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METROLOGY OF GASEOUS AIR POLLUTANTS

Jari Waldén

ACADEMIC DISSERTATION

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Authors
Jari Walden

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Abstract

In recent times the importance of metrology has increased in the World Trade Organization (WTO), where the issues of human health and the environment have become part of the trade policy. The costs and amount of unnecessary measurements, lack of accuracy in the measurement results are issues for which a general solution has been sought. The need for mutual recognition of accurate measurement results made by competent laboratories has been very widely accepted at the international level. A partial solution to the problem was made by the International Committee for Weights and Measures (CIPM) in setting up the Mutual Recognition Arrangement (CIPM MRA), which was signed by National Metrology Institutes (NMI) around the world. The core idea of the CIPM MRA is to have global arrangements for the mutual acceptance of the calibration certificates of National Metrology Institutes. The CIPM MRA covers all the fields of science and technology for which NMIs have their national standards.

The infrastructure for the metrology of the gaseous compounds carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and ozone (O_3) has been constructed at the national level at the Finnish Meteorological Institute (FMI). The calibration laboratory at the FMI was constructed for providing calibration services for air quality measurements and to fulfil the requirements of a metrology laboratory. The laboratory successfully participated, with good results, in the first comparison project, which was aimed at defining the state of the art in the preparation and analysis of the gas standards used by European metrology institutes and calibration laboratories in the field of air quality. To confirm the competence of the laboratory, the international external surveillance study made by an expert from the National Metrology Institute of the Netherlands was conducted at the laboratory. The survey confirmed the expertise of the laboratory to manage the tasks of a metrology laboratory. Based on the evidence obtained from the survey and the comparison results, the Centre for Metrology and Accreditation (MIKES) designated the calibration laboratory at the Finnish Meteorological Institute (FMI) as a National Standard Laboratory in the field of air quality. The designation was declared to the regional metrology organization in Europe and to the International Bureau of Weights and Measures (BIPM). With this designation, the MIKES-FMI Standards Laboratory became a member of CIPM MRA, and Finland was brought into the internationally-accepted forum in the field of gas metrology. The FMI is the national representative in the Metrology organization at the European level. The designation also brought responsibilities, whose fulfillment is mandatory to the NMIs and Designated Institutes of the CIPM MRA. The concept of ‘once measured - everywhere accepted’ is the leading theme of the CIPM MRA.

The calibration service of the MIKES-FMI Standards Laboratory realises the SI traceability system for the gas components, and is constructed to enable it to meet the requirements of the European air quality directives. The standards used to obtain the measurement results are traced to the base unit of the quantity of amount of substance, the *mole,* although the unit used for gas concentration is the mole fraction. In addition, all the relevant uncertainty sources that influence the measurement results have been evaluated, and the uncertainty budgets for the measurement results have been created.

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Nimeke

Kaasumaisten epäpuhtauksien metrologia

Tiivistelmä

Viimeaikoina metrologian merkitys on kasvanut Maailman Kauppajärjestössä (WTO), jossa asiakokonaisuudet kuten ihmisen terveys ja ympäristö ovat tulleet osaksi kauppapolitiikkaa. Kokonaiskustannukset, tarpeettomien mittausten lukumäärä ja mittaustulosten huono laatu ovat asioita, joihin kokonaisvaltaista ratkaisua ollaan etsimässä. Tunnustettujen asiantuntijalaboratorioiden tekemien luotettavien mittaustulosten vastavuoroinen tunnustaminen on ollut laajasti hyväksytty periaate kansainvälisellä tasolla. Käytännön ratkaisuna Kansainvälinen Painojen ja Mittojen Komitea (CIPM) laati sopimuksen kalibrointitodistusten vastavuoroisesta hyväksynnästä, ekvivalenssisopimus (Mutual Recognition Arrangement, CIPM MRA), jonka on hyväksynyt kansalliset metrologialaitokset maailmanlaajuisesti. CIPM MRA sopimuksen ydin on se, että sopimuksen piirissä olevat kansalliset mittanormaalilaboratoriot tunnustavat toistensa antamat mittaus- ja kalibrointitodistukset tasavertaisiksi. CIPM MRA sopimus kattaa kaikki tieteen ja teknologian osa-alueet, joilla kansallisilla metrologialaitoksilla on kansalliset mittanormaalit.

Kaasumaisten yhdisteiden metrologinen järjestelmä hiilimonoksidin (CO), typpimonoksidin (NO), typpidioksidin (NO_2), rikkidioksidin (SO_2) ja otsonin (O_3) osalta on rakennettu kansallisella tasolla Ilmatieteen Laitoksella (IL). Kalibrointilaboratorio rakennettiin Ilmatieteen Laitokselle täyttämään ilmanlaadun mittausten vaatimat kalibrointitarpeet sekä metrologiselle laboratoriolle asetetut vaatimukset. Laboratorio osallistui menestyksellisesti ensimmäiseen vertailuprojektiin, jonka tavoitteena oli selvittää ilmanlaatumittauksissa käytettävien kaasunormaalien valmistuksen ja analysoinnin senhetkinen tilanne. Projekti oli suunnattu ilmanlaadun alueella toimiville eurooppalaisille metrologialaitoksille ja kalibrointilaboratorioille. Kalibrointilaboratorion teknisen pätevyyden osoittamiseksi järjestettiin kansainvälinen arviointikäynti laboratoriossa, jonka suoritti Hollannin metrologialaitoksen asiantuntija. Arvioinnissa vahvistui laboratorion pätevyys suoriutua metrologialaboratoriolta vaadittavista tehtävistä. Niinpä Mittatekniikan keskus nimesi Ilmatieteen laitoksen kalibrointilaboratorion kansalliseksi mittanormaalilaboratorioksi pätevyysalueena ilmanlaatu. Päätös perustui tehdyn arvioinnin lopputulokseen sekä laboratorion tuloksiin vertailumittauksissa. Tehty nimitys vahvistettiin sekä Euroopan metrologialaitosten yhteistyöelimessä, että Kansainvälisessä Painojen ja Mittojen Toimistossa (International Bureau of Weights and Measures, BIPM). Tällä nimityksellä MIKES-IL mittanormaalilaboratorio tuli osalliseksi ekvivalenssisopimusta (CIPM MRA) ja Suomi kytkeytyi osaksi kansainvälisesti hyväksyttyä mittausjärjestelmää kaasujen metrologiassa. Ilmatieteen laitos on myös kansallinen taho Euroopan metrologialaitosten välisessä järjestelmässä. Nimitys toi mukanaan MIKES-IL mittanormaalilaboratoriolle myös velvoitteita, joiden täyttäminen on ekvivalenssisopimuksen piirissä oleville tahoille pakollista. ’Kerran mitattu – kaikkialla hyväksytty’ on ekvivalenssisopimuksen johtava ajatus.

Kalibrointien jäljitettävyys kaasujen osalta on MIKES-IL mittanormaalilaboratoriossa järjestetty SI-yksikköön. Samalla luotu jäljitettävyysketju täyttää Euroopan ilmanlaadun direktiiviin kirjatun vaatimuksen mittausten jäljitettävyydestä kansallisella tasolla. Laboratorion käyttämät mittanormaalit on jäljitetty ainemäärän yksikköön, *mooliin*. Pitoisuudesta puhuttaessa yksikkönä on *mooliosuus (mol/mol)*. Laboratorio on laatinut kalibrointi- ja mittaustuloksille mittausepävarmuusbudjetin, mikä käsittää kaikki mittaustulokseen liittyvät epävarmuuskomponentit.

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ABREVIATIONS

BIPM	The International Bureau of Weights and Measures Bureau Internationals des Poids et Mesures
BMC	Best Measurement Capability
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CCM	Consultative Committee for Mass
CCQM	Consultative Committee for Amount of Substance Comité Consultatif pour la Quantité de Matière
CEM	Centro Espanol de Metrologia
CGPM	General Conference of Weights and Measures
CHMI	Czech Hydro-Metrological Institute
CIPM	International Committee for Weights and Measures
CMC	Calibration and Measurement Capabilities
CRM	Certified Reference Material
CSIR-NMI	National Metrology Institute, South Africa
DI	Designated Institute
DMU	Danmarks Miljoundersogelser
EC	European Commission
EMPA	Swiss Federal Laboratories for Materials Testing and Research
EP	European Parliament
ERLAP	European Reference Laboratory of Air Pollution
EU	European Union
EURACHEM	European Association for Analytical Chemistry
EURAMET e.V.	European Association of National Metrology Institutes
EUROMET	European Collaboration in Measurement Standards
FMI	Finnish Meteorological Institute
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatograph
GL	Finnish Geodetic Institute
GPT	Gas Phase Titration
GUM	Guide to the Expression of Uncertainty in Measurements
GUM	Central Office of Measures, Physical Chemistry Division (Poland)
HAMAQ	Harmonisation of air quality measurements in Europe
HFTLS	How Far the Light Shines-statement
IDMS	Isotope Dilution Mass Spectroscopy
IEP	Institute for Environmental Protection
ILC	Interlaboratory Comparison
INRIM	Instituto Nazionale di Ricerca Metrologia
IPQ	Instituto Portuguese de qualidade
IRCEL	Interwestelijke Cel voor het Leefmilieu
ISCIII	Instituto de Salud Carlos III
ISO	International Organization for Standardization
ITM	Institute of Applied Environmental Research

JCRB	Joint Committee of the Regional Metrology Organizations and the BIPM
JRC	Joint Research Centre
KC	Key Comparison
KCRV	Key Comparison Reference Value
KRISS	Korean Research Institute of Standards and Science
LFE	Laminar Flow Element
LNE	Laboratoire National D'Essais
METAS	Bundesamt fűr Metrologie
MetChem	Metrology in Chemistry
MFC	Mass Flow Controller
MFM	Mass Flow Meter
MIKES	Centre for Metrology and Accreditation
MRA	Mutual Recognition Arrangement
NERI	National Environmental Research Institute
NIES	National Institute for Environmental Studies, Japan
NILU	Norsk Instituut for Luftforskning
NIST	National Institute of Standards and Technology
NMI	National Metrology Institute
NMi	Nederlands Meetinstituut – Van Swinden Laboratorium
NPL	National Physical Laboratory
NRL	National Reference Laboratory
NSL	National Standards Laboratory
OLR	Orthogonal Linear Relation
PMM	Primary Method of Measurement
PRM	Primary Reference Materials
PTB	Physikalisch-Technischen Bundesanstalt
RIVM	Rijksinstituut voor Volksgezondheid en Milieu
RMO	Regional Metrology Organization
RvA	Dutch Accreditation Council
SHMI	Slovak Hydrometeorological Institute
SI	International System of Units
SOP	Standard Operation Procedures
SP	Technical Research Institute of Sweden
SRM	Secondary Reference Materials
SRP	Standard Reference Photometer
STUK	Radiation and Nuclear Safety Authority
UBA (A)	Umwelt Bundes Amt, Austria
UBA(D)	Umwelt Bundes Amt, Deutchland
VDI	Verein Deutscher Ingenieure, The Association of German Engineers
VSL	Van Swinden Laboratorium (former NMi-VSL) March 1, 2009
WG	Working Group
VNIIM	D.I. Mendeleyev Institute for Metrology
VTT	Technical Research Centre of Finland

CONTENTS

1. INTRODUCTION

Metrology is the science of measurements and its application (VIM, 2008) and thus it is not restricted to any specific science. It includes the whole field of science and technology where measurements of any kind are made. To obtain the measurements, issues such as what is the quantity, the measurand, the unit, and how accurate are the measurements, have to be addressed and solved. In addition, some general requirements have to be fulfilled, e.g., that the measurement results have to be repeatable and comparable to similar measurements under the same conditions, and that they are related to an acceptable reference. The last requirement implies that there is a common, global reference to which the measurement device or the measurement probe is linked. The accuracy of the measurements is connected to the fact that there are always uncertainty components associated with the measurements. The question is to what extent the uncertainties can be avoided or corrected.

Throughout the centuries there has been an urgent need to make measurements, e.g., to measure the length of fabric, weigh goods in the market place or define the volume of a wine jar. In ancient Egypt, 3000 years BC, when building the temples and pyramids of the Pharaohs, the architects were responsible for calibrating the standard for the unit of length, i.e., the reference standard for the measurement of length, at each full moon. The death penalty ensued for disregarding the calibration of the standards. The reference standard was defined as the length of the forearm from the elbow to the middle finger of the ruling Pharaoh plus the width of his hand. The reference standard was carved into a granite stone, and copies of the standard (working standards) were used at the working sites. As a result of the reference standard for length, the pyramids and temples are symmetric and straight, as can still be seen to this day (Howarth and Redgrave, 1999).

Even though the technology for conducting the measurements was not advanced, there were well-recognised requirements, so that falsification of the measurements was punishable. In addition to this, there were well-identified references with which the measurements ought to be compared. Nowadays the needs for obtaining measurements in every field of endeavour (human health, environment, industry, science and technology) have expanded considerably. This has led to the practice that in almost every nation there are institutions that are responsible for providing and monitoring reliable weights and measures. A clear indication of this is a label put on a device proving that the calibration of the device has been taken care of by an authorised institution. These kinds of labels can be found on scales in shops, on the fuel meter at the filling stations, on the radar meter of police measuring the speed of a car or on the breathalyser determining the amount of alcohol in the breath.

The basic vocation of metrology is to trace the units and standards of any measurements to a stated reference, and to know all the sources of uncertainties associated with these measurements. Nowadays metrology has an important role to play in world trade, as well as in the fields of human health and the environment (Kaarls, 2003).

The structure of metrology includes all the knowledge required for obtaining the measurements, and ensuring that the measurements are repeatable. It also includes the requirements for well defined standards to which the measurement results can be traced and for the standards to be international. In many areas of the physical sciences, the measurements of a quantity can be made using a calibrated measurement device, e.g., weighing the mass of a certain material with a balance, measuring the temperature of a gaseous, liquid or solid material with a temperature probe, measuring time and frequency with a clock or a frequency meter, and the dimensions of a solid material with a micrometer. Therefore the term physical metrology is often used. In the case of other sciences, e.g., chemistry, biology and especially microbiology, the metrological structure is not always well-defined, due to the presence of a strong sample dependence, matrix dependence, living organism, or to reactions and changes of content during storage. However, there are fields of chemistry where the metrological structure follows that of physical metrology (De Bièvre et al. 1996, Williams, 2000, Meinrath and Kalin 2005, De Bièvre, 2008).

