	0.8% Br_2 0.7% total Br_2	30 h^{-1}	[85]
2003	sulphate	Natural and waste waters	Spectrophotometry	Use of an air bubble for minimise dispersion and improve mixing, turbid metric determination (BaCl)	10–100 mg L^{-1}	10 mg L^{-1}	5%	20 h^{-1}	[86]
2003	Sulphide	Simulated water samples	Spectrophotometry	Based in formation of methylene blue dye, calibration with in-line dilution of a single standard	0.17–1.0 mg L^{-1}	0.04 mg L^{-1}	5.20%	38 h^{-1}	[87]
2003	Tween-80	Well water, tap water and seawater all spiked	Fluorimetry	Enhancement of fluorescein fluorescence in the presence of Tween-80	10–2100 μg L^{-1}	1.7 μg L^{-1}	2.70%	–	[88]
2003	Al	Tap water spiked	Fluorimetry	Enhancement of the fluorescence of the complex aluminium–morin with Tween-20	50–1000 μg L^{-1}	3 μg L^{-1}	2.90%	–	[89]
2003	Cd	Reference river and natural water	Electrothermal atomic absorption spectrometry	Coupling bead injection with lab-on-valve for on-line matrix removal and preconcentration	0.05–1 μg L^{-1}	15 ng L^{-1}	3.10%	12 h^{-1}	[90]
2003	Cr(VI)	River and lake water samples	Spectrophotometry	Comparative studies of diffusion samplers using diphenylcarbazide (DPC)	0–1.6 mg L^{-1} (without membrane)	20 mg L^{-1}	1.10%	–	[91]
2003	Cu	Mineral and tap water	Spectrophotometry	Reaction with cuprizone, sandwich SIA compared to FIA	0.06–4 mg L^{-1}	0.004 mg L^{-1}	0.71%	48 h^{-1}	[92]
2003	Hg (total)	River water samples spiked	Spectrophotometry	Bead injection with Chelex resin and dithizone for colorimetric reaction	0–30 mg L^{-1}	0.9 mg L^{-1}	9%	20 h^{-1}	[93]
2003	Mn(II) Mn(VII)	River water samples and effluents streams	Spectrophotometry	Determination of Mn(II) and total Mn (Mn(VII) by the difference)	0.02–0.50 mg L^{-1} Mn(II) 0.025–0.55 mg L^{-1} total Mn	0.005 mg L^{-1} Mn(II) 0.008 mg L^{-1} total Mn	0.27% Mn(II) 0.34% total Mn	30 h^{-1}	[94]
2002	Chloride	Ground, surface and waste water	Spectrophotometry	Turbidimetric determination based in the reaction between silver nitrate and chloride	2–400 mg L^{-1}	2 mg L^{-1}	3.7%	55 h^{-1}	[95]
2002	Nitrite nitrate	Surface water	Spectrophotometry	Direct determination of nitrite, reduction of nitrate to nitrite in a copperised-cadmium column	0.05–1.00 mg N L^{-1} 0.50–50.0 mg N L^{-1}	0.015 mg N L^{-1} 0.10 mg N L^{-1}	1.10% 1.32%	14 h^{-1}	[96]
2002	Fluorophores	Tap and mineral water	Variable angle scanning fluorescence spectrometry	Multicomponent mixtures coupling the detection with multivariate least squares regression	From 0.05–5 μg L^{-1} to 13–720 μg L^{-1}	From 0.02 μg L^{-1} to 10 μg L^{-1}	<1.0%	17 h^{-1}	[97]
2002	Al	Drinking and tap water	Spectrofluorimetry	Reaction between Al and hydroxyquinoline and fluorimetric detection of the complex	2.2–300 μg L^{-1}	LOQ = 2.8 μg L^{-1}	1.5%	20 h^{-1}	[98]

2002	Cd	Natural waters	Electrothermal atomic absorption spectrometry	SI for on-line solvent extraction-back extraction	0.05–0.8 $\mu g\,L^{-1}$	2.7 $ng\,L^{-1}$	1.8%	13 h^{-1}	[99]
2002	Cd	Natural waters	Electrothermal atomic absorption spectrometry	SI for on-line matrix removal and preconcentration	0.02–0.2 $\mu g\,L^{-1}$	1.2 $ng\,L^{-1}$	1.5%	16 h^{-1}	[100]
2002	Cd, Cu, Pb and Zn	Drinking and waste waters	Voltammetry	Comparison of between a flow injection system and a sequential injection system (still in study)	From 10–70 $\mu g\,L^{-1}$ to 470–700 $\mu g\,L^{-1}$	From 6 $\mu g\,L^{-1}$ to 4700 $\mu g\,L^{-1}$	<9.8%	–	[101]
2002	Al, As, Co, Cu, Mn, Mo, Ni, Pb and V	Sea water	ICP-MS	Comparison of different resins for preconcentration	0–100 $\mu g\,L^{-1}$	–	<5%	–	[102]
2002	Fe(III) Fe(II)	Effluents streams	Spectrophotometry	Determination of Fe(III) and total Fe, oxidation, (Fe(II) by the difference)	0.15–100 $mg\,L^{-1}$ 0.30–80 $mg\,L^{-1}$	0.10 $mg\,L^{-1}$ 0.15 $mg\,L^{-1}$	1.3% Fe(III) 0.8% Fe(II)	30 h^{-1}	[103]
2002	Cr(III) Cr(VI)	Water samples (not specified)	Spectrophotometry	Direct determination of Cr(VI) and total Cr (oxidation of Cr(III) to Cr(VI)), Cr(III) by the difference	0.85–25 $mg\,L^{-1}$ 0.16–20 $mg\,L^{-1}$	0.042 $mg\,L^{-1}$ 0.023 $mg\,L^{-1}$	0.70%	30 h^{-1}	[104]
2002	^{90}Sr	Mineral, ground and marine water	Low-background gas-flow proportional counter	Si for on-line wetting-film extraction and sample handling	0.07–0.30 Bq	–	3.0%	–	[105]
2001	fluorberidazole thiabenzadole	Natural water	Scanning fluorescence spectrometry	Simultaneous determination of both pesticides	0.04–10 $\mu g\,L^{-1}$ 0.08–20 $\mu g\,L^{-1}$	1 $\mu g\,L^{-1}$ 0.02 $\mu g\,L^{-1}$	0.30% 0.50%	–	[106]
2001	Nitrogen Phosphate	Lake and tap water	Spectrophotometry	Determination of nitrite, nitrate (reduced copperised-cadmium column) and orthophosphate	30–4000 $\mu g\,L^{-1}$ 1.0–30.0 $\mu g\,L^{-1}$	3.91 $\mu g\,L^{-1}$ 9.92 $\mu g\,L^{-1}$	<1.22%	48 h^{-1}	[107]
2001	Oxidised nitrogen	Natural waters	Spectrophotometry	Determination of nitrate + nitrite as N after reduction of nitrate (cadmium)	0.0–5 $mg\,L^{-1}$	0.01 $mg\,L^{-1}$	1.20%	36 h^{-1}	[108]
2001	Chloride	Mineral and drinking waters	Spectrophotometry	Determination based on the thiocyanate method, formation of red iron(III) thiocyanate complex	0–50 $mg\,L^{-1}$	3.01 $mg\,L^{-1}$	2.5%	37 h^{-1}	[109]
2001	Iodide	Drinking water samples and pharmaceuticals	Spectrophotometry	Based in the catalytic effect of iodide on redox reaction between Ce(IV) and As(III)	1–60 $mg\,L^{-1}$	1.5 $mg\,L^{-1}$	–	15 h^{-1}	[110]
2001	benzo[A]pyrene	Tap and distilled water	Variable angle fluorescence spectrometry	Extraction and preconcentration prior to detection	7.5–280 $ng\,L^{-1}$	2.5 $ng\,L^{-1}$	1.10%	4.5 h^{-1}	[111]
2001	Hg	River water	Cold-vapour atomic absorption spectrometry	Standard addition SI method with on-line UV-digestion	20–1000 $ng\,L^{-1}$	–	5–30%	–	[112]
2001	Ni	Waste water	Electrothermal atomic absorption spectrometry	Coupling SI in-line preconcentration with renewable micro column ion-exchange beads	0.02–1.20 $\mu g\,L^{-1}$	10.2 $ng\,L^{-1}$	5.80%	12 h^{-1}	[113]
2001	Cr(III) Cr(VI)	Effluent and natural water	Flame atomic absorption spectroscopy	Speciation of chromium with anionic and cationic resins	0.5–1.5 $mg\,L^{-1}$ –	81 $\mu g\,L^{-1}$ 42 $\mu g\,L^{-1}$	<10%	12 h^{-1}	[114]
2000	Boron	Liquid fertilizers and effluent water samples	Spectrophotometry	*In-situ* preparation of azomethine-H (salicyaldehyde and H-acid in boron's presence)	0.61–100 $mg\,L^{-1}$	0.61 $mg\,L^{-1}$	1.40%	30 h^{-1}	[115]
2000	Nitrite, nitrate, sulphate, phenolic compounds	Waste waters	Spectrophotometry	Griess reaction for nitrite, nitrate reduced (Cd column), turbidimetry for sulphate, phenolic compounds through oxidative properties	From 0.05–15 $mg\,L^{-1}$ to 5–200 $mg\,L^{-1}$	From 0.03 $mg\,L^{-1}$ to 19 $mg\,L^{-1}$	<2.2%	12 h^{-1}	[116]