The objective of this study was to construct the infrastructure for gas metrology at a national level in Finland and to link it to the global metrology system. The infrastructure includes the personnel and facilities at the calibration laboratory which:

1. Fulfils the criteria required internationally of a metrology laboratory and is accredited according to an international standard (ISO, 2005).
2. Is designated in the International Metrology Organization as a National Standard Laboratory in the field of gas metrology.
3. Constructs the calibration and measurements capability of the laboratory in such a way that this can be realised through the international comparison projects aimed at Metrology Institutes and Designated Institutes
4. Has the resources and capability for scientific work and development of the calibration methods in the field of expertise.
5. Can serve society with high-quality, traceable calibration services.

The gas components considered here are carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO_2), ozone (O_3), and sulphur dioxide (SO_2). Although gas compounds of benzene, toluene, ethylbenzene and o-, m-, and p-xylene (known together as BTEX) are included into the scope of the laboratory they are not considered more detailed in here. The task of the calibration laboratory is the development, maintenance and dissemination of the reference standards of the laboratory and the provision of calibration services to its customers (industry, government, different areas of society). The calibration services for these gas components are constructed to fit the purposes set out in the European air quality directives (Council Directive 2008/50/EC). The results of the global and regional comparison projects, in which the National Metrology Institutes (NMI) and Designated Institutes (DI) (CIPM-MRA, 2003) are entitled to participate, are used to validate the calibration and measurement capability of the laboratory (CMC). The CMCs of a laboratory defines its capability with respect to each of the quantities and their ranges. The CMCs are evaluated and approved by the regional Metrology organization and are finally accepted at a global level and published in a database open to the general public.

The operation of the laboratory covers all the facilities needed for the calibration of instruments, and the standards used for the measurements are traced to a base unit, the amount of substance, or to internationally-accepted methods or standards. The uncertainty budget of the measurement results has been constructed and the major sources of uncertainties that influence the measurement results have been characterized. The quality system of the laboratory is accredited according to an international standard (ISO-17025, 2005). The calibration facilities include different methods that, with cross-check studies, can serve as an independent support to the principal calibration method.

2. BACKGROUND

2.1. Terminology in metrology

The main task of the metrology includes the following items (EUROMET 595, 2000):

- The definition of internationally-accepted units of measurements, e.g., the metre
- The realisation of units of measurement by scientific methods, e.g., the realisation of a metre through the use of laser beams
- The establishment of traceability chains in documenting the accuracy of a measurement, e.g., the documented relationship between the micrometer screw in a precise engineering workshop and a metrology laboratory for optical length

To fulfil these tasks metrology is normally divided into three categories with different levels of complexity and accuracy:

1. *Scientific metrology* deals with the organization and development of measurement standards together with their maintenance (highest level)

2. *Industrial metrology* has to ensure the adequate functioning of measurements used in industry as well as in production and testing processes.

3. *Legal metrology* is concerned with the accuracy of measurements where its influence on the transparency of economical transactions, and on health and safety, is important.

In general the structure of metrology is a well-formulated field of science with the quantities and the units. The realisation of *mass* is carried out by an artefact standard, the international prototype of the kilogram, while the realisation of *length* is defined by the primary method. The definition of the metre is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second. Besides the SI unit, there are quantities that are not well-defined but are commonly used. For example, the hardness of materials and the smoothness of printing paper, which are widely used as quality indicators in material production (paper, steel etc) and, that have to be measured accurately. These quantities need support from the scientific and technical point of view to provide the best definitions and the standards to make the measurements accurate and comparable.

Scientific metrology works with the definitions and development of the quantities, units and measurement systems. As an example, the definition of the base unit for mass, e.g., through the prototype of the kilogram has been under debate for some years, and a proposal that mass unit shall be linked to Planck's constant has made good progress (Becker et al. 2007, Mills et al. 2005 and Mills et al. 2006). The redefinition of the *mole* has also been under debate since its definition is not unique. The most prominent attempt is to define the *mole* with the help of Avogadro's constant. The discussion has arisen since it is a fixed number (a scaling factor) and not a universal constant (Leonard 2007 and Milton et al. 2007). Scientific metrology follows, among others, progress in modern quantum field theory i.e., unified quantum field theory. Universal constants combining the different field theories (gravitation, electromagnetism, etc) will also be the foundation in metrology for redefinitions of the units.

Industrial metrology is mainly responsible for the application and obtainability of calibration services among users: industry, trade, the environment, etc. The services provided by a National Metrology Institute (NMI) should be designed in such a way that the customers (industry, trade, etc) can really benefit from its expertise. A good example for this is the South Korean NMI (KRISS) which has close cooperation with electronic technology (Jin Seog Kim, 2005) In Europe, NMIs from the UK and from the Netherlands have good cooperation with the gas industry. Similarly, the MIKES has good co-operation with high technology enterprises in Finland.

The objective of legal metrology is to establish the credibility of measurements that are associated with trading at national and international levels. Legal metrology is devoted to the entirety of the legislative, administrative and technical procedures established by, or by reference to, public authorities, and implemented on their behalf in order to specify and to ensure, in a regulatory or contractual manner, the appropriate quality and credibility of measurements related to official controls, trade, health, safety and the environment (www.oiml.org). It covers a wide area of needs that society has in trade, health, the environment and safety. Examples of such topics are market scales, meters for petrol, gas, electricity, water, and taxis; equipments in medical use, instruments for measuring noise levels, air and water pollution; and equipment for monitoring the speed of a vehicle, testing the blood alcohol levels of motorists and tyre-pressure gauges.

2.2. Traceability of the measurement results

The traceability of a measurement result is one of the most important issues to take care of when building up a measurement system from which reliable results are expected or of which the results are credible. It does not in itself tell how accurate the measurement actually is. One cannot verify the traceability through the results of interlaboratory comparison (ILC), e.g., a key comparison by BIPM, or by proficiency tests, as has been discussed in the literature (De Bièvre, 2002, Rassberry, 2001, Papadakis and Taylor, 2001). Traceability is defined (VIM, 2008) as

"*the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty*".

Traceability is a property of a measurement result and should be build into the measurement system. Wherever possible, the value of the measurement is ultimately made traceable to an SI *unit* (or units) (VIM, 2008; EURACHEM, 2002) through realisations of those units. If this is not possible, the final link is made to a unit on an internationally-recognized scale (De Bièvre et al. 1997).

In the most favourable situation, the traceability chain can be connected directly to the primary method. If this is not applicable, one should choose the shortest as practical way to link the measurement results to SI units. This can be done by the use of reference material prepared by or having a direct link to the primary method to calibrate the scale of the measurement equipment (measurement signal) against the scale of the reference material. It should be kept in mind that calibrations of the standards are made at each of the steps in the chain in order to maintain the traceability chain unbroken. Therefore the uncertainty budget of the measurement results increases at each step along the traceability chain when calibration of the standard takes place. The uncertainty of the reference material and the traceability to stated references must be documented with identifiable reference numbers on the certificate. This requirement has been stated by the International Organization for Standardization, ISO (ISO-17025, 2005 and GUM, 1995).

It should also be remembered in mind that the traceability of the results is complete only if the traceability chain is unbroken, and that all the parameters or quantities that are essential for obtaining the result are themselves traceable to stated references (SI units).

For example, a laboratory may prepare gas mixtures of known concentration by dynamic dilution of the reference standard. In this case, knowledge of the composition of the dilution gas, as well as its flow rate, temperature and pressure is needed for calculation of the actual concentration. The traceability of the result is not achieved if the standard gas alone is traceable to an SI unit. In addition standards for each of the quantities that affect the results, e.g., the flow measurements, the temperature measurements and the pressure measurements all have to be traceable to SI units in order to achieve a complete traceability for the measurement results.

The laboratory can, for certain reasons, built the calibration and measurement system in such a way that the traceability chains for each of the reference standards of the laboratory lead to an SI unit. Such reasons may be, e.g., the status of the laboratory as being a reference laboratory or the type of sample the laboratory is analysing (e.g., quality of food, blood serum, forensic evidence, etc) where the results of the measurements have very far-reaching consequences. To prove of the competence of the laboratory and the comparability of the results, the laboratory can participate in comparison measurements (Richter 2000, Rasberry, 2001). On the other hand, if all the quantities that are essential for obtaining the measurement results are traceable to SI units, the results are comparable.

2.3. Uncertainty in measurements

When reporting the result of a measurement of a quantity (physical or chemical) it is essential to have information about the uncertainty associated with the result. The uncertainty of the measurement result is needed in order to know the quality of the result and the measurement system. To characterise the quality of the result there must be a generally accepted procedure to evaluate and express the parameter, which defines the range inside which the result lies. The measurement uncertainty is defined as (VIM, 2008):

"*uncertainty is a non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used.*"

A very comprehensive review of the definition of the measurand and the concept of the measurement result has been made by De Bièvre (2008).

It is important that the evaluation of the uncertainty of the measurements follows universal methods in order to establish the credibility of the measurements. The uncertainty of measurement results should be built up from the components that make contributions to the results, i.e., these should form an uncertainty budget for the measurement results. The uncertainty of the measurements should also be transferable, i.e., it should be possible to use the uncertainty evaluated for one result as a component in evaluating the uncertainty of another measurement in which the first result is used. (GUM, 1995).

To quantify the uncertainty of the measurement results the presentation prepared by ISO (GUM, 1995) is followed. According to this, the uncertainties can be divided into two groups, types A and B, depending on the method of evaluation of the uncertainty components. The definitions of these uncertainty types are:

Type A evaluation: *method of evaluation of uncertainty by the statistical analysis of a series of observations*

Type B evaluation: *method of evaluation of uncertainty by means other than the statistical analysis of a series of observations*

If an A-type quantity varies randomly and is not correlated in any way with the results of the measurements then the arithmetic mean can be a good approximation of the expected value of the quantity. Also the standard deviation of the mean describes the distribution of the measurement results around the mean. If, however, the results are correlated in some way, then more sophisticated statistical methods should be applied in describing the results of the quantity.

For a B-type quantity, repeated measurements are not useable. One should therefore analyse the standard uncertainty of the result of a quantity using all the information that is available associated with the measurement results (previous measurements, performance characteristics of the measurement method, calibration data and estimation of the uncertainty of the calibration standard).

A procedure to calculate the uncertainty of the measurement result is to start with the independent quantities and follow the procedure presented by ISO (GUM, 1995). Let Y be a measurand, a physical quantity or a random variable that can be determined from N other quantities $X_1, X_2, \ldots, X_N$ through a functional relationship

$$Y = f\,(X_1, X_2, X_N) \tag{2.1}$$

The quantities X_i ($i = 1 ,.., N$) may also depend on other quantities, so a complete functional relationship between the quantity Y and the quantities X_i may be rather complicated. The functional relationship between Y and X_i also includes the factors from the error sources that contribute significantly to the measured result.

Let y be the estimate of the measurand Y which can be obtained from the input estimates $x_1, x_2, \ldots, x_N$ for the values of the N quantities X_i ($i = 1, \ldots, N$) using Equation (2.1), i.e.,

$$y = f(x_1, x_2, \ldots, x_N) \tag{2.2}$$

Note that y is the result of the measurement and can be obtained, e.g., from the arithmetic mean of n independent determinations Y_k of Y:

$$y = \overline{Y} = \frac{1}{n}\sum_{k=1}^{n} Y_k = \frac{1}{n}\sum f(X_{1,k}, X_{2,k}, ..., X_{Nk}) \qquad (2.3)$$

Since y is an estimate of the measurand Y, the estimated standard uncertainty associated with the output estimate y, denoted by $u_c(y)$, is determined from the estimated standard uncertainties associated with each input estimate x_i, denoted by $u(x_i)$. Since each standard uncertainty of $u(x_i)$ makes a contribution to the standard uncertainty of $u_c(y)$, the latter is therefore defined as the combined standard uncertainty. The variance of the standard uncertainty can be expressed in the form (GUM, 1995):

$$u_c^2 = \sum_{i=1}^{n}\left(\frac{\partial f}{\partial w_i}\right)^2 u_i^2 + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{\partial f}{\partial w_i}\frac{\partial f}{\partial w_j}u_i u_j \rho_{ij} \qquad (2.4)$$

Equation (2.4) is also known to as the law of propagation of errors. The square root of u_c^2 in Equation (2.4) is the combined standard uncertainty and includes all the uncertainty components associated with the results of the measurements. The covariance term (the second term on the right-hand side) in Equation (2.4) needs to be taken into account when it is about the same size as the independent part in Equation (2.4). The need for the covariance term has been discussed from a theoretical standpoint, e.g., by Bremser and Hässelbarth (1998), and the covariance terms have been calculated and used in uncertainty analysis e.g. by Alink and van der Veen (2000).

When the covariance term is negligible, Equation (2.4) simplifies to the form:

$$u_c^2 = \sum_{i=1}^{n}\left(\frac{\partial f}{\partial w_i}\right)^2 u_i^2 = \sum_{i=1}^{n} c_i^2 \cdot u_i^2 = \sum_{i=1}^{n} u_i^2 \quad , \qquad (2.5)$$

where $c_i = \partial f / \partial w_i$ is the sensitivity factor for the standard uncertainty u_i for each index i $(1, ..., n)$. The variance terms, u_i^2 on the right-hand side of Equation (2.5), are assumed to be independent variables with $c_i^2 = 1$, for each i. The variance terms in Equation (2.5) can be defined experimentally through repeatable measurements, be estimated from the measurements, or taken from the literature or some other reliable source. The procedure used in building the uncertainty budget of the measurements or measurement method is part of the validation of the measurements. When all the components of the standard uncertainties associated with the method or measurements are known, the expanded uncertainty can be calculated as follows:

$$\boldsymbol{U} = \boldsymbol{k} \cdot \sqrt{\boldsymbol{u}_y^2} = \boldsymbol{k} \cdot \boldsymbol{u}_y \tag{2.6}$$

where k is the coverage factor and u_y is the combined standard uncertainty from Equation (2.4). The coverage factor k is defined based on the confidence level required for the uncertainty. Often the coverage factor is defined as k = 2. This means that the level of confidence is approximately 95 % if there is not an exact knowledge of the distributions. If the distribution is of Gaussian type, then the level of confidence is exactly 95 %.

Knowing the uncertainty of the results, the measurand can be expressed as:

$$\boldsymbol{Y} = \boldsymbol{y} \pm \boldsymbol{U} \tag{2.7}$$

The expression of Equation (2.7) can also be rewritten in the form:

$$\boldsymbol{y} - \boldsymbol{U} \leq \boldsymbol{Y} \leq \boldsymbol{y} + \boldsymbol{U} \tag{2.8}$$

Equation (2.8) means that the result can lie at any point between the lower and upper end of the range representing the result of the measurand. Equation (2.7) is the format in which the measurement result should be expressed. There has been a debate in the literature as to whether or not the term “true value” of the measurand should be used or avoided as well as the term “accuracy” (De Bièvre, 2000, Meinrath, 2002). The consensus appears to be that the results of the measurement are as accurate (qualitatively) as the uncertainty of the measurements. Moreover, results without a statement of the uncertainty are meaningless.

When one has built the uncertainty budget and has found the range within which the result lies (Equation 2.8), one measurement result is enough to describe the result of the measurand **Y**. Guidance for building the uncertainty budget for the measurements can be found from various different sources. For example EURACHEM, the European Association for Analytical Chemistry, has prepared a guide to the uncertainty analysis of measurements with examples and the use of cause-and-effect analysis (the fish-tail diagram) of the various uncertainty components (EURACHEM, 2002).

2.4. International organization

Since the beginning of the industrialization era, but particularly at the First Universal Exhibition in Paris in 1878, it became apparent that there was a need for universal units for defining the length, mass and volume of a substance (Quinn, 2004). Development in the fields of mechanics and astronomy in the nineteenth century brought up three independent units, i.e., metre, gram and second for representing the quantities of length, mass and time, respectively. These units formed the basis of the Metric System and were proposed by Gauss (Karl Friedrich Gauss 1777 – 1855) in 1832 (BIPM: www.bipm.fr/enus/3_SI/si-history.html). These units formed a coherent system of units (cgs, centimetre, gram and second) for the physical sciences. The further development of electricity and magnetism by Gauss and Weber (Wilhelm Eduard Weber 1804 – 1891) and especially by Maxwell (James Clerk Maxwell 1831 - 1879) and Thomson (Thomson, Sir Joseph John 1856 - 1940) brought the cgs-system into wider use in the physical sciences. In addition, the base electric units of the *ohm* for electric resistance, the *volt* for electromotive force, and the *ampere* for electric current were established. Already a few years before the Universal Exhibition in Paris, on 20 May 1875, a diplomatic conference on the metre took place in Paris. Altogether 17 governments signed a treaty - "The Metre Convention" – in which the base units of metre, kilogram and second were established.

The signatories decided to create and finance a permanent scientific institute, The International Bureau of Weights and Measures - Bureau International des Poids et Mesures (BIPM). The task of the institute is to ensure worldwide unification of physical measurements and their traceability to the International System of Units, the SI (adopted in 1960), formerly the metric system. The task of the BIPM (BIPM, 2001) is:

- To establish fundamental standards and scales for the measurement of the principal physical quantities and maintain the international prototypes;
- To carry out comparisons of national and international standards;
- To ensure the co-ordination of corresponding measurement techniques;
- To carry out and co-ordinate measurements of the fundamental physical constants relevant to these activities

The BIPM operates under the exclusive supervision of the International Committee for Weights and Measures (CIPM). The CIPM has members from each member state and is mandated by The General Conference of Weights and Measures (CGPM). The CGPM is the highest organization in Metrology, presently meeting every fourth year at governmental level. The CGPM discusses and examines the work performed by the National Metrology Institutes (NMI). The functions of the CGPM meetings are (BIPM, 2002):

- To discuss and initiate the arrangements required to ensure the propagation and improvement of the SI;
- To confirm the results of new fundamental metrological determinations and various scientific resolutions of international scope;
- To take all major decisions concerning the finance, organization and development of the BIPM

The 10th CGPM meeting in 1954 approved the *Ampere* (A), the *Kelvin* (K) and the *Candela* (cd) as the base units of electric current, thermodynamic temperature and luminous intensity, respectively. The seventh base unit, the *mole* for the quantity of amount of substance was established in 1971, completing the present SI. In Appendix 1 the base units of the SI-system and their definitions are presented. In the field of amount of substance a derived unit, the katal, for catalytic activity was accepted in 2002. The units of the katal are $[s^{-1} \cdot mol]$.

The definition of the *mole* was given by the CIPM in 1967 and was adopted by the 14th CGPM (Terrien, 1972). The definition includes two parts:

1. The *mole* is the amount of substance of a system which contains as many elementary entities as there are atoms in 0,012 kilogram of carbon 12
2. When the *mole* is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

The CIPM set up bodies known as consultative committees, whose function is to provide it with information on matters that it refers to them for study and advice. These consultative committees, which may form temporary or permanent working groups to study special topics, are responsible for co-ordination of the international work carried out in their respective fields and for proposing recommendations to the CIPM concerning units (BIPM, 2001). At the present time there are ten different subject fields in which the metrological structure is defined (BIPM, 1998): mass and related quantities (CCM), electricity and magnetism (CCEM), length (CCL), time and frequency (CCTF), thermometry (CCT), ionizing radiation (CCRI), photometry and radiometry (CCPR), acoustics, ultrasound and vibration (CCAUV), and amount of substance (CCQM). In addition there is the committee of units, which is concerned with the development of the International System of Units (SI) (www.bipm.org). The Consultative Committee for Amount of Substance (Comité Consultatif Pour la Quantité de Matière, CCQM) was founded in 1993.

The definition of the primary method of measurement (PMM) was made in 1995 (BIPM, 1995) at the first meeting of the CCQM (BIPM, 1995), and after three years the definition was revised. In its present form, the PMM is the following (BIPM, 1998):

A primary method of measurement is a method having the highest metrological qualities, whose operation can be completely described and understood for which complete uncertainty statement can be written down in terms of SI units

A primary direct method: measures the value of an unknown without reference to a standard of the same quantity.

A primary ratio method: measures the value of a ratio of an unknown to a standard of the same quantity; its operation must be completely described by a measurement equation.

The definition of the PMM has raised a number of questions about the contents of the definition. The overall criticism is aimed at the requirements that the PMM should produce measurement results that are of “the highest metrological qualities” and “whose operation can be completely described and understood” (Taylor et al., 2001; Milton and Quinn, 2001, Milton and Marschal, 2001). The clearest statement in the definition is the requirement that “the complete uncertainty statement can be written down in terms of SI units”. If the measurement equation of the measurement method cannot be expressed in terms of SI units, then automatically the method is not primary or is not being used in the way that is meant by the PMM. The CCQM considered a few of the methods used in chemistry in order to see if they have potential for being PMMs. Based on the survey, methods like gravimetry, coulometry, isotope dilution mass spectrometry and freezing-point depression were listed.

Under the authority given to it in the Metre Convention, the CIPM draw up an arrangement for the mutual recognition of national measurement standards and of calibration and measurement certificates issued by NMIs. This arrangement, the Mutual Recognition Arrangement (CIPM MRA), was signed by the directors of the NMIs at the

21st CGPM meeting on October 14, 1999. The objectives of the CIPM MRA are (www.bipm.org):

- To establish the degree of equivalence of national measurement standards maintained by NMIs
- To provide for the mutual recognition of calibration and measurement certificates issued by NMIs
- Thereby to provide governments and other parties with a secure technical foundation for wider agreements related to international trade, commerce and regulatory affairs.

In the CIPM MRA the competence of an NMI is evaluated through the processes of:

- International comparisons of measurements, to be known as key comparisons
- Supplementary international comparisons of measurements
- Quality systems and demonstrations of competence by NMIs.

The outcome of the CIPM MRA is the general principle: “Measured once, accepted everywhere”. The key element is that only the signatory bodies of the CIPM MRA (NMIs and DIs) are included within the mutual acceptance of the calibration certificates. The competence of the measurements by the NMIs and the DIs is recognized through their statements of the calibration and measurement capabilities (CMC). For each quantity, the signatory bodies of the CIPM MRA prepare CMCs that are based on the detailed analysis of the uncertainty budget for the range of measurement results. The uncertainty statement is expressed as expanded uncertainty using the coverage factor of 2 (level of 95 % confidence). The NMI submits the CMCs to the RMO for international evaluation. The CMCs of an NMI may include a number of lines under the same quantity, but with different service categories and different components (e.g. chemical compounds). The evaluation is based on the results of the key comparison results of the NMI. In addition, supporting evidence (written documents) may be requested by the evaluators if needed. After evaluation and approval by the RMOs, the final acceptance is made by the Joint Committee of the Regional Metrology Organizations and the BIPM – the JCRB. After this the CMCs of the NMI are stored on the database maintained by the BIPM. The database is publicly available on the internet. As stated previously, participation in key comparison projects is restricted to the signatories of the CIPM MRA. It is also the obligation. If an NMI or DI neglects or refuses participation in a KC for which it has CMCs, or the result of a comparison differs from the KCRV by more than the uncertainty of the result stated by the NMI or DI, the CIPM can withdraw the entries of the CMC. The same holds if the quality system of the laboratory is terminated by the accreditation body or if the quality system is for some reason out of order (www.bipm.org).

Earlier, the body for European collaboration in measurement standards (EUROMET) carried the responsibilities of the RMO in Europe. Since 2007 EUROMET has been known as The European Association of National Metrology Institutes (EURAMET e.V.). EURAMET has formed sub-committees for the specific quantities. In the field of metrology in chemistry, EURAMET and EURACHEM (www.eurachem.org) formed a joint technical committee, Metrology in Chemistry (MetChem). MetChem has four working groups to cover different fields of chemical metrology, i.e., the electrochemistry, organic chemistry, inorganic chemistry and gas groups. MetChem holds technical steering group meetings and sub-committee meetings on an annual basis. The most important items at the meetings are the new or revised entries for the CMC tables, evaluation of the CMCs from other RMOs and preparing and conducting the various types of collaboration. These may be:

- Cooperation in research
- Comparison of measurement standards
- Traceability
- Consultation on facilities.

The NMI directors, in signing the CIPM MRA with the approval of the appropriate authorities in their own country, thereby:

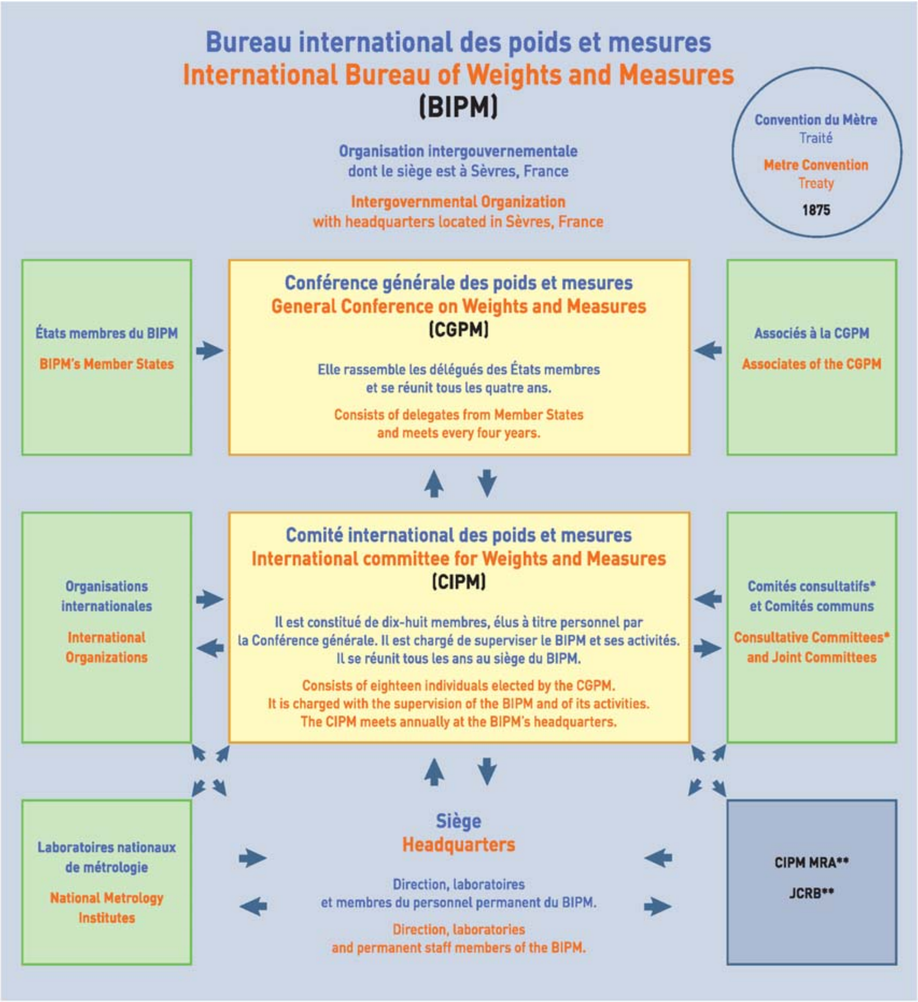
- Accept the process specified in the CIPM MRA for establishing the database;
- Recognize the results of key and supplementary comparisons as stated in the database;

- Recognize the calibration and measurement capabilities of other participating NMIs as stated in the database.

The CIPM MRA obligates NMIs and DIs, but also provides them with the opportunity to make use of the mutual international acceptance of calibration certificates, thus avoiding the unnecessary repeated measurements by every party involved without any loss of reliability in the measurement results. The cost savings achieved with the CIPM MRA have been estimated prior to and after the CIPM MRA per NMI. At the global level, the annual reduction in non-tariff barriers to trade due to the effect of CIPM MRA is estimated to be around $4.2 \cdot 10^9$ € (Kaarls, 2003). Also the responsibility for the results of calibrations and measurements rests wholly with the NMI that makes them and is not, through the CIPM MRA, extended to any other participating NMI. The overall co-ordination of the CIPM MRA is by the BIPM. The Consultative Committees of the CIPM, RMOs and BIPM are responsible for carrying out the key and supplementary comparisons.

In addition to participation in key comparison projects, the NMIs and the designated laboratories participating in the CIPM MRA were engaged to prepare and follow the quality system of the NMIs according to ISO Guide 25 or its equivalent, and to be assessed by an accreditation body. EUROMET adopted ISO/IEC 17025 as the reference standard to cover calibration activities. In agreement with the CIPM MRA, accreditation and self-declaration are considered by EURAMET as equivalent means for NMIs and DIs to obtain confidence in the operation of their quality system (QS). Nowadays EURAMET has a quality technical committee (TCQ), which among its other duties collects information on the QS of each NMI and the designated laboratories on an annual basis. At time intervals of six years the whole QS of the NMI is evaluated by the TCQ to determine whether "the attending NMIs have sufficient confidence in the QS presented and in its ability to fulfil the requirements of the CIPM MRA" (www.euramet.org).