Table 1 (*Continued*)

Year	Analyte	Sample	Detection system	Determination conditions	Dynamic range	LOD	RSD	Determination rate	Ref.
2000	Nitrite Nitrate	Waste waters	Spectrophotometry	Griess reaction for nitrite, nitrate reduced to nitrite (copperised cadmium column)	0.05–25 mg L^{-1} 0.05–15 mg L^{-1}	0.01 mg L^{-1} 0.01 mg L^{-1}	2.0% 1.3%	24 h^{-1}	[117]
2000	Nitrite	Rain, tap water, ground, pond and sea water	Spectrophotometry	Isolation, preconcentration and determination of nitrite based on the Shinn reaction	13.4–160 mg L^{-1} 0.83–20 mg L^{-1}	5.9 mg L^{-1} 0.32 mg L^{-1}	4.00%	15 h^{-1} 3 h^{-1}	[118]
2000	Phosphate Silicate	River reservoir water samples, sediments and culture mediums	Spectrophotometry	Reaction with molybdenum blue avoid interferences of each other with oxalic acid	0.2–7 mg L^{-1} 5–50 mg L^{-1}	0.1 mg L^{-1} 1 mg L^{-1}	–	75 h^{-1} 40 h^{-1}	[119]
2000	Phosphate and silicate	Waste waters	Spectrophotometry–diode array	Determination based on different reaction rates of . . . of phosphomolybdenium blue	0.026–0.485 P, 0.125–2.848 Si (mmol L^{-1})	7.4 P, 37.38 Si (mmol L^{-1})	2.10% 1.10%	30 h^{-1}	[120]
2000	Sulphuric acid	Effluents	Spectrophotometry	SI titration with sodium hydroxide	0.006–0.178 M	0.002 M	<0.75%	23 h^{-1}	[121]
2000	Sulphate	Waste waters	Ultraviolet-spectrophotometry	Formation of a cation between iron and sulphate	10–1000 mg L^{-1}	5 mg L^{-1}	2.40%	72 h^{-1}	[122]
2000	Thiocyanate	Waste water samples from effluent streams	Spectrophotometry	Reaction between thiocyanate and iron(III), formation of the coloured complex	2.0–150 mg L^{-1}	1.1 mg L^{-1}	1.20%	24 h^{-1}	[123]
2000	Hg	River water	Cold-vapour atomic absorption spectrometry	SI for standard addition method, on-line UV-digestion and sample handling	20–1000 ng L^{-1}	10 ng L^{-1}	<10%	3 h^{-1}	[124]
2000	Hg (total)	Lake and tap water and tuna samples	Cold-vapour atomic absorption spectrometry	Improvement in comparing with FI with same detection	1.0–20 mg L^{-1}	0.46 mg L^{-1}	0.90%	45 h^{-1}	[125]
2000	Cd	Drinking, mineral, river and sea water	Electrothermal atomic absorption spectrometry	SI for on-line solvent extraction	0–80 ng L^{-1}	0.5 ng L^{-1}	2.1%	12 h^{-1}	[126]
2000	Fe (total), as Fe(III)	Pharmaceuticals, natural waters and effluent streams	Spectrophotometry	Reduction of Fe(III) to Fe(II) with cadmium and reaction of Fe(II) with 1,10-phenanthroline	0.002–0.50 mg L^{-1}	0.18 mg L^{-1}	2.50%	24 h^{-1}	[127]
2000	Mn(II)	Tap water	Spectrophotometry	Use of a solid-phase lead(IV) dioxide reactor	1–7 mg L^{-1}	062 mg L^{-1}	3.0%	50 h^{-1}	[128]
1999	Pb	Natural waters	Flame atomic absorption spectroscopy	Pb preconcentration in poly(vinylpyrrolidone) – PVP, coupled SIA/FAAS	11.8–400 mg L^{-1}	4.9 mg L^{-1}	3.0%	16 h^{-1}	[129]
1999	Cu	Food samples (water soluble) and water samples	Spectrophotometry	Based on the reaction between Cu(II) with diethyldithiocarbamate (DDTC)	0.5–5.0 mg L^{-1}	0.2 mg L^{-1}	4.5%	7 h^{-1}	[130]
1998	Nitrite	Feed, dam and waste water, effluent stream and fertilizer	Spectrophotometry	Nitrite is diatonised with *N*-(1-naphthyl)ethylenediammonium dichloride resulting a coloured azo dye	0.05–5.0 mg L^{-1}	0.053 mg L^{-1}	2.63%	49 h^{-1}	[131]
1998	Nitrate and nitrite	Tap, mineral and sea water	Spectrophotometry–diode array	Sandwich arrangement with Griess reagent (nitrate reduced to nitrite – cadmium)	0.5–40 NO_2^-, 2–100 NO_3^- (mmol N L^{-1})	0.1 NO_2^-, 0.45 NO_3^- (mmol N L^{-1})	<2%	10 h^{-1}	[132]
1998	Warfarin	Domestic water samples spiked	Fluorimetry	Enhancement of the fluorescence resulting from the complex with b-cyclodextrin	0.1–1 mg L^{-1}	0.02 mg L^{-1}	1.50%	26 h^{-1}	[133]