The schematic presentation of the Metre Convention organization is presented in Figure 2.1.



Bureau international des poids et mesures
International Bureau of Weights and Measures
(BIPM)

Organisation intergouvernementale
dont le siège est à Sèvres, France

Intergovernmental Organization
with headquarters located in Sèvres, France

Convention du Mètre
Traité

Metre Convention
Treaty

1875

États membres du BIPM

BIPM's Member States

Conférence générale des poids et mesures
General Conference on Weights and Measures
(CGPM)

Elle rassemble les délégués des États membres
et se réunit tous les quatre ans.

Consists of delegates from Member States
and meets every four years.

Associés à la CGPM

Associates of the CGPM

Organisations internationales

International Organizations

Comité international des poids et mesures
International committee for Weights and Measures
(CIPM)

Il est constitué de dix-huit membres, élus à titre personnel par
la Conférence générale. Il est chargé de superviser le BIPM et ses activités.
Il se réunit tous les ans au siège du BIPM.

Consists of eighteen individuals elected by the CGPM.
It is charged with the supervision of the BIPM and of its activities.
The CIPM meets annually at the BIPM's headquarters.

Comités consultatifs* et Comités communs

Consultative Committees* and Joint Committees

Laboratoires nationaux de métrologie

National Metrology Institutes

Siège
Headquarters

Direction, laboratoires
et membres du personnel permanent du BIPM.

Direction, laboratories
and permanent staff members of the BIPM.

CIPM MRA**

JCRB**

* ▶ Actuellement au nombre de dix, ils sont chargés de conseiller le CIPM et le Siège, notamment sur des questions techniques, et d'aider à l'administration du CIPM MRA.
▶ There are currently ten CCs which advise the CIPM and the Headquarters, e.g. on technical matters, and the administration of CIPM MRA.

** ▶ Le JCRB est le sigle utilisé pour désigner le Comité mixte des organisations régionales de métrologie et du BIPM. Le CIPM MRA fait référence à l'Arrangement de reconnaissance mutuelle du BIPM rédigé par le CIPM.
▶ The JCRB refers to the Joint Committee of the Regional Metrology Organizations and the BIPM. The CIPM MRA refers to the Mutual Recognition Arrangement of the BIPM drawn up by the CIPM.

Figure 2.1. The Metre Convention organization.

2.5. Finnish metrological organization

The Centre for Metrology and Accreditation (MIKES) supports the competitiveness of Finnish trade and industry, and promotes the quality and reliability of national testing and inspection services. (www.mikes.fi). MIKES also participates actively in international co-operation and ensures that Finnish metrology is following international requirements (MIKES, 2002).

Metrology in Finland started at the end of the nineteenth century when the legislation of weights and measures by the Russian emperor, Alexander III, took effect; Finland joined the Metre Convention during 1887-92. The Metre Convention is a treaty signed in Paris in 1875. Russia and Finland were among the first countries in Europe to join the agreement. Prototypes of the metre and kilogram for Finland were purchased in 1890 from the CIPM.

MIKES Metrology realises the SI of measurement units in Finland, performs high-level metrological research and develops measuring applications in partnership with industry. The National Measurement Standard System was established in 1978 by the government decree. The Council of State appointed a number of National Research Institutes and laboratories as National Standards Laboratories (NSL) to be responsible for the maintenance, development and support of the base units and some of the derived SI units. The structure of the National Measurement Standard System is shown in Figure 2.2, including the NSLs and the DIs. The DIs are designated by MIKES Metrology to carry out the calibration services and the maintenance of reference standards for the specific units within their field of expertise. In this respect the Finnish Meteorological Institute is responsible for the gas metrology, especially as it relates to air quality (Document Dnro 165/71/2001 by MIKES Metrology). In Figure 2.3 the traceability chain of the Finnish national and/or the reference standards are presented.

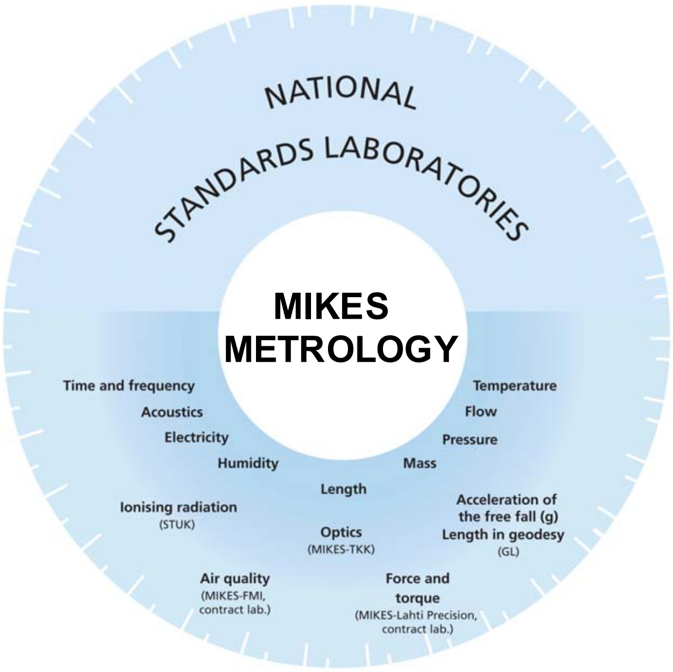


Figure 2.2. The national standards laboratories for the SI base quantities (MIKES Metrology), and those for ionization radiation (the Radiation and Nuclear Safety Authority, STUK), for optics (MIKES-TKK), for acceleration of the free fall (g) and length in geodesy (the Finnish Geodetic Institute, GL), for Force and torque (MIKES-Lahti Precision) and for Air quality (MIKES-FMI) comprise the measurement system in Finland.

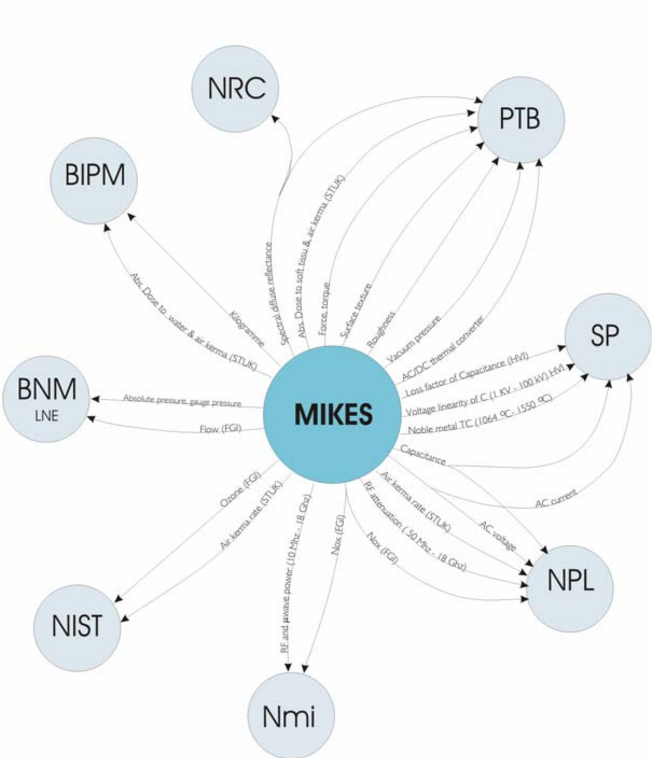


Figure 2.3. The traceability chart of the Finnish reference and/or national standards in 2006.

3. THE CALIBRATION LABORATORY FOR GASEOUS POLLUTANTS

3.1. Task of the laboratory

The Finnish Meteorological Institute (FMI) is a governmental research and service institute. The main objective of the FMI is to provide the best possible information about the atmosphere above and around Finland, to ensure public safety relating to atmospheric and airborne hazards and to satisfy requirements for specialised meteorological products (FMI, 2007).

Among its other duties, the FMI has been nominated as a National Reference Laboratory (NRL) in the field of air quality. The nomination was made according to the environmental protection law (FI-86/2000, 2000) by the Ministry of the Environment. The common duties of the NRLs within the European Union, are set out in *Article 3*, of the Directive on ambient air quality and cleaner air for Europe, Directive 2008/50/EC of the European Parliament and the Council (CAFE-Directive, former Frame Work Directive, 96/62/EC). The scope of the NRL at the FMI covers the service and maintenance of the traceable calibration, sampling and tests of air quality analysers and measurement methods. For more details of the task of the NRL see Appendix 2.

EU-directives approved by the European Parliament (EP), have to be implemented through the legislation of each member state. Therefore the duties set out for the NRLs are in principal the same all over Europe. However, differences in the tasks of an NRL may occur, depending on the structure of the responsibilities for air quality measurements at the national level, e.g., whether or not the air quality measurements are carried out by an NRL. In Finland, local authorities are responsible for maintaining awareness of the air quality situation in their own area and for conducting air quality measurements, while the FMI is responsible for the duties of the NRL.

The most important activities of the NRL are dissemination of a traceable calibration service and organization of intercomparison exercises for local air quality networks, participating in intercomparison exercises organized by the EC and organizing ongoing training for local authorities.

The dissemination of a traceable calibration service is made by direct calibration of the calibration or measurement facilities of the consultants or of the networks that run the air quality measurements. From audits conducted in the air quality networks by the NRL, it has been estimated that the traceable calibrations from the NRL cover more than 98 % of the air quality measurements. The major part (90 %) is covered by consultants, while about 10 % is covered by the networks (Walden et al. 2008).

The NRL has organized two national intercomparison exercises and the field audits for the local networks for gaseous compounds (Walden et al. 2004, Walden et al. 2008). According to the latest comparison, the results of the local air quality networks were very good. In total of 94 % of the measurement results were within the range of "satisfactory" based on the z-score method (ISO GUIDE 43-1, 1997).

As stated in the previous chapter, MIKES designated the FMI for maintaining calibration facilities according to the CIPM MRA (see Ch. 2.4). With this designation the FMI became part of the National Standards Laboratory System, responsible for the duties of a National Standards Laboratory in gas metrology, with emphasis on air quality (see Figure 2.3). The Calibration Laboratory in the Air Quality division (FMI-Calibration Laboratory) is the core of the National Standards Laboratory for gas metrology (MIKES-FMI Standards Laboratory) and is the National Reference Laboratory. The FMI-Calibration Laboratory carries out accreditation on certain calibration methods and gas compounds. In Figure 3.1 the schematic figure on how the different laboratories have been integrated into the FMI-Calibration Laboratory.

The roles of an NRL in the field of air quality and an NSL in the field of metrology combine resources which are feasible. A very comprehensive report of the role and the responsibilities of the NRL have been prepared by P. Woods (2009) where the traceability and the responsibility of the NMI have also been combined. A structure in which an expert laboratory carries the responsibilities of the measurement institutes (metrology institutes) in an area where the NMI has no resources or no plan to recruit resources is met with especially in the field of chemistry (Richter and Güttler, 2003; Taylor, et al., 2004). This structure has also been recognised by the CCQM (CIPM, 2003).

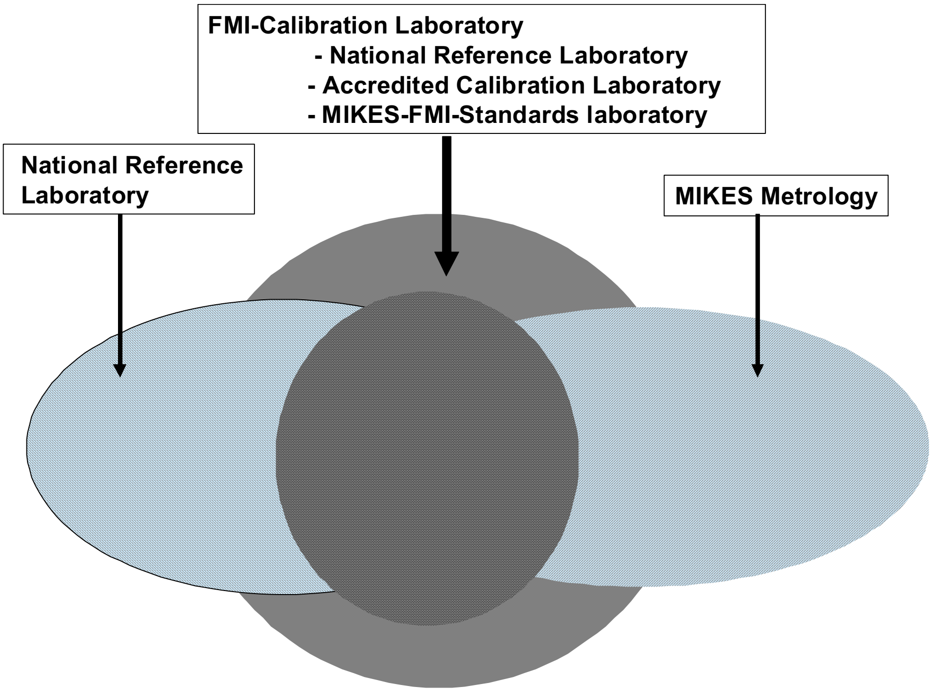


Figure 3.1. Schematic presentation of the integration of the National Reference Laboratory (on the left) and MIKES Metrology (on the right) into the FMI-Calibration Laboratory (large circle in the middle), part of which is accredited (smaller circle in the middle).

The process for designation of the FMI as the NSL in the field of air quality followed the process accepted by the CIPM MRA. It included the inspection of the quality system of the laboratory, assessment of the calibration facilities, traceability and the uncertainty estimation of the measurement results, proof of the measurement capability based on a comparison project (pilot- or key comparison by EURAMET or CCQM), and the competence of the personnel of the laboratory. The inspection was made by Dr. Rob Wessel from the Van Svinden Laboratory (former NMi-VSL) of the Netherlands (Wessel, 2001).

3.2. Quality system of the calibration laboratory

The quality system of the FMI-Calibration Laboratory is constructed according to SFS-EN ISO /IEC 17025 (2005). The laboratory received accreditation in 2001 as a calibration laboratory (Code K043). The surveillance of the accreditation was made by the Finnish Accreditation Service (FINAS). The technical assessment was made by an expert from the Dutch Accreditation Council (RvA). Besides the surveillance by the accreditation body, the quality system was also checked by the TC-Q of the EURAMET through a questionnaire following the requirements of the CIPM MRA.

The quality system of the laboratory includes the quality manual, the standard operation procedures (SOP), and the registers. The quality manual states the quality policy, shows the laboratory organization, responsibilities of the personnel and all the planned actions involved with calibration and the customers.

The standard operation procedures cover all the technical and practical procedures in order to perform the calibration and the measurements of the gas compounds. In addition, training of personnel, calculation of the calibration results and their uncertainties, preparing the calibration certificates, and maintaining the capability of the calibration and measurement method at the level stated by the laboratory have been described in the SOPs. The scope of the accreditation includes the ranges and the uncertainty estimates of the best measurement capability (BMC) for the gas compounds of sulphur dioxide (SO_2), nitrogen monoxide (NO), nitrogen dioxide (NO_2), carbon monoxide (CO), ozone (O_3), benzene (C_6H_6), toluene (C_7H_8), ethyl benzene (C_8H_8), and xylene (o-, and p/m). The calibration and measurement methods are followed by the EN standards and the standard operation procedure (SOP) prepared for the method in the laboratory. The scope of accreditation is shown in Appendix 3.

The laboratory supports registers for all the necessary items that are important for the laboratory. Such registers includes the items of equipment, reference and working standards, training of personnel, register for the intercomparison exercises in which the laboratory has participated and a register of all the documents.

To demonstrate the measurement capability of the laboratory, the laboratory participates in the comparison projects (key-, supplementary-, pilot comparisons) organized by the BIPM, CCQM, and EURAMET or in the intercomparison exercises of the European Commission.

3.3. Traceability of the FMI-Calibration Laboratory measurement results

The traceability chain of the FMI-Calibration Laboratory for the calibration measurement results has been connected to the SI units through a primary method of measurement, through the NMIs, or is traceable to internationally-accepted references. The traceability chain includes all the quantities, (e.g., gas compound, pressure, temperature, gas flow) that make a contribution to the preparation of gas mixtures for calibration purposes in the laboratory. The statement of the traceability of the laboratory measurement results (calibration) is found in the calibration certificate given by the laboratory. The statement covers all the reference standards that are necessary for obtaining the measurement result, and it is ensured that there is no gap in the traceability chain. The strategy of the laboratory is to have the traceability chain to the given SI unit as short as possible.

The measurement standards of the laboratory are divided into reference standards and working standards. The hierarchy of the measurement standards is organized according to the standard operating procedures of the laboratory. The best measurement capability (BMC) of the laboratory is achieved by the use of the highest order of standards and the most accurate calibration methods of the laboratory. The normal procedure is the use of BMC for the calibrations performed for customers, unless otherwise agreed.

The laboratory has reference standards for gas compounds, measurement of the gas flow rate, and measurements of the pressure, temperature, and relative humidity. The traceability chain of the reference standards of the laboratory is shown in Appendix 4.

Working standards are of lower quality than the reference standards, are cheaper, and their expanded uncertainty is larger than that of the reference standard. The working standards are for use where the best quality of the standard is not needed and to save costs where possible. The policy of the laboratory is to define (calibrate) the working standards against the reference standards of the laboratory and to establish the traceability of a working standard to the relevant SI unit.

The reference standards of carbon monoxide (CO), sulphur dioxide (SO_2) and nitrogen monoxide (NO) are gas cylinders labelled as primary reference materials (PRM), certified reference materials (CRM) or secondary reference materials (SRM) depending on the preparation method of the gas mixture. The sources of the uncertainty components for gas standards prepared by a gravimetric method include the uncertainty associated with the method itself, the influence of the inner material of the cylinders, the impurities in the diluents and pure gas and the stability of the gas under test. The traceability of the concentration of the gas cylinders is linked to the base unit through a PMM at the NMI (Alink and van der Veen 2000, Holland et al. 2001).

The reference standard of ozone is the UV-photometric method (ISO 13964, 1998) as realised by the Standard Reference Photometer (SRP) No: 37 of the National Institute of Standards and Technology (NIST, USA). The photometer is the reference instrument for ground level ozone measurements, and fulfils the definition of a PMM (BIPM, 1998). At present, the Bureau International des Poids et Mesures (BIPM) maintains several Standard Reference Photometers by NIST to provide frequent comparison with national ozone photometers (Wielgosz et al. 2003).

The reference standard of nitrogen dioxide is the known concentration of NO_2 obtained by the gas phase titration method (GPT). The GPT method links the reference standards of O_3 and NO through the chemical reaction giving an exact concentration of NO_2 as the reaction product. The method is described in more detail in chapter 3.4.5. The ozone source of the method is calibrated against the ozone standard of the laboratory. The concentration of the NO is prepared from the reference standard of NO.

Gas mixtures of sulphur dioxide and nitrogen dioxide are also prepared by the permeation method. The method can be used as a PMM. However, there are points where the requirement of “the highest metrological qualities” is not always fulfilled. Problems may arise, e.g., from impurity of the source gas or in the stability of the working conditions (temperature, pressure) of the method. Because of this the uncertainty budget of the method is not as good as would be expected.

The hierarchy of the standards used in the calibration laboratory is shown in Appendix 4, while the methods used to determine the working standards in the laboratory are shown in Appendix 5.

3.4. Calibration methods of the FMI-Calibration Laboratory and their uncertainty

For its calibration services the FMI-Calibration Laboratory provides traceability to SI. The uncertainties in the concentrations of the gas mixtures for calibrations have been calculated according to the guideline of the International Standardization Organization (GUM, 1995). For obtaining the calibration concentrations of the gas component, five calibration methods are available in the laboratory: the dynamic dilution method, the permeation method, the static volumetric method, the gas phase titration method (GPT) and the UV-photometric method.

The PMMs, defined by the CCQM that are used in the laboratory are the permeation method, the gas phase titration method, the UV-photometric method by the SRP-37 and the static volumetric method. The accuracies of the permeation method and the static volumetric method are not, however, the best that exist at the laboratory. The dynamic dilution method is more accurate, and is used instead. The laboratory maintains different methods for the preparation of gas mixtures for calibration purposes in order to have flexibility in serving its customers, but also to check the result obtained with another method if some doubts concerning the result exist.

3.4.1. Dynamic dilution method

The dynamic dilution method is used to dilute the gas standard from the gas cylinder (compressed gas) or from the permeation gas source. The dilution is made in two types of gas dilutors operated by the thermal mass flow controllers (ISO 6145/7-2001) or by the critical orifices (ISO 6145/6-1986). Both methods have been evaluated in the laboratory.

Thermal mass flow controllers (MFC) or meters (MFM) are widely used for the measurements of gas flow rate. The flow rates vary from about 5 ml/min to about 500 l/min. The operation is based on the thermal properties of the gas. The gas passes through a tube containing two thermal sensors, of which the first one (the upstream) is heated and the second one is at the gas temperature. The heat loss consequent on the gas flow past the first, heated element creates a temperature difference between the temperature sensors. The temperature difference is proportional to the mass flow of the gas. It depends on the thermal properties of the gas as well as the flow rate. Therefore the temperature difference caused by the mass flow can create a different flow rate because of the different gas properties. Both thermal mass flow controllers and meters use this technique, and are usually designed in such a way that the flow is divided into two laminar flows: a sensor flow and a bypass flow. Only the sensor flow goes through the thermal sensors up to 5 ml/min of the full scale of the flow in order to have correct operation of the temperature sensors. The ratio of the sensor to the bypass flow is constant in order to enable correct calculation of the total flow.

The mass flow controllers are designed to keep the flow rate constant at a pre-set value with the help of the pressure difference between the input and output flow, while the mass flow meter measures the flow in the prevailing conditions.

The performance characteristics of the mass flow controllers and meters have been studied by a number of research groups (Wright and Murdoc, 1994, Tison, 1996) in which the uncertainty of the devices has also been defined (Kruh, 2000 and Goody and Milton, 2002). In addition, an ISO standard for the use of mass flow controllers for the calibration purposes has been set up (ISO 6145/7, 2001). In Appendix 6 the uncertainty calculation for the concentration of gas mixtures prepared by the use of mass flow controllers is described. The standard uncertainty components and the expanded uncertainty of the NO-, SO_2- and CO-gas compounds are presented as a function of gas concentration in Appendix 7.

The other method for obtaining gas calibration concentrations by the dynamic dilution method is the use of critical orifices. The operation of the orifices is based on the characteristics of gas flow through an orifice (nozzle) at the velocity of sound. An ISO standard has been prepared for the use of critical orifices (ISO6145/6, 1986). The performance characteristics of critical orifices have not been evaluated as widely in the literature as have MFCs.

In the case of a critical orifice, a commercial dilution device by LN-Industries (Sonimix 6000 A1, 1998) is used. The schematic layout of the dilution method is shown in Figure 3.2.

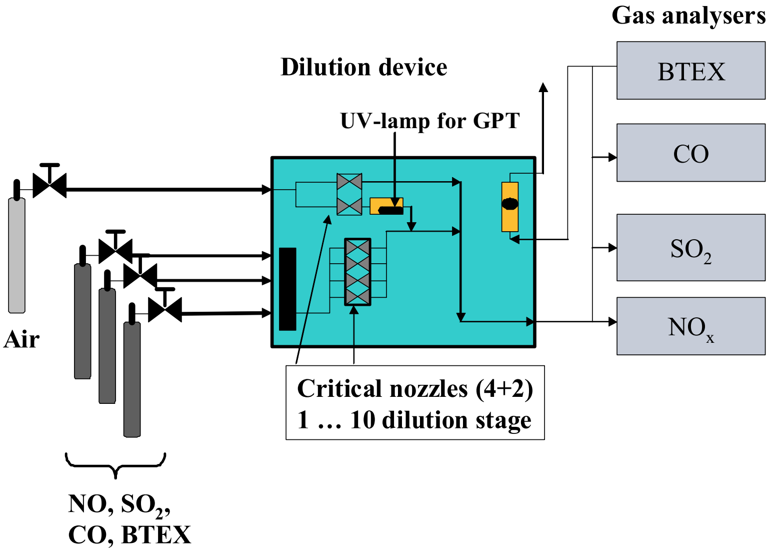


Figure 3.2. The schematic layout of the dynamic dilution system operated by the Sonimix 6000 A1. The device is equipped with four critical nozzles for the CRM and two for the dilution gas giving ten different dilution stages.

The mass flow (q_m) passing isotropically through the sonic orifice provided that the critical conditions across the orifice are fulfilled, i.e., the ratio of upstream pressure to downstream pressure exceeds the value of 2 and the ratio of the diameter of the orifice to the diameter of the upstream tube remains below 0.2, can be expressed in the form (Landau, Lifshitz, 1987)

$$q_m = A_c C_d \cdot \frac{p_1}{\sqrt{T_1}} \cdot \sqrt{\frac{M}{R}\gamma\left(\frac{\gamma}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} = \frac{m}{t} \tag{3.1}$$

where

q_m = mass flow

A_c = the cross-section area of the sonic nozzle

C_d = the concentration coefficient of the gas jet (discharge coefficient)

p_1 = upstream pressure, absolute (hPa)

T_1 = upstream temperature (°K)

M = molar mass of the gas

γ = ratio of the mass thermal capacities c_p/c_v

R = gas constant of an ideal gas

m = mass of the gas flow

t = time

From Equation (3.1) one can see that the mass flow through the sonic nozzle depends on the upstream temperature and pressure, and, that the coefficient A_cC_d depends on the characteristics of the flow dynamics and the geometry of the nozzle.

Equation (3.1) can be expressed in the form (ISO 6145-6 1986):

$$q_m = A_c C_d C^* \cdot \frac{p_1}{\sqrt{T_1}} \tag{3.2}$$

Where from Equation (3.1) the coefficient C^* is:

$$C^* = \sqrt{\frac{M}{R}\gamma\left(\frac{\gamma}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}}, \tag{3.3}$$

and depends on the thermal properties of the gas (the ratio of c_p/c_v).

By applying Equation (2.4) to Equation (3.2) one can express the variance u_c^2 in the form:

$$u_c^2 = \left(\frac{u(A_c)^2}{A_c^{\,2}} + \frac{u(C_d)^2}{C_d^2} + \frac{u(C^*)^2}{C^{*2}} + \frac{u(p_1)^2}{p_1^{\,2}} + \frac{1}{2}\cdot\frac{u(T_1)^2}{T_1}\right)\cdot q_m^2 . \tag{3.4}$$

where $u(A_c)^2$, $u(C_d)^2$, $u(C^*)^2$, $u(p_1)^2$, and $u(T_1)^2$ are the variances of the cross-section area of the nozzle A_c, the discharge coefficient C_d, the coefficient of C^*, the upstream pressure p_1, and the upstream temperature T_1, respectively. The combined standard uncertainty u_c of Equation (3.4) has to be calculated for each of the sonic nozzles. The nozzle in the Sonimix 6000 A1 are produced individually, and no clear definition of the cross section area of the nozzle, A_c, is given. Instead, the uncertainty of the flow through the nozzle can be measured by flow measurements. Therefore a different approach is used here.