1998	Phosphate	River waters	Spectrophotometry	Molybdenum blue method, comparison to FIA	0–70 mg L^{-1}	0.5 mg L^{-1}	0.9%	18 h^{-1}	[134]
1998	Fe(II), phosphate	Tap waters and ground waters	Spectrophotometry–diode array	Sample as carrier, reaction between Fe(II) and phenanthroline and reaction of molybdate for phosphate	0.25–6 mg L^{-1} Fe(II), 0.1–1 mg L^{-1} P	0.06 mg L^{-1} Fe(II), 0.02 mg L^{-1} P	1.7% Fe(II), 4.1% P	–	[135]
1998	Fe(III)	Mine waters	Spectrophotometry	Investigation of the use of mixing chambers, reaction between iron and tiron	0–200 mg L^{-1}	0.03 mg L^{-1}	0.28%	24 h^{-1}	[136]
1998	Fe(II)	Natural waters	Spectrophotometry	New strategies of sampling, reaction between Fe(II) and phenantroline	–	–	1.1%	–	[137]
1998	Co(II) Ni(II)	Water samples with known quantities of the analytes	Spectrophotometry	Kinetic determination based on different reaction rate between the analytes and citrate, colour reaction with PAR	0–10 mg L^{-1}	0.20 mg L^{-1} 0.14 mg L^{-1}	1.20%	11 h^{-1}	[138]
1997	Ammonia	Water samples and effluent streams	Spectrophotometry	Based on the reaction of ammonia with hypochlorite forming monochloramine that reacts with phenol reagent (blue indophenol-type)	0–50 mg L^{-1}	0.36 mg L^{-1}	1.80%	16 h^{-1}	[139]
1997	Ammonium, nitrite, orthophosphate	Waste waters	Spectrophotometry	Bromothymol blue for ammonium, Griess reaction for nitrite, vanadomolybdate for orthophosphate	2–60 (NH_4^+), 0.5–25 (NO_2^-), 0.5–50 (PO_4^{3-}) mg L^{-1}	–	–	–	[140]
1997	Phosphate Silicate	Urban waste water	Spectrophotometry	Reaction with molybdate eliminating mutual interference with appropriated acidity and segmentation with oxalic acid	0–12 mg L^{-1} P 0–36 mg L^{-1} Si	0.2 mg L^{-1} P 0.9 mg L^{-1} Si	1.38% 3.87%	23/(46 h^{-1})	[141]
1997	Orthophosphates	Natural and waste waters	Spectrophotometry	Study of three methods with: vanadomolybdate, malachite green, molybdenum blue	0–18, 0–0.4, 0–4 mg P L^{-1} (respectively)	0.15, 0.01, 0.01 mg P L^{-1}	2.1%, 18%, 1.7%	30 h^{-1}	[142]
1997	Fe(III)	Potable water	Atomic absorption spectrophotometry	Without the preconcentration step Preconcentration in a Chelex resin	1–20 mg L^{-1} 0.02–0.4 mg L^{-1}	0.088 mg L^{-1} 0.006 mg L^{-1}	2.00% 4.80%	6 h^{-1}	[143]
1997	Fe(III)	Water samples	Spectrophotometry	Based on thiocyanate reaction, modelling through a neural network system using genetic algorithm	5–20 mg L^{-1}	–	–	110 h^{-1}	[144]
1997	Cr(VI) Cr(III)	Tap water, lake water and sea water	Spectrophotometry	Reaction product of Cr(VI) with diphenylcarbazide extracted to a wet film, oxidation of Cr(III) (determination by difference with total chromium)	2.0 mg L^{-1} Cr(VI)	2.0 mg L^{-1} Cr(VI)	2.80%	17 h^{-1}	[145]
1996	Ammonium	Urban waste water samples, aqueous extracts of atmospheric aerosols	Spectrophotometry–diode array	Formation of ammonia that diffuses through an hydrophobic membrane into an acid–base indicator	0–60 mg L^{-1}	2 mg L^{-1}	2.50%	–	[146]
1996	Ammonium	Waste water	Conductimetry	Coupled of a selection valve with a injection valve for sample preconcentration with a gas diffusion unit	0–180 mg L^{-1}	0.1 mg L^{-1}	3.0%	–	[147]

Table 1 (*Continued*)

Year	Analyte	Sample	Detection system	Determination conditions	Dynamic range	LOD	RSD	Determination rate	Ref.
1996	Chloride and pH	Waste water	Potentiometry	Simultaneous determination of both analytes	–	–	1.0% Cl^-, 1.2% pH	–	[148]
1996	Chloride and fluoride	Mineral and tap water	Potentiometry	Simultaneous determination of both analytes	20–500 mg L^{-1} Cl^-, 0.5–200 mg L^{-1} F^-	–	1.0% Cl^-, 3.7% F^-	–	[149]
1996	Sulphate	Natural waters and industrial effluents	Spectrophotometry	Turbidimetric determination based in the reaction between sulphate and barium chloride	10–200 mg L^{-1}	–	3.90%	26 h^{-1}	[150]
1996	Ca	Water, control sample and urine	Spectrophotometry	Complexation between Ca and cresolphthalein complexone	0–20 mg L^{-1}	0.05 mg L^{-1}	1.40%	43 h^{-1}	[151]
1996	Fe(III)	Public water supplies, underground water (well) and sea water	Spectrophotometry–diode array	Preconcentration in a Chelex resin, reaction between Fe(III) and thiocyanate	0.05–0.6 mg L^{-1}	0.02 mg L^{-1}	3.00%	37 h^{-1}	[152]
1995	Ca and Mg	Drinking and waste water	Spectrophotometry–diode array	Reaction of Ca and Mg with PAR	1–20 mg L^{-1} Mg, 2–40 mg L^{-1} Ca	–	2.0% Ca, 4.0% Mg	60 h^{-1}	[153]
1995	Ca	White water samples from paper mills	Spectrophotometry	Complexation between Ca and cresolphthalein complexone masking Mg with hydroxiquinoline	5–500 mg L^{-1}	5 mg L^{-1}	2.50%	–	[154]
1995	Nitrite Nitrate	Aqueous extracts of atmospheric aerosol filters, waste water	Spectrophotometry	Griess reaction for nitrite, nitrate reduced to nitrite (hydrazine in alkaline medium)	0–18.4 mg L^{-1} 0–24.8 mg L^{-1}	0.07 mg L^{-1} 0.2 mg L^{-1}	1.50% 3.10%	–	[155]

Fig. 3. Schematic representation of a hybrid SIA–FI system for the spectrophotometric determination of lead in water samples with in-line preconcentration of lead and elimination of interferences (adapted from [81]): Pi – peristaltic pumps, S – sample, C1 – column filled with an anionic resin for interference elimination, C2 – column filled with a cationic resin for lead preconcentration, MG – malachite green, Eluent – nitric acid solution for eluting the preconcentrated lead.