In the following the contribution of the uncertainty of the critical nozzles to the concentration levels is calculated. The calibration concentration of a single dilution stage in the Sonimix 6000 A1 can be calculated according to

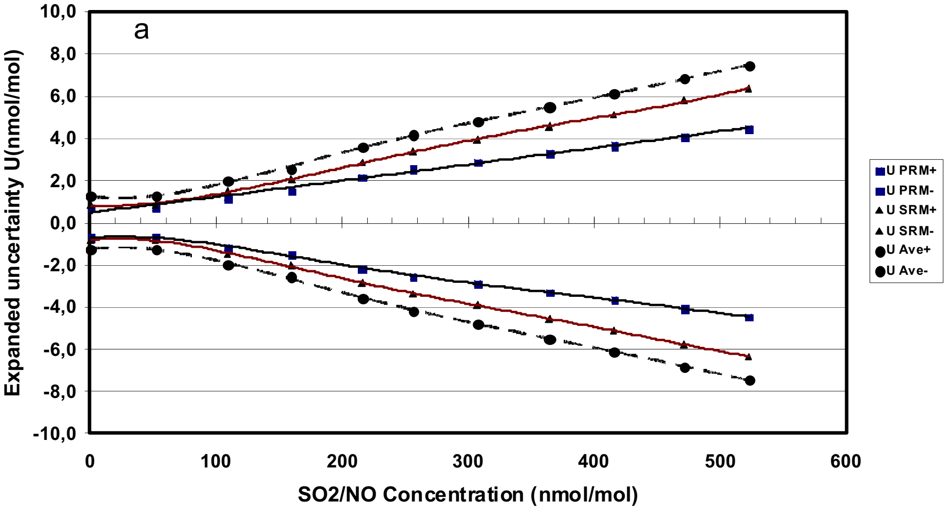
$$C(i) = \frac{f(i)_{\text{span}}}{f(i)_{\text{span}} + f_{\text{dil}}} C_{ST} + \frac{f_{\text{dil}}}{f(i)_{\text{span}} + f_{\text{dil}}} C_{\text{dil}} \tag{3.5}$$

Where $C(i)$ is the concentration (mole fraction) at dilution stage i (i =1, …, 10), C_{ST} is the concentration (mole fraction) of the gas standard, C_{dil} is the impurity (mole fraction) of the dilution gas (zero gas) and f_{tot} is the total flow rate, $f_{\text{tot}} = f_{\text{span}} + f_{\text{dil}}$ [ml/m^3]. The span flow rate, $f(i)_{\text{span}}$ [ml/m^3] and the dilution flow rate $f(i)_{\text{dil}}$ [ml/m^3] are obtained from the truth table of the manual (Sonimix 6000 A1, 1998). The exact equation for the calibration level, $C(1)$, is presented in Appendix 8. When the functions describing the concentrations of the each dilution stages are known, the variances of the dilution steps can be calculated according to Equation (2.4). The covariance terms in Equation (2.4) can be omitted as second-order term, which simplifies the variance of the first dilution stage to the form:

$$u(C(1))^2 = \left(\frac{C_{ST}}{f(bs1) + f(bs2)}\right)^2 u(bs4)^2 + \left(\frac{f(bs4) \cdot C_{ST}}{(f(bs1) + f(bs2))^2}\right)^2 (u(bs1)^2 + u(bs2)^2) + \left(\frac{f(bs4)}{f(bs1) + f(bs2)}\right)^2 u(C_{ST})^2 + u(C_{dil})^2 \tag{3.6}$$

where the flow rates *f(bsi)* of the sonic nozzles are from the truth table (see in Appendix 8). The variances of the standard uncertainty components $u(bsi)^2$, $u(C_{ST})^2$ and $u(C_{dil})^2$ need to be calculated or estimated. All the partial derivatives needed for Equation (3.6) are shown in more detail in Appendix 8, as also are the standard uncertainties by components.

The expanded uncertainty for the calibration concentrations obtained by the Sonimix 6000 A1 dilutor is shown in Figures 3.3a and b. The calibration capability is calculated using the highest quality of the gas standard, the primary reference material (PRM), having an expanded uncertainty of 0.5 %. The second highest quality of the gas standard, secondary reference material (SRM), has an expanded uncertainty of 1.0 %. The average calibration capability (Ave) is the mean of the best and the normal operation of the laboratory. The concentrations of the PRM and the SRM standards for sulphur dioxide and nitrogen monoxide are 100 μmol/mol, and the expanded uncertainty of the calibration capability is shown in Figure 3.3.a. For carbon monoxide the concentrations of the PRM and SRM are 10 mmol/mol, and the calibration capability is shown in Figure 3.3.b



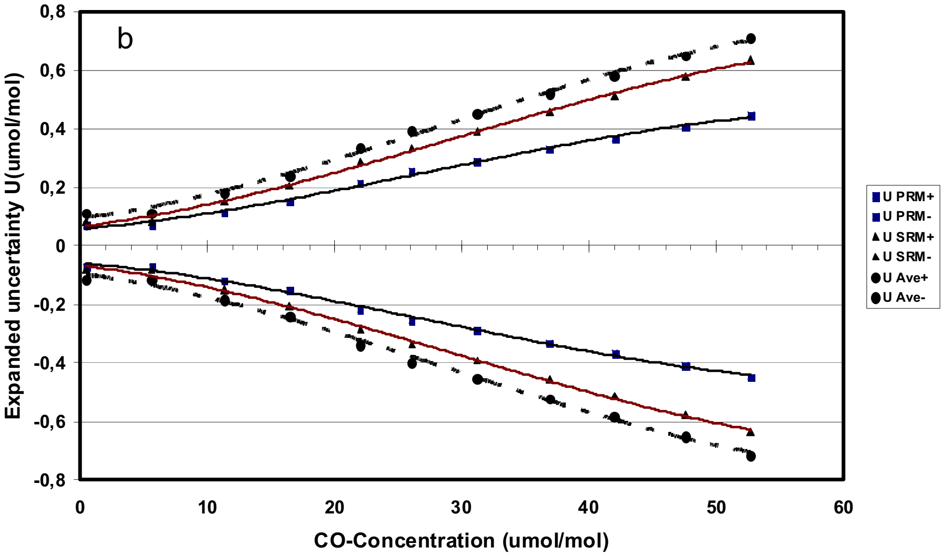


Figure 3.3a-b. The expanded uncertainties of the calibration concentration of sulphur dioxide (SO_2) and nitrogen monoxide (NO) produced in the calibration concentration range of 0 to 500 nmol/mol (Figure 3.3a) and of carbon monoxide (CO) in the calibration concentration range of 0 to 50 µmol/mol (Figure 3.3b). The best measurement capability is U PRM, the second-best is U SRM and the third is U Ave.

From the Figures 3.3a and b, the calculated relative expanded uncertainty is about 0,8 % for the best measurement capability. This means that the uncertainty of dilution and the uncertainty of the impurity of the dilution gas are of the same order as the gas standard. This has been the advantage of the use of the SRM instead of the PRM. There are not many improvements foreseen regarding the uncertainty of the dilution method. An accurate analysis of the impurities, e.g., by Fourier transform infrared spectroscopy (FTIR-analysis) can provide a better method for quantifying the amount of impurities and therefore also for decreasing the estimated uncertainty contribution to the uncertainty budget.

The Sonimix 6000 A1 is calibrated in the laboratory two to four times a year. In addition, one of the dilutors has been calibrated twice at MIKES and twice at LNE (France). The calibrations of the Sonimix 6000 A1 at MIKES and at LNE were based on the measurement of flow rates through the sonic orifices by synthetic air (dilution line) and by nitrogen (gas line). In the laboratory, the calibration of the Sonimix 6000 A1 has been carried out with the calibrated CO-analyser. Calibration of the analyser has been done with zero gas and with a CO-standard (PRM) with a nominal concentration so low that it has been injected directly into the analyser. The results of the calibrations of the dilutor are shown in chapter 5.

3.4.2. Permeation method

The phenomenon of a gas or vapour penetrating through a membrane, i.e., an elastic material is fairly familiar, e.g., the loss of helium from a balloon or the gas exchange through the wall of a living cell. The penetration of the gas or vapour depends on the membrane material and the gas itself. In permeation the following processes occur (Amman, 1998):

- Absorption of the gas molecules into the membrane material (entry side)
- Dissolving of the gas molecules in the membrane material
- Diffusion of the gas molecules through the membrane in the direction of decreasing concentration and pressure
- Desorption on the gas component (exit side).

Permeation of a gas through a membrane is a widely-used method for the preparation of gas mixtures for calibration purposes. The permeation takes place in a tube, in which the source is in the liquid phase. The tube is tightly closed at both ends, but in the tube wall there is a membrane, through which the gas can permeate out of the tube. The tube is installed in a vessel through which the carrier gas passes, flushing the permeated gas, and causing a gradient of gas concentration between the tube and the vessel. The vessel is kept in a temperature-controlled oven (water bath, block of concrete) in order to maintain constant conditions (temperature, pressure) for the tube. As a result of the stationary conditions, the permeation rate of the gas through the membrane is constant.

The permeability, P, through the membrane of the tube can be expressed as:

$$P = D \cdot S, \tag{3.7}$$

Where D is the diffusion coefficient of the gas and S is the solubility of the membrane. The unit of permeability through the membrane is formed: [the amount of substance·thickness of material/(time·surface area·partial pressure difference)]. Therefore large variety of units can be used for P, e.g., [mol mm/(min cm^2 hPa)]. There are many materials, that have been tested for permeation (see ISO 1629) as well as various gas components (Polymer Handbook, 1989). The laboratory maintains two different configurations of the permeation method. In the conventional method, the permeation rate (mass per unit time) of the gas is defined by weighing the tube at regular intervals and calculating the loss of mass of the contents over the period between two consecutive weighings. The method is well described by the ISO standard (ISO 6145-7 2001). The magnetic suspension method, which is the other permeation method in use at the laboratory, measures the loss of the gas by a continuous weighing of the permeation tube on a balance (Knopf, 2001)

The permeation method can fulfil the criteria for a PMM (see Ch. 2.4) and therefore the gas component is directly traceable to the SI. One of the most difficult tasks in the operation of the method relates to the environmental conditions (temperate, pressure and flush flow) in the permeation oven. These need to be kept constant during the period between consecutive weighings of the tube. The time between two consecutive weighings can vary from some weeks to some months depending on the size of the tube, the tube material and the sensitivity of the balance. In addition, the amount of impurities in the gas can be problematic if not known. In the magnetic suspension method, where the weighing of the permeation tube is continuous, a change in environmental conditions can be directly observed as a change in the permeation rate. The method has been used in a few metrological institutes in Europe. A very detailed study including the uncertainty budget associated with the method has also been published (Knopf, 2001). The magnetic suspension method of the laboratory is undergoing the validation process, and the results are not discussed here. Instead, a description of the conventional permeation method is given below.

The calibration laboratory of the FMI is equipped with a conventional permeation device by Kin-Tek (Model 491M-B Operation manual, 1996). The device consists of a permeation oven and the gas dilution unit. The dilution of the gas concentration into an exact gas concentration is performed by the dynamic dilution method operated by mass flow controllers. Calibration gases of sulphur dioxide and nitrogen dioxide are obtained with the method. The schematic layout of the permeation apparatus used in the laboratory is shown in Figure 3.4.

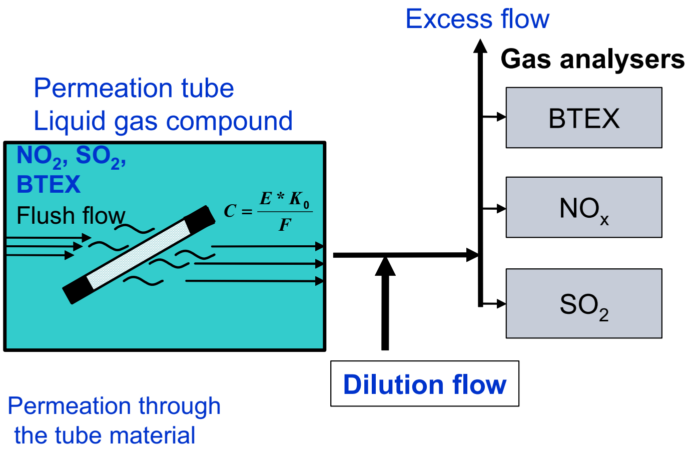


Figure 3.4. Principle of the conventional permeation apparatus.

The sources of error linked to the permeation method are for the following:

1) Impurities in the permeation gas source and in the flush and dilution gases.
   - The manufacturer of the tube should analyse the gas content for possible impurities (for example by Gas Chromatograph, GC, or Fourier Transform Infra Red Spectrometer, FTIR) and the results should be reported in the tube certificate. Impurities in the tube cause a higher apparent emission rate, as measured by weighing, than the actual rate of transfer of the permeation gas.
   - Impurities in the flush and dilution gases can either be the same gas component as the permeation gas or cause a similar response in the analyser as the permeation gas. The impurities in the flush and dilution gases can be removed/reduced using different types of filter cartridges. Known impurities can be taken into account when preparing the uncertainty calculations.

2) The emission rate of the permeation tube is determined wrongly.
   - The balance used for the weighing of the permeation tube is not calibrated
   - If the mass of the air replaced by the volume of the tube is large enough to affect weighing result, the effect of buoyancy needs to be taken into account. Similarly if the environmental conditions (temperature, pressure, and humidity) in the weighing room differ considerably between the consecutive tube weighings, the buoyancy effect should take into account.

The mass of the permeation tube as weighed with the balance can be expressed as $m_{pt} = m_w - \rho V$, where m_{pt}, is the mass of the permeation tube, m_w, is the weighing result and the last term, ρV, is due to the buoyancy. The true loss of mass of the permeation tube between the two consecutive weighings can be calculated according to the equation:

$$\Delta m = m_{w1} - m_{w2} + (\rho_1 - \rho_2)V_{\mathrm{rf}}\,, \tag{3.8}$$

where

m_{w1} and m_{w2} are the results of consecutive tube weighings,

ρ_1 and ρ_2 are the respective air densities in the weighing room during the consecutive weighings, and

V_{rf} is the volume of the permeation tube.

3) The environmental conditions in the permeation oven (the temperature, and the humidity and pressure of the flush gas), have not been kept constant.

- A change in the oven temperature changes the emission rate of the permeation tube. The change of temperature should be within ± 0.1 ºC in order to keep the changes in permeation rate acceptable (Scaringelli et al, 1970). Larger temperature fluctuations change the permeation rate by an order of several percentiles. To avoid a change in emission rate, the temperature of the oven is set well above room temperature, is thermostatically controlled and is measured continuously. The flow rate through the oven is stabilized with a critical orifice and recorded with a flow meter.

The calibration concentration obtained by the permeation method can be expressed according to the equation:

$$C = \frac{E \cdot K_o}{F} \tag{3.9}$$

where C is the output concentration (mole fraction), E is the permeation rate (ng/min), K_o is a coefficient for converting the mixing rate by volume into mass concentration, and F is the dilution (= F_d + F_s) gas flow (l/min). The coefficient K_o can be expressed in the form:

$$K_o = \frac{V_M}{M} \tag{3.10}$$

where V_M is the molar volume (= 22.4 l) and M is the molecular weight of the compound at NTP.