There were also at least two references to coupling SIA with HPLC [49,54] showing how effective SIA can be in preparing the sample prior to injection. In the work described by Burakham et al. [49], SIA is responsible not only for the preconcentration step but also for the selection of reagents in the different metals determination. In the work described by Sabarudin et al. [58], a solid phase extraction was carried out in a SIA method prior to injection, which enabled the application to waste waters.

In combining SIA with spectrophotometric determinations, different approaches were observed. In some cases, when gaseous analytes were involved, the separation was obtained using a hydrophobic membrane [69,146]. In other cases, the separation involved an extraction, either liquid–liquid [41,54,73] or solid–liquid [31,33,81,93,118,152]. These solid–liquid extractions used resins and the analyte was retained, even after the colorimetric reaction [31]. In some of these cases, the analyte was not only extracted from the matrix but also preconcentrated before determination, enabling enhanced limits of detection, e.g. 25 μg Pb L^{-1} [81] (Fig. 3) and 20 μg Fe L^{-1} [152].

Changes in oxidation state

The use of in-line chemical treatments aims mainly to change the oxidation state of a specific analyte. For some determinations it is important to know the oxidation state and/or to convert the analyte to the same oxidation state. This is particularly important in the determination of metals such as chromium [61,72,104,145]. In this case, the in-line treatment aimed for either the oxidation of chromium(III) to chromium(VI) [38,61,104,145], or the reduction of chromium(VI) to chromium(III) [72] depending upon the appropriate oxidation state for the determination. The result was a bi-parametric determination of chromium (III) and chromium (VI).

The same was observed in a couple of iron determinations [103,127], where the reduction of iron(III) to iron(II) resulted in the determination of both ionic forms. Other papers that describe the determination of iron also reported the previous iron reduction but present the results as total amount of iron [59,74].

As for manganese, there was only one description of the determination of both manganese(II) and manganese(VII) [94] resulting from the reduction of manganese(VII) to manganese(II). In another work, manganese(II) determination involved the oxidation of manganese(II) to permanganate prior to the direct determination of this anion [128]. In all of these works, the inclusion of either several reagents or devices in the SI system reinforces the versatility attributed to sequential injection analysis, by performing multi-determinations with the same basic configuration.

Oxidation and reduction treatments were not limited to the determination of metals as the determination of nitrite and nitrate is also very common [96,107,108,116,117,132,155]. In all these works, nitrate is reduced to nitrite, most of them involving a cadmium column [96,107,108,116,117,132] once again emphasising the easy assembly of a device (column) to a SI system.

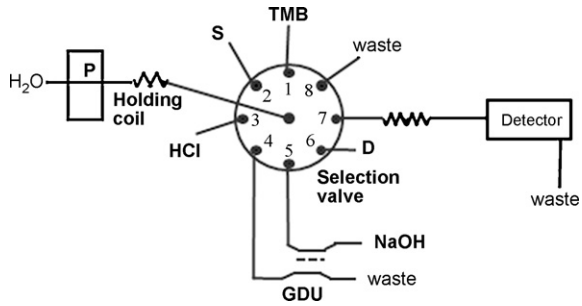

Fig. 4. Schematic representation of a SIA system for the spectrophotometric determination of chlorine with or without matrix separation (adapted from [44,69]): P – peristaltic pump, S – sample, TMB – tetramethylbenzidine reagent used for the determination without separation, GDU – gas diffusion unit, D – dianisidine reagent used for the determination with gas diffusion separation.

There was one exception to the use of the cadmium column as Oms et al. [155] described the reduction with hydrazine. In the end, most of these works represent a bi-parametric determination of both anions [96,116,117,132,155] but a couple present the results as total nitrogen [107,108]. The work by Thomas et al. [140] described the determination of nitrite and total nitrogen (obtained from sample digestion) but made no reference to the value of nitrate.

Another application of an in-line oxidation process for determination of two oxidation states was observed in the work by van Staden et al. [85]. The authors described the determination of both bromine and bromide; while the value of bromine was obtained by the direct determination, for bromide it was calculated by the difference with total bromine (after oxidation of bromide).

Another application of the oxidation/reduction process is the determination of chlorine described by Mesquita and Rangel [69] in which hypochlorite was reduced to chlorine in order to diffuse through a hydrophobic membrane and subsequently oxidised back to hypochlorite for the colorimetric determination. In Fig. 4, a sequential injection manifold is presented in which chlorine could be determined with either a selective reagent (tetramethylbenzidine) or with matrix separation and a non-selective reagent (dianisidine).

Metals determination

The range of analytes covered by the works listed in Table 1 is fairly extensive, but a little more than half (56%), described the determination of metal cations in water. The importance of metal cations in water is mainly related to their toxicity, which depends upon their concentration. Most regulations for water quality have strict limits for metals.

Among these, iron is the most determined metal in waters, if the two possible ionic forms are considered [49,59,71,74,83,103,127,135–137,143,144,152]. This fact can be explained as iron determination can be fairly easy to obtain with spectrophotometric detection, due to well-known reactions. It seems pertinent to highlight some of those described works as they constitute a significantly different approach to the determination. That was the case of the work developed by Makchit et al. [71]; the authors designed a home-made sequential injection system providing valuable information for "a do it yourself SI manifold". Other examples are described by Vieira et al. [137] and Mas et al. [135], involving different strategies of sampling and the use of sample as carrier stream.

For the determination of chromium, spectrophotometric [60,61,91,104,145], atomic absorption [39,72,73,114] and ICP detection [50] was used. All the methodologies described with AAS detection used a preconcentration step.

Metals such as copper [48–51,59,74,92,101,102,113], cadmium [40,47,50,51,83,90,99–101,126] and lead [40,41,50,51,58,81–83,101,102,129] were mainly determined with ICP [50,51,58,102] and AAS [41,47,48,88,99,100,126,129] because these metals are found at very low concentrations in waters. In fact, there was only one spectrophotometric method described for cadmium [83], two for lead [81,82] and four for copper [59,74,92,130] as spectrophotometric determinations normally imply higher detection limits.

A rather different approach was the use of voltammetric determination of several metals by Chuanuwatanakul et al. in the determination of lead, cadmium and zinc [40] and by Suteerapataranon et al. in the determination of copper, cadmium and lead [101].

Mercury is a heavy metal with very low concentrations in natural waters, so highly sensitive detection methods are required for its determination. Cold-vapour AAS was exclusively applied for the determination of mercury [80,112,124,125] providing detection limits as low as 10 ng L^{-1} [124]. A new alternative with a lab-on-valve micro-scale vapour generation chamber coupled with atomic fluorescence detection was recently described by Yu et al. [46], exploiting new applications of the cold-vapour generation. There were only a few descriptions of spectrophotometric detection [83,93] for the determination of mercury and, despite the use of a preconcentration procedure, the detection limit obtained was only about 1 mg L^{-1}.

Other metals such as manganese, nickel and cobalt, although not commonly determined in water samples, may be indicators of contamination. Taljaard and van Staden [138] described the determination of nickel and cobalt based on the same colorimetric reaction but with different kinetics for each analyte, while the individual determination of nickel involving separation of the analyte from the sample with AAS detection has been described [56,113].

Spectrophotometric method have been described for the determination of manganese, either as manganese(II) [128] or manganese(II) and (VII) [94].

Other metals (silver, uranium [51], barium [45], molybdenum [102] and vanadium [51,102]) were determined using multiparametric methodologies involving ICP-AES detection [51], ICP-MS [102] and potenciometric detection [45].

Only one method has been described for the determination of strontium: the aim was to develop a new extraction procedure. In this work, by Miró et al. [105], sequential injection was used to carry out the wet film extraction procedure prior to determination of radioactive strontium by low-background gas-flow proportional counter.

Recently, sequential injection was coupled with an array of potentiometric detectors described as an "electronic tongue" [34,35,45,59]. The aim of this technique is to mimic the human sense of taste, and this approach involves the simultaneous determination of metal ions such as sodium, potassium, calcium, magnesium and barium. In order to "taste the sample", a mathematical model had to be created based in the determination of different concentrations of the different ions, a process called training. Sequential injection was used to automate this training step.

Non-metals determination

Anions

The determination of anions represents about 46% of the papers listed in Table 1, which can be easily explained as most macro nutrients present in waters are included in this category.

Spectrophotometry was the most widely used method of detection, although there were also quite a few methods that involved electrochemical detection. Almost 20% each of the listed references, described the determination of nitrite [67,96,107,118,116,117,132,131,140,155] and phosphate [52,77,107,120,119,135,134,140–142]. For monitoring aquatic media, it is important not only the determination of these anions individually, but also the ratio

between them, currently called N:P content. In fact, a couple of the mentioned methodologies enabled to obtain that ratio [107,140].

Although nitrate is the ionic form of nitrogen that is biologically available, most nitrate determinations involve its prior reduction to nitrite before detection by the Griess method (see Section 4.4.2). So, in the end, those methodologies described the determination of both nitrate and nitrite [96,107,118,116,132,155].

As a major dissolved component of rain water, sulfate is also commonly found in natural waters. All of the methods described for the determination of sulfate used spectrophotometric detection [86,116,122,150] were based on the turbidimetric reaction between sulfate and barium chloride. Only Lapa et al. [122] described an alternative to turbidity measurement, namely the determination of sulfate by direct UV detection.

Also relevant in water analysis is the determination of chloride due to its aesthetic effects in drinking water and due to salinity measurement in natural waters.

Most of the described works for chloride determination involved potentiometric detection [53,70,148,149]. Furthermore, except for the work by Jakmunee et al. [70], the described methods were multiparametric, reinforcing the versatility of sequential injection analysis. There were also a couple of methods that used spectrophotometric detection, one based on the turbidimetric reaction between chloride and silver nitrate [95], and another using the colorimetric reaction of chloride with thiosulfate [109]. Due to the influence of chloride on the taste of water, one of the recent applications of sequential injection analysis to the training of the "electronic tongues" also included the determination of chloride [34].

The determination of silicate and phosphate are often described together [120,119,141] because detection of both involves similar colorimetric reaction.

Some anions are not significantly present in natural waters and hence are rarely measured. It is the case of the spectrophotometric determination of bromate [75]. As for fluoride, the developed methods described for its determination used potentiometric detection [32,149]. There were some works for the determination of sulfide [87], bromide [85], iodide [110] and thiocyanate [123] where the main application was not water samples but other matrices such as effluents [85,123], pharmaceuticals [110] and simulated samples [87].

Other analytes

Sequential injection techniques were not commonly applied to the analysis of gaseous analytes. The most recent application was to the determination of chlorine [44,69], which has become a significant contaminant due to the excessive use of disinfection products in water treatments. In the work by Mesquita and Rangel [69], the ability of gaseous chlorine to cross through a gas diffusion unit was used to remove it from a water sample prior to colorimetric determination. A different approach was used by Mesquita et al. [44], in which chlorine was oxidised to hypochlorite prior to determination, based on the colorimetric reaction with a specific reagent.

The use of gas diffusion has also been described by van Staden and Taljaard [139] for the determination of ammonia.

Recently the determination of a number of human-health related water quality parameters have been described, e.g. determination of pharmaceuticals [54] in water streams. Their presence results from human consumption and excretion and their environmental impact is yet not fully known but is an area of concern. Other emerging analytes in natural and drinking waters include surfactants (nonionic [30], anionic [65] and cationic [64]). These parameters are the consequence of sources of contamination that were not previously considered, in most cases excess of disinfectants and/or detergents used to clean up the water supplies. The contamination may result by the disinfectants and/or detergents themselves or by their by-products. In fact, there are already contaminants such as linear alkylbenzene sulfonates [30] which result from the search of more biodegradable alternatives to highly toxic disinfectants and/or detergents previously used. Another known source of water contamination, namely ground water, is the excess use of pesticides. New pesticides are developed regularly resulting in new contaminants to search in water such as methyl parathion [29], an insecticide.

Off-line pre-treatment

Some of the previously described systems were applicable to both untreated samples or to samples subject to a previous off-line treatment (for example filtration of waste waters), depending on the sample characteristics. A little over 45% of all the publications have no reference of any treatment or clearly state that none was made. Some determinations, namely for metals, imply acidification of the sample at the time of collection as part of the sampling procedure. Spiking the samples was made to enable the determination within the described dynamic range and not required for the methodology to be applied, so it was also not classified as previous treatment.

In about 30% of the publications, the described methodology required a previous treatment. Most of those mentioned previous treatments were as simple as a filtration of the sample when waste water was involved [64,67,91,118,119,141,142,146]. In the work by Nyman and Ivaska [154], centrifugation of the sample was used with the same purpose. Other pre-treatments were more complex such as acidic digestion of the sample for the determination of total iron [71] and total mercury [93]. Although extraction procedures were already mentioned in Section 3.4.1 as in-line pre-treatments, in the work by Roerdink and Aldstadt [66] for the determination of *p*-arsenilic acid, solid phase extraction was used as a previous treatment.

Conclusions

The sequential injection concept proved to be a suitable choice for meeting the purpose of turning water analysis into a faster, more efficient and automatic procedure. The use of sequential injection analysis enabled, with the same basic equipment and configuration, to perform a wide variety of determinations and unit operations. This can be achieved just by using different reagents on the ports of the selection valve or then by coupling devices such as gas diffusion/dialysis systems, packed columns or mixing chambers. These approaches can also be efficient tools for analyte speciation.