Taking into account the impurity of the dilution gas, Equation (3.9) can be expressed as:

$$C = \frac{E \cdot K_o}{F} + C_o , \tag{3.11}$$

where C_o is the amount of impurity (mole fraction) in the dilution gas or in the flush gas. Following the same procedure as above, the quadratic term of combined standard uncertainty can be expressed in the form (for more details, see Appendix 9):

$$u_p^2 = \left(\frac{K_o}{F}\right)^2 \cdot u_E^2 + \left(\frac{K_o E}{F^2}\right)^2 \cdot \left(u_{Fs}^2 + u_{Fd}^2\right) + u_{Co}^2 =$$

$$\left(\frac{K_o E}{F}\right)^2 \cdot \left[\left(\frac{u_E}{E}\right)^2 + \left(\frac{u_{Fs}}{F}\right)^2 + \left(\frac{u_{Fd}}{F}\right)^2\right] + u_{Co}^2 \tag{3.12}$$

where the quadratic term of the standard uncertainty of the permeation gas, u_p^2, depends on the output of the permeation tube (u_E^2), the dilution and flush flows (u_{Fs}^2 and u_{Fd}^2) and the impurity of the dilution gas (u_{Co}^2).

The loss of mass of the permeation gas source determined by weighing can be rewritten from Equation (3.8):

$$\Delta m = m_{\mathrm{pg}} + m_{\mathrm{pi}} + \left(\rho_1 - \rho_2\right) \cdot V_{\mathrm{rf}} = m_{\mathrm{pg}} + m_{\mathrm{pi}} + m_{\mathrm{buo}} \tag{3.13}$$

where m_{pg} is the mass of the permeated gas, m_{pi} is the mass of the possible impurity in the permeation source, and m_{buo} is the mass of air involved in the buoyancy. Note that if $m_{\mathrm{pi}} = 0$, then $m_{\mathrm{pg}} = m_{w1} - m_{w2}$.

The standard uncertainty of the output of the permeation tube (u_E^2) can be expressed according to Equation (2.5) in the form (see in Appendix 9):

$$u_E^2 = \left(\frac{1}{\Delta t}\right)^2 \cdot \left[u_{\mathrm{pg}}^2(m) + u_{\mathrm{pi}}^2(m) + u_{\mathrm{buo}}^2(m) + (m_{\mathrm{pg}} + m_{\mathrm{pi}} + m_{\mathrm{buo}})^2 \cdot \left(\frac{u_{\Delta t}}{\Delta t}\right)^2\right] \tag{3.14}$$

where Δt is the time interval between two consecutive weighings of the permeation tube, and $u_{\Delta t}$ is the uncertainty in the time interval.

Next the effect of buoyancy is considered more closely. The density of air depends on its ambient pressure, temperature and humidity. The correction term for air density was studied by Jones (1978), and amended in further studies by other researchers (Giacomo, 1982; Davis, 1992). The air density can be calculated starting from the ideal gas law and applying the compressibility factor (Z) to the reference of real gas ($pV = nZRT$). The molar mass of an air molecule can be written in the form $M_{air} = (1-x_v)M_a + x_vM_v$, where x_v is the mole fraction of water vapour, M_a is the molar mass of dry air and M_v is the molar mass of moist air (M_v). The density of air ($\rho = m/V = pM/ZRT$) can be expressed as follows (Giacomo, 1982):

$$\begin{aligned}\rho_{air} &= \frac{pM_a}{ZRT}\left[1 - x_v\left(1 - \frac{M_v}{M_a}\right)\right] \\ &= \frac{a_1}{T}\left[p - a_2 H \exp(AT^2 + BT + C + \frac{D}{T})\right]\end{aligned} \tag{3.15}$$

where the last identity was proposed by the Working Group of the CCM in 1976 and published by the BIPM in French (BIPM, 1981) and in English (Giacomo, 1982). The values of the coefficients are as follows: $a_1 = 3.48488\ 10^{-3}$, and $a_2 = 0.37952$ are constant and $A = 1.2811805 \times 10^{-5}\ K^{-2}$, $B = -1.9509874 \times 10^{-2}\ K^{-1}$, $C = 34.04926034$ and $D = -6.3536311 \times 10^{3}\ K$ are correction parameters that were defined by the Working Group of the CCM. The parameters from A to D were updated following a better determination of the molar gas constant, R, in 1991 (Davis 1992). A more detailed description of the behaviour of the compressibility of the air is presented in Appendix 10.

The mass of air of volume V_{pt} that is displaced by the volume of the permeation tube can be calculated from:

$$m_{buo,i} = (\rho_{air,i} - \rho_{air,i+1})V_{pt} \tag{3.16}$$

The effect of buoyancy can be estimated by calculating the maximum and minimum values of air density between the consecutive weighings according to Equation (3.15). In Table 3.1 the air density is presented at three different water contents (30 %, 50 % and 70 %) between temperatures of 293 to 303 K and ambient pressures of 95 kPa, 100 kPa and 105 kPa.

Table 3.1. The density of moist air calculated according to Equation (3.15) at different pressure (kPa), mole fractions of water (x_v) and temperature (K).

P(kPa)	**95**	**100**	**105**	**95**	**100**	**105**	**95**	**100**	**105**
Xv	**0.3**	**0.3**	**0.3**	**0.5**	**0.5**	**0.5**	**0.7**	**0.7**	**0.7**
Temp (K)									
293	*1.007*	*1.060*	*1.113*	*0.929*	*0.978*	*1.027*	*0.854*	*0.898*	*0.943*
294	*1.004*	*1.056*	*1.109*	*0.926*	*0.975*	*1.023*	*0.850*	*0.895*	*0.940*
295	*1.000*	*1.053*	*1.105*	*0.923*	*0.971*	*1.020*	*0.847*	*0.892*	*0.936*
296	*0.997*	*1.049*	*1.102*	*0.919*	*0.968*	*1.016*	*0.844*	*0.888*	*0.933*
297	*0.993*	*1.046*	*1.098*	*0.916*	*0.964*	*1.012*	*0.841*	*0.885*	*0.929*
298	*0.990*	*1.042*	*1.094*	*0.913*	*0.961*	*1.009*	*0.837*	*0.882*	*0.926*
299	*0.986*	*1.038*	*1.090*	*0.909*	*0.957*	*1.005*	*0.834*	*0.878*	*0.922*
300	*0.983*	*1.035*	*1.087*	*0.906*	*0.954*	*1.002*	*0.831*	*0.875*	*0.919*
301	*0.980*	*1.031*	*1.083*	*0.903*	*0.950*	*0.998*	*0.828*	*0.872*	*0.915*
302	*0.976*	*1.028*	*1.079*	*0.900*	*0.947*	*0.994*	*0.825*	*0.868*	*0.912*
303	*0.973*	*1.024*	*1.076*	*0.897*	*0.944*	*0.991*	*0.822*	*0.865*	*0.908*

As one can see from Table 3.1, the density of the air varies with air pressure, air temperature and water content. The maximum air density under the conditions shown in Table 3.1 is 1.113 g/dm^3 (T = 293 K, P = 105 kPa and x_v =0.3) while the minimum value is 0.822 g/dm^3 (T = 303 K, P = 95 kPa and x_v = 0.7). The difference of the air density is then 0.3 g/dm^3. The volume of the permeation tubes is about 3 cm^3. According to Equation (3.16), the mass of the displaced air is then 0.6 mg, which is about 1.5 % of the loss of the gas between adjacent weighings. If the environmental conditions changes that much the buoyancy effect is the same order as the expanded uncertainty of the method. On the other hand the effect of buoyancy has very little influence on the result of the weighing of the permeation tube when the pressure and water content are kept constant in the weighing room, even though the temperature changes by a few degrees Celsius. In the literature few examples of the calculation of the buoyancy from Equation (3.12) exist (Alink and van der Veen, 2000; Alink, 2001).

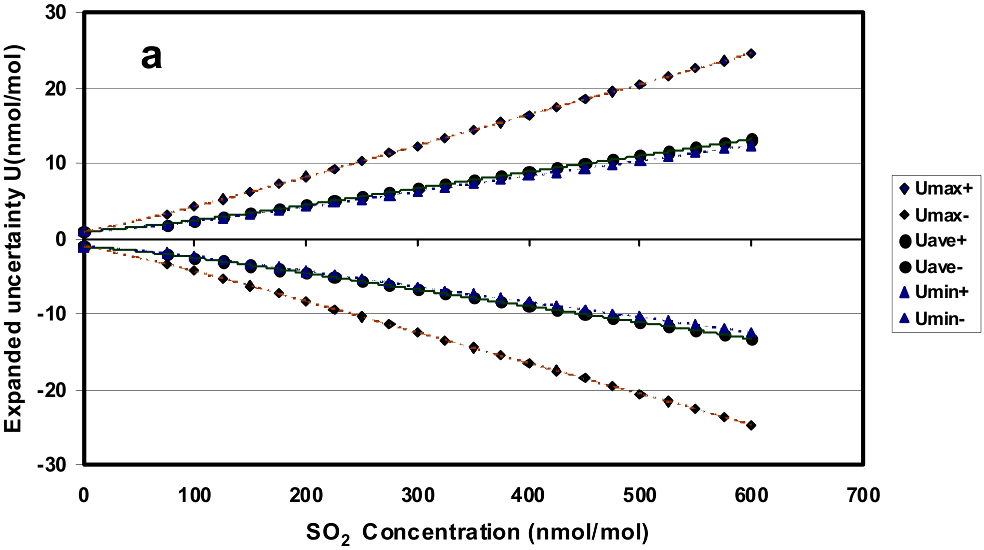
If the impurity in the permeation gas is negligible and if the buoyancy effect in weighing the tube can be neglected, Equation (3.14) is simplified and the Equation (3.12) can be rewritten in the form:

$$u_p^2 = \left(\frac{K_o E}{F}\right)^2 \cdot \left[\left(\frac{u_E}{E}\right)^2 + \left(\frac{u_{Fs}}{F}\right)^2 + \left(\frac{u_{Fd}}{F}\right)^2\right] + u_{Co}^2 =$$

$$= \left(\frac{K_o E}{F}\right)^2 \cdot \left[\left(\frac{m_{\mathrm{pg}}}{E \cdot t}\right)^2 \cdot \left[\left(\frac{u_{\mathrm{pg}}(m)}{m_{\mathrm{pg}}}\right)^2 + u_t^2\right] + \left(\frac{u_{Fs}}{F}\right)^2 + \left(\frac{u_{Fd}}{F}\right)^2\right] + u_{Co}^2 \qquad (3.17)$$

where the variance of the standard uncertainty, u_E^2, depends on the variances associated with the mass of the permeation source and the time interval between the consecutive weighings of the tube. The uncertainty of the flush flow (u_{Fs}) is taken from the certificate of the critical nozzles, and the uncertainty of the dilution flow (u_{Fd}) is calculated from the flow meter of the dilution device (Kin-Tek 491M or Environnement MGC 101 depending on the dilution configuration).

The values of the standard uncertainties obtained for each of the uncertainty components associated with the uncertainty budget of the permeation method are given in Appendix 11. The expanded uncertainty of the permeation method as a function of the produced calibration concentration is shown in Figures 3.5a and b at different values of the accuracy of the measurements (min, max values).



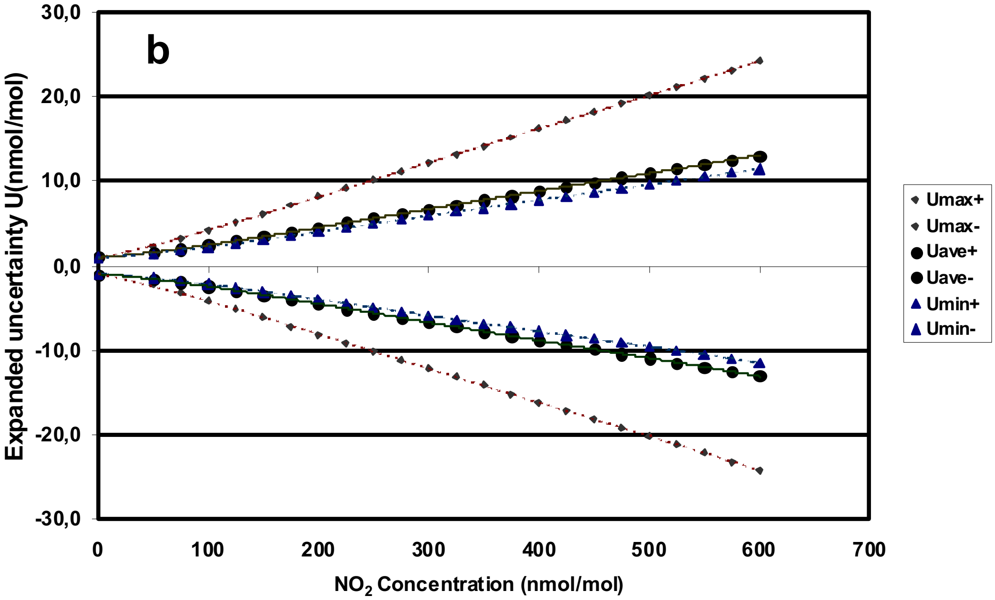


Figure 3.5 a to b. The expanded uncertainty of the produced calibration concentration of sulphur dioxide (SO_2) in the calibration concentration ranges from 75 to 600 nmol/mol (Figure 3.5a) and of nitrogen dioxide (NO_2) in the calibration concentration ranges from 50 to 600 nmol/mol (Figure 3.5b). The curve U_{min+-} indicates the best measurement capability and U_{max+-} the worst measurement capability of the method used. The parameters used in the calculations are listed in Appendix 11.

3.4.3. Static volumetric method

The use of the static volumetric method can provide a PMM for the preparation of gas mixtures for calibration purposes. The static volumetric method has been used routinely for more than 20 years at the Pilot Station of the Federal Environmental Agency of Germany (UBA(D)). Since its introduction there, the method has also been adopted at several other environmental laboratories in Europe. The method has been evaluated and described in detail by a VDI-standard (VDI 3490, 1994) and an ISO-standard (ISO 6144, 2003). The uncertainty calculation of the static volumetric method has been analysed by the European Reference Laboratory of Air Pollution, ERLAP, (Gerboles et al 1998). The basic idea of the static volumetric method is to prepare a known concentration of gas mixture by dilution of pure gas of known volume with dilution gas of known volume. The mixing of the two components takes place in a vessel of known volume at a known pressure and temperature. The volume fraction of the prepared gas mixture is calculated according to the following equation (ISO 6144, 2003 or VDI 3490, 1994):

$$C_v() = C_v(g_s) \cdot \frac{p_s \cdot V(g_s)}{p_d \cdot V(g_d) + p_s \cdot V(g_s)} \approx C_v(g_s) \cdot \frac{p_s \cdot V(g_s)}{p_d \cdot V(g_d)} \tag{3.18}$$

where

$C_v()$ is the concentration of the calibration gas by volume fraction obtained with the volumetric static chamber,

$C_v(g_s)$ is the concentration of the pure gas (span gas) by volume fraction,

p_s is the pressure of the gas mixture in the mixing chamber when injecting the pure gas,

p_d is the pressure of the gas mixture in the mixing chamber at the end of the filling of the chamber with the dilution gas,

$V(g_s)$ is the volume of the injected pure gas component referred to the same temperature as that of the mixing chamber,

$V(g_d)$ is the volume of the dilution gas in the mixing chamber.