As SIA systems are necessarily controlled by computer, they could be further explored towards intelligent automated systems. If a feedback system is implemented and a suitable program is developed, the operation conditions (for example injection volumes, flow-rates) could be readjusted according to the first sample reading. This way, the same configuration could be used for a wide variety of concentration ranges and thus be applicable to different types of waters or then to control a waste water treatment process.

Being composed of relatively small, but robust equipment, it can be used for at-line determinations. This is also possible due to the low reagent consumption and effluent production of SIA systems.

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References

[1] Water Frame Directive – directive 2000/60/EC of the parliament and of the council, Official Journal of the European Communities L 327/1, of 23 October 2000, establishing a framework for Community action in the field of water policy.
[2] R. Greenwood, G.A. Mills, B. Roig, Trends Anal. Chem. 26 (2007) 263.
[3] EPA – United States Environmental Protection Agency, July 2007 (last access), Current drinking water standards – List of contaminants. http://www.epa.gov/safewater/mcl.html.
[4] S.D. Richardson, Anal. Chem. 79 (2007) 4295.
[5] P.T. Anastas, Crit. Rev. Anal. Chem. 29 (1999) 167.
[6] J. Růžička, G.D. Marshall, Anal. Chim. Acta 237 (1990) 329.
[7] J. Růžička, E.H. Hansen, Anal. Chim. Acta 78 (1975) 145.
[8] B.F. Reis, M.F. Giné, E.A.G. Zagatto, J.L.F.C. Lima, R.A. Lapa, Anal. Chim. Acta 293 (1994) 129.
[9] V. Cerdà, J.M. Estela, R. Forteza, A. Cladera, E. Becerra, P. Altimira, P. Sitjar, Talanta 50 (1999) 695.
[10] R.A.S. Lapa, J.L.F.C. Lima, B.F. Reis, J.L.M. Santos, E.A.G. Zagatto, Anal. Chim. Acta 466 (2002) 125.
[11] J. Růžička, Analyst 125 (2000) 1053.
[12] J. Růžička, L. Scampavia, Anal. Chem. 71 (1999) 257A.
[13] V. Cerdà, A. Cerdà, A. Cladera, M.T. Oms, F. Mas, E. Gómez, F. Bauzá, M. Miro, R. Forteza, J.M. Estela, Trends Anal. Chem. 20 (2001) 407.
[14] M. Miró, J.M. Estela, V. Cerda, Talanta 60 (2003) 867.
[15] M. Miró, J.M. Estela, V. Cerda, Talanta 62 (2004) 1.
[16] M. Miró, J.M. Estela, V. Cerda, Talanta 63 (2004) 201.
[17] A.F. Dŭnec, M. Cheregi, J.M. Calatayud, J.V.G. Mateo, H.Y.A. Enein, Crit. Rev. Anal. Chem. 31 (2001) 191.
[18] A.F. Dŭnec, M. Cheregi, J.M. Calatayud, J.V.G. Mateo, H.Y.A. Enein, Crit. Rev. Anal. Chem. 33 (2003) 57.
[19] V. Cerda, J.M. Estela, Int. J. Environ. Anal. Chem. 85 (2005) 231.
[20] J. Wang, E.H. Hansen, Trends Anal. Chem. 22 (2003) 836.
[21] Y. Wang, M.-L. Chen, J.-H. Wang, Appl. Spectrosc. Rev. 42 (2007) 103.
[22] S. Armenta, S. Garrigues, M. de la Guardia, Trends Anal. Chem. 26 (2007) 775.
[23] M. Gallignani, M.R. Brunetto, Talanta 64 (2004) 1127.
[24] M. Burguera, J.L. Burguera, Spectrochim. Acta, Part B 62 (2007) 884.
[25] A. Gutés, F. Céspedes, M. del Valle, Anal. Chim. Acta 600 (2007) 90.
[26] S. Gray, G. Hanrahan, I. McKelvie, A. Tappin, F. Tse, P. Worsfold, Environ. Chem. 3 (2007) 3.
[27] S. Motomizu, Z.-H. Li, Talanta 66 (2005) 332.
[28] T.P. Rao, P. Metilda, J.M. Gladis, Crit. Rev. Anal. Chem. 35 (2007) 247.
[29] L.B.O. Santos, J.C. Masini, Anal. Chim. Acta 606 (2008) 209.
[30] J.R. Jiménez, M.D.L. Castro, Electrophoresis 29 (2008) 590.
[31] G. Chen, D. Yuan, Y. Huang, M. Zhang, M. Bergman, Anal. Chim. Acta 620 (2008) 82.
[32] A.C.L. Conceição, M.M.C. Santos, M.L.S.S. Gonçalves, Talanta 76 (2008) 107.
[33] J. Ma, D. Yuan, Y. Liang, Mar. Chem. 111 (2008) 151.
[34] A. Ipatov, N. Abramova, A. Bratov, C. Domínguez, Sens. Actuators, B 131 (2008) 48.
[35] D. Calvo, A. Durán, M. Valle, Sens. Actuators, B 131 (2008) 77.
[36] A. Ipatov, N. Abramova, A. Bratov, Talanta 77 (2008) 581.
[37] R.B.R. Mesquita, A.O.S.S. Rangel, J. Braz. Chem. Soc. 19 (2008) 1171.
[38] A.-M. Zou, X.-W. Chen, M.-L. Chen, J.-H. Wang, J. Anal. At. Spectrom. 23 (2008) 412.
[39] A.-M. Zou, X.-Y. Tang, M.-L. Chen, J.-H. Wang, Spectrochim. Acta, Part B 63 (2008) 607.
[40] S. Chuanuwatanakul, W. Dungchai, O. Chailapakul, S. Motomizu, Anal. Sci. 24 (2008) 589.
[41] A.N. Anthemidis, Talanta 77 (2008) 541.
[42] R. Zang, H. Nakajima, N. Soh, K. Nakano, T. Masadome, K. Nagata, K. Sakamoto, T. Imato, Anal. Chim. Acta 600 (2007) 105.
[43] L.B.O. Santos, J.C. Masini, Talanta 72 (2007) 1023.
[44] R.B.R. Mesquita, M.L.F.O.B. Noronha, A.I.L. Pereira, A.C.F. Santos, A.F. Torres, V. Cerdà, A.O.S.S. Rangel, Talanta 72 (2007) 1186.
[45] D. Calvo, M. Größl, M. Cortina, M. del Valle, Electroanalysis 19 (2007) 644.
[46] Y.-L. Yu, Z. Du, J.-H. Wang, J. Anal. At. Spectrom. 22 (2007) 650.
[47] A.-M. Zou, M.-L. Chen, Y. Shu, M. Yang, J.-H. Wang, J. Anal. At. Spectrom. 22 (2007) 392.
[48] Y. Yong-Liang, D. Zhou, W. Jian-Hua, Chin. J. Anal. Chem. 35 (2007) 431.
[49] R. Burakham, S. Srijaranai, K. Grudpan, J. Sep. Sci. 30 (2007) 2614.
[50] R.K. Katarina, N. Lenghor, S. Motomizu, Anal. Sci. 23 (2007) 343.
[51] A. Sabarudin, N. Lenghor, M. Oshima, L. Hakim, T. Takayanagi, Y.-H. Gao, S. Motomizu, Talanta 72 (2007) 1609.
[52] C. Frank, F. Schroeder, R. Ebinghaus, W. Ruck, Microchim. Acta 154 (2006) 31.
[53] M. Cortina, A. Duran, S. Alegret, M. del Valle, Anal. Bioanal. Chem. 385 (2006) 1186.
[54] J.B. Quintana, M. Miró, J.M. Estela, V. Cerdà, Anal. Chem. 78 (2006) 2832.
[55] A.D. Idowu, P.K. Dasgupta, Z. Genfa, K. Toda, Anal. Chem. 78 (2007) 7088.
[56] X. Long, M. Miró, R. Jensen, E.H. Hansen, Anal. Bioanal. Chem. 386 (2006) 739.
[57] A.N. Anthemidis, Spectrosc. Lett. 39 (2007) 699.
[58] A. Sabarudin, N. Lenghor, Y. Living, Y. Furusho, S. Motomizu, Spectrosc. Lett. 39 (2006) 669.
[59] S. Ohno, N. Teshima, T. Sakai, K. Grudpan, M. Polasek, Talanta 68 (2006) 527.
[60] V. Gómez, M.S. Larrechi, M.P. Callao, Anal. Chim. Acta 571 (2006) 129.
[61] J. Wang, B. Xue, Anal. Sci. 22 (2006) 1233.
[62] G. Liu, S.L. Riechers, C. Timchalk, Y. Lin, Electrochem. Commun. 7 (2005) 1463.
[63] S. Feng, X. Chen, J. Fan, Z. Hu, Int. J. Environ. Anal. Chem. 85 (2005) 63.
[64] M.L.C. Passos, M.L.M.F.S. Saraiva, J.L.F.C. Lima, Anal. Sci. 21 (2005) 1509.
[65] R. Burakham, S. Lapanantnoppakhun, J. Jakmunee, K. Grudpan, Talanta 68 (2005) 416.
[66] A. Roerdink, J.H. Aldstadt III, Anal. Chim. Acta 539 (2005) 181.
[67] M. Baeza, J. Bartrolí, J. Alonso, Talanta 68 (2005) 245.
[68] L.B.O. Santos, M.S.P. Silva, J.C. Masini, Anal. Chim. Acta 528 (2005) 21.
[69] R.B.R. Mesquita, A.O.S.S. Rangel, Talanta 68 (2005) 268.
[70] J. Jakmunee, L. Patimapornlert, S. Suteerapataranon, N. Lenghor, K. Grudpan, Talanta 65 (2005) 789.
[71] J. Makchit, S. Kruanetr, P. Prasertgitwatana, T. Lelasattarathkul, S. Liawruangrath, S. Upalee, W. Oungpipat, Instrum. Sci. Technol. 33 (2005) 565.
[72] X. Long, M. Miró, E.H. Hansen, J. Anal. At. Spectrom. 20 (2005) 1203.
[73] X. Long, M. Miró, E.H. Hansen, Anal. Chem. 77 (2005) 6032.
[74] I.P.A. Morais, M.R.S. Souto, A.O.S.S. Rangel, J. AOAC Int. 88 (2005) 639.
[75] J.F. van Staden, L.V. Mulaudzi, R.I. Stefan, Talanta 64 (2004) 1196.
[76] A. Economou, D.G. Themelis, H. Bikou, P.D. Tzanavaras, P.G. Rigas, Anal. Chim. Acta 510 (2004) 219.
[77] F. Mas-Torres, J.M. Estela, M. Miró, A. Cladera, V. Cerdà, Anal. Chim. Acta 510 (2004) 61.
[78] R.B.R. Mesquita, A.O.S.S. Rangel, Anal. Sci. 20 (2004) 1205.
[79] C. Brach-Papa, B. Coulomb, C. Branger, A. Margaillan, F. Theraulaz, P. Loot, J.-L. Boudenne, Anal. Bioanal. Chem. 378 (2004) 1652.
[80] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, Talanta 64 (2004) 1053.
[81] R.B.R. Mesquita, S.M.V. Fernandes, A.O.S.S. Rangel, Talanta 62 (2004) 395.
[82] N.Z. Aracama, A.N. Araújo, R. Perez-Olmos, Anal. Sci. 20 (2004) 679.
[83] J.F. van Staden, R.E. Taljaard, Talanta 64 (2004) 1203.
[84] P.J. Fletcher, J.F. van Staden, Anal. Chim. Acta 485 (2003) 187.
[85] J.F. van Staden, L.V. Mulaudzi, R.I. Stefan, Anal. Bioanal. Chem. 375 (2003) 1074.
[86] I.P.A. Morais, M.R.S. Souto, T.I.M.S. Lopes, A.O.S.S. Rangel, Water Res. 37 (2003) 4243.
[87] M.S.P. Silva, C.X. Galhardo, J.C. Masini, Talanta 60 (2003) 45.
[88] S.M.Z. Al-Kindy, F.E.O. Suliman, S.B. Salama, M. Aoudia, S.N. Al-Bahry, H.S. Al-Bahlany, Anal. Sci. 19 (2003) 737.
[89] S.M.Z. Al-Kindy, F.O. Suliman, S.B. Salama, Microchem. J. 74 (2003) 173.
[90] M. Miró, S. Jończyk, J. Wang, E.H. Hansen, J. Anal. At. Spectrom. 18 (2003) 89.
[91] M.A.S. Pressman, J.H. Aldstadt, Microchem. J. 74 (2003) 47.
[92] P. Rumori, V. Cerdà, Anal. Chim. Acta 486 (2003) 227.
[93] R.P. Sartini, E.C. Vidotti, C.C. Oliveira, Anal. Sci. 19 (2003) 1653.
[94] J.F. van Staden, L.V. Mulaudzi, R.I. Stefan, Anal. Chim. Acta 499 (2003) 129.
[95] R.B.R. Mesquita, S.M.V. Fernandes, A.O.S.S. Rangel, J. Environ. Monit. 4 (2002) 458.
[96] Z. Legnerová, P. Solich, H. Sklenářová, D. Šatínský, R. Karlíček, Water Res. 36 (2002) 2777.
[97] G. Armas, M. Miró, J.M. Estela, V. Cerdà, Anal. Chim. Acta 471 (2002) 173.
[98] C. Brach-Papa, B. Coulomb, J.-L. Boudenne, V. Cerdà, F. Theraulaz, Anal. Chim. Acta 457 (2002) 311.
[99] J. Wang, E.H. Hansen, Anal. Chim. Acta 456 (2002) 283.
[100] J. Wang, E.H. Hansen, J. Anal. At. Spectrom. 17 (2002) 248.
[101] S. Suteerapataranon, J. Jakmunee, Y. Vaneesorn, K. Grudpan, Talanta 58 (2002) 1235.
[102] M.S. Jiménez, R. Velarte, J.R. Castillo, Spectrochim. Acta, Part B 57 (2002) 391.
[103] L.V. Mulaudzi, J.F. van Staden, R.I. Stefan, Anal. Chim. Acta 467 (2002) 35.
[104] L.V. Mulaudzi, J.F. van Staden, R.I. Stefan, Anal. Chim. Acta 467 (2002) 51.
[105] M. Miró, E. Gómez, J.M. Estela, M. Casas, V. Cerdà, Anal. Chem. 74 (2002) 826.
[106] G. de Armas, E. Becerra, A. Cladera, J.M. Estela, V. Cerdà, Anal. Chim. Acta 427 (2001) 83.
[107] C.-H. Wu, J. Růžička, Analyst 126 (2001) 1947.
[108] E.B. Naidoo, J.F. van Staden, Water SA 27 (2001) 355.
[109] J.F. van Staden, S.I. Tlowana, Fresenius J. Anal. Chem. 371 (2001) 369.
[110] J.A. Erustes, R. Forteza, V. Cerdà, J. AOAC Int. 84 (2001) 337.
[111] J.A. Erustes, A. Andrade-Eiroa, A. Cladera, R. Forteza, V. Cerdà, Analyst 126 (2001) 451.
[112] O. Elsholz, C. Frank, B. Stachel, H. Reincke, R. Ebinghaus, Anal. Chim. Acta 438 (2001) 251.
[113] J. Wang, E.H. Hansen, Anal. Chim. Acta 435 (2001) 331.
[114] M.J. Marqués, A. Morales-Rubio, A. Salvador, M. de la Guardia, Talanta 53 (2001) 1229.
[115] J.F. van Staden, T.A. Merwe, Analyst 125 (2000) 2094.
[116] R.A.S. Lapa, J.L.F.C. Lima, I.V.O.S. Pinto, Analusis 28 (2000) 295.
[117] R.A.S. Lapa, J.L.F.C. Lima, I.V.O.S. Pinto, Anal. Sci. 16 (2000) 1157.
[118] M. Miró, A. Cladera, J.M. Estela, V. Cerdà, Analyst 125 (2000) 943.
[119] C.X. Galhardo, J.C. Masini, Anal. Chim. Acta 417 (2000) 191.
[120] F. Mas-Torres, A. Muñoz, J.M. Estela, V. Cerdà, Int. J. Environ. Anal. Chem. 77 (2000) 185.
[121] H. du Plessis, J.F. van Staden, Talanta 52 (2000) 83.
[122] R.A.S. Lapa, J.L.F.C. Lima, I.V.O.S. Pinto, J. Braz. Chem. Soc. 11 (2000) 170.
[123] J.F. van Staden, A. Both, Anal. Chim. Acta 403 (2000) 279.
[124] O. Elsholz, C. Frank, B. Matyschok, F. Steiner, O. Wurl, B. Stachel, H. Reincke, M. Schulze, R. Ebinghaus, M. Hempel, Fresenius J. Anal. Chem. 366 (2000) 196.
[125] W.E. Doering, R.R. James, R.T. Echols, Fresenius J. Anal. Chem. 368 (2000) 475.
[126] Z.-R. Xu, H.-Y. Pan, S.-K. Xu, Z.-L. Fang, Spectrochim. Acta, Part B 55 (2000) 213.
[127] E.B. Naidoo, J.F. van Staden, S. Afr. J. Chem. 53 (2000) 191.
[128] E.B. Naidoo, J.F. van Staden, Fresenius J. Anal. Chem. 370 (2000) 776.
[129] A.N. Araújo, R.C.C. Costa, J.L.F.C. Lima, Anal. Sci. 15 (1999) 991.

[130] J.F. van Staden, A. Botha, Talanta 49 (1999) 1099.
[131] J.F. van Staden, T.A. Merwe, Microchim. Acta 129 (1998) 33.
[132] A. Cerdà, M.T. Oms, R. Forteza, V. Cerdà, Anal. Chim. Acta 371 (1998) 63.
[133] L.X. Tang, F.J. Rowell, Anal. Lett. 31 (1998) 891.
[134] J.F. van Staden, R.E. Taljaard, Microchim. Acta 128 (1998) 223.
[135] F. Mas, A. Cladera, J.M. Estela, V. Cerdà, Analyst 123 (1998) 1541.
[136] T. McCormack, J.F. van Staden, Anal. Chim. Acta 367 (1998) 111.
[137] J.A. Vieira, I.M. Raimundo, B.F. Reis, E.A.G. Zagatto, J.L.F.C. Lima, Anal. Chim. Acta 366 (1998) 257.
[138] R.E. Taljaard, J.F. van Staden, Anal. Chim. Acta 366 (1998) 177.
[139] J.F. van Staden, R.E. Taljaard, Anal. Chim. Acta 344 (1997) 281.
[140] O. Thomas, F. Théraulaz, V. Cerdà, D. Constant, P. Quevaullier, Trends Anal. Chem. 16 (1997) 419.
[141] F. Mas-Torres, A. Muñoz, J.M. Estela, V. Cerda, Analyst 122 (1997) 1033.
[142] A. Munõz, F. Mas-Torres, A. Munõz, J.M. Estela, V. Cerdà, Anal. Chim. Acta 350 (1997) 21.
[143] E. Rubí, M.S. Jiménez, F.B. Mirabó, R. Forteza, V. Cerdà, Talanta 44 (1997) 553.
[144] J. Garcia, M.L.M.F.S. Saraiva, A.N. Araújo, J.L.F.C. Lima, M. del Valle, M. Poch, Anal. Chim. Acta 348 (1997) 143.
[145] Y. Luo, S. Nakano, D.A. Holman, J. Růžička, G.D. Christian, Talanta 44 (1997) 1563.
[146] M.T. Oms, A. Cerdà, A. Cladera, V. Cerdà, R. Forteza, Anal. Chim. Acta 318 (1996) 251.
[147] M.T. Oms, A. Cerdà, V. Cerdà, Electroanalysis 8 (1996) 387.
[148] J. Alpízar, A. Crespí, A. Cladera, R. Forteza, V. Cerdà, Lab. Rob. Autom. 8 (1996) 165.
[149] J. Alpízar, A. Crespí, A. Cladera, R. Forteza, V. Cerdà, Electroanalysis 11 (1996) 1051.
[150] J.F. van Staden, R.E. Taljaard, Anal. Chim. Acta 331 (1996) 271.
[151] J.F. van Staden, R.E. Taljaard, Anal. Chim. Acta 323 (1996) 75.
[152] E. Rubí, R. Forteza, V. Cerdà, Lab. Rob. Autom. 8 (1996) 149.
[153] E. Gómez, C. Tomás, A. Cladera, J.M. Estela, V. Cerdà, Analyst 120 (1995) 1181.
[154] J. Nyman, A. Ivaska, Anal. Chim. Acta 308 (1995) 286.
[155] M.T. Oms, A. Cerdà, V. Cerdà, Anal. Chim. Acta 315 (1995) 321.