The right-hand side of Equation (3.18) is the approximation when $V(g_d) >> V(g_s)$. Conversion from the unit of volume fraction into the unit of mole fraction is made according to:

$$C() = C_v(g_s) \cdot \frac{p_s \cdot V(g_s) \cdot V_m(g_d)}{p_d \cdot V(g_d) \cdot V_m(g_s)} \tag{3.19}$$

where $C()$ is the concentration of the calibration gas by mole fraction, $V_m(g_d)$ and $V_m(g_s)$ are the molar volumes of the diluent gas and the gas compound, respectively.

There are two basic types of static chambers, one operated slightly above ambient pressure (up to 1.5 bars) and the other one working at a still higher pressure (up to 10 bars). The first types of static chambers are made of glass, mostly borosilicate glass, while the others are made of stainless steel with a proper treatment of the surface, or of some other material suitable for the purpose. In general the size of the glass vessel is 100 l or larger, while the volume of the stainless steel vessel is 10 l to 50 l. The volume of the available gas mixtures for calibration purposes is of the same order in both vessels.

The use of a static injection chamber as a PMM relies on the fact that the concentration of the prepared gas mixture in the chamber can be traced to SI, i.e., the volume of the chamber, the volume of the syringe, and the pressure and temperature meters of the static chamber. The purity of the gas component (= 100 %) and the purity of the dilution gas can be estimated based on chemical analysis, and the complete uncertainty budget can be prepared from Equations (3.18) and (3.19).

Both the static chambers at the FMI are made of stainless steel. One is coated with ceramics while the other is untreated. The ceramic chamber was found to be not inert with sulphur dioxide, but works well with nitrogen monoxide and carbon monoxide. The problem with the ceramic chamber with sulphur dioxide is the adsorption of the sulphur dioxide onto the wall of the chamber. In the case of nitrogen monoxide, a certain amount of nitrogen dioxide and nitric acid (HNO_3) can be formed inside the chamber due to the reaction with water vapour (Froelich, 2007). The uncoated stainless steel chamber was also found to face the same problems as the ceramic chamber, although the adsorption of the sulphur dioxide was not so severe. Both of the chambers worked well with carbon monoxide. The volume of the ceramic chamber was determined by a volumetric method at the reference laboratory of the UBA(D). The volume of the other chamber was defined by a direct comparison of the concentrations with a gas analyser: a gas mixture was prepared both with the ceramic chamber and with the uncoated stainless steel chamber, using the same volumes of pure gas and filling the chambers with the dilution gas at the same pressure.

The schematic of the static chamber is shown in Figure 3.6. The vacuum pump is for evacuation of the gas mixture from the chamber prior to injecting a new concentration of the gas or when changing the gas component. The dilution gas can be either air (synthetic or pressurised air) or nitrogen. The syringe is used to inject the pure gas into the chamber.

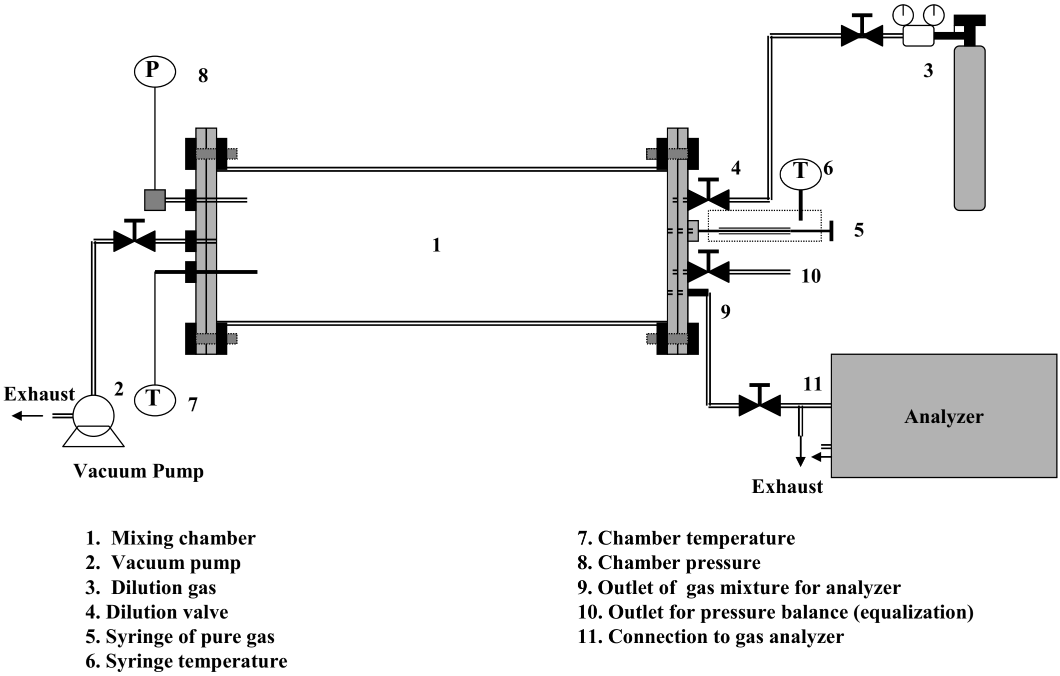


Figure 3.6. Schematic presentation of the static volumetric system. The vessel is made of stainless steel but coated with ceramics.

It can be stored in a reservoir in order to have the same temperature as that of the chamber, but the needle needs to close, in order to prevent the diffusion of pure gas from taking place. Preparation of the known volume of the pure gas in the syringe is made at a separate filling station. The operation of the filling station for preparing the pure gas component must be carried out inside a ventilation chamber. A photograph of the filling station is shown in Figure 3.7.

The operating principle of the static injection system is as follows. Before the preparation of the gas mixtures for calibration purposes, the chamber has to be evacuated and filled with dilution gas at least three times in order to be sure that the chamber is clean after previous use. After this, the chamber is filled with dilution gas up to the ambient pressure. By opening the balance valve (10, see Figure 3.6), the equilibrium with the environment pressure is reached. The balance valve is then closed, and pure gas is injected with a syringe into the chamber through the septum. One should be aware of the loss of pure gas in the needle of the syringe by diffusion immediately after preparation, so the injection should take place within a few seconds after filling (Gerboles et al. 1998). After the injection of the pure gas, dilution gas is added up to a certain pressure to reach the correct volume for the desired gas concentration. After reaching equilibrium with the environment temperature, the actual concentration of the gas mixture can be calculated according to Equation (3.18). The gas mixture is ready to use for calibration purposes. For this operation, the valve in the outlet line (9) is opened and connected to the sample inlet of the analyser via a T-connector in order to decrease the sample pressure to the ambient value. With a regulation valve the flow rate from the chamber can be adjusted to provide at least 20 % of excess flow compared to that of the sample flow to the analyser.

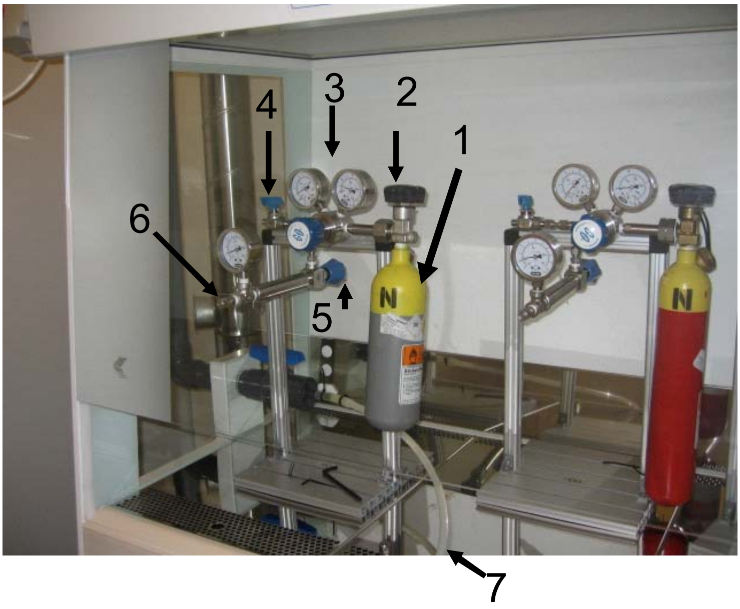


Figure 3.7. A photograph of the station for filling the pure gas syringe. For the numbers, see the text.

The purpose of the filling station is to fill the syringe with the precise volume of pure gas to be injected into the mixing chamber, as described above. The filling station comprises a gas cylinder of pure gas (1), a pressure manometer for the gas cylinder (2), a pressure regulating valve (3), a ball valve (4), a gas stock valve (5), a stock volume for sample gas for filling the syringe (6), and a vacuum pump (7). The reservoir (6) needs to be filled and evacuated at least five times with the pure gas before filling the syringe with a known volume of pure gas (from a few *μl* up to a few tens of *ml*). The filling of the reservoir is made by closing the ball valve (4) and valve (3) and opening the valve of the gas cylinder (1). This will pressurize the connection tube between the valve (3) and the gas cylinder. The pressure manometers (2) show the pressure of the gas cylinder (right-hand side) and the downstream pressure (left-hand side). The opening of the valves (3) and (5) allows the gas to fill the reservoir (6) up to a working pressure of 1 – 2 bar set by the regulator (3). For evacuation, the valves (3), (4) and (5) should be opened. The pump should turn on, then evacuating the whole volume of tubes and reservoir (6) up to the valve of the gas cylinder. After reaching the recommended low pressure, the ball valve (4) should be closed and the reservoir can be filled again. After repeating this procedure five times, the nut of the head of the reservoir is opened and the needle of the syringe is pushed through the rubber seal. The filled syringe should be quickly brought to the gas-mixing chamber to inject the correct volume of pure gas into the chamber, as described in previous chapter. Instead of using a syringe, a sample loop of known volume can be used for the injection of pure gas. This method is described in more detail by Lagler et al. (2007).

In Figure 3.8 the concentration contour (from Equation 3.14b) as a function of the volume of the pure gas in the syringe and the pressure of the mixing chamber is presented for carbon monoxide.

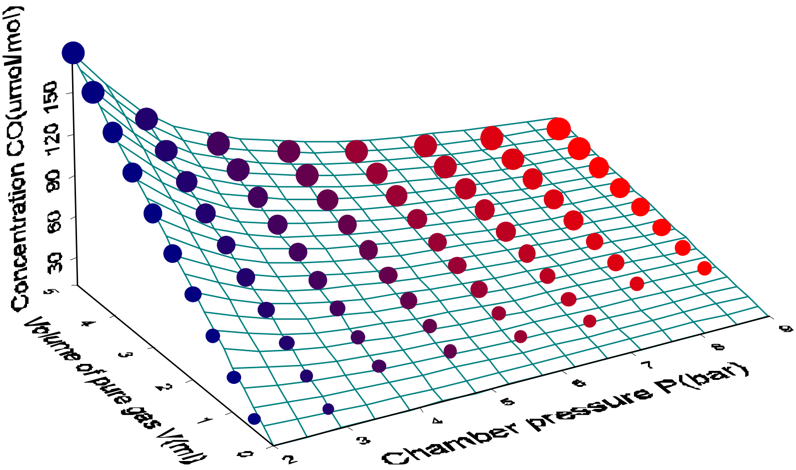


Figure 3.8. Concentration contours as a function of the volume of the pure gas in the syringe and the pressure of the mixing chamber for carbon monoxide.

As can be seen from Figure 3.8, for preparation of a higher concentration (larger spheres) a larger volume of pure gas and a lower chamber pressure of dilution gas are needed. In addition, the increase of concentration is proportional to the volume of the pure gas at a fixed chamber pressure.

An application in which the mixing chamber is not evacuated after the first preparation of the gas mixture, but is filled again up to a certain pressure with the dilution gas to produce a new concentration of the gas mixture, is used quite frequently. Repeating this again and again makes it possible to produce several different concentrations of gas mixtures for multipoint calibration of the analyser in a very short time. Also one of the advantages is that the filling of the pure gas is only needed once. The concentration of the gas mixture at each of the dilution steps can be calculated according to Equation (3.18) or (3.19).

A third way of using the static injection chamber is the use of a certified reference material instead of the pure gas. A known concentration of CRM (or SRM) is injected into the chamber through a tube. By measuring the change of pressure caused by the injected gas mixture one can calculate the volume of the CRM. Filling the chamber with the dilution gas up to a certain pressure, the concentration of the gas mixture can be calculated according to Equation (3.18) or (3.19).

The expanded uncertainty of the gas mixture obtained by the static volumetric method can be calculated. Substituting Equation (3.18) into Equation (2.5), one can rewrite it in the form:

$$\boldsymbol{u}_c^2(\boldsymbol{y}) = \sum_{\boldsymbol{i}=1}^{N} \left(\frac{\partial C}{\partial x_i} \right)^2 \cdot \boldsymbol{u}^2(\boldsymbol{x}_i) = \sum_{\boldsymbol{i}=1}^{N} \left(\frac{\partial C(\boldsymbol{g}_s) \cdot \dfrac{\boldsymbol{p}_s \cdot \boldsymbol{V}(\boldsymbol{g}_s)}{\boldsymbol{p}_d \cdot \boldsymbol{V}(\boldsymbol{g}_d)}}{\partial \boldsymbol{x}_i} \right)^2 \cdot \boldsymbol{u}^2(\boldsymbol{x}_i) \tag{3.20}$$

The same procedure is used as in Ch 3.4.1 to calculate Equation (3.20) which can be expressed in the form (ISO 6144, 2003)

$$\begin{aligned} u_c^2(C()) = & \left(\frac{p_s\, V(g_s)}{p_d\, V(g_d)} \right)^2 u(C(g_s))^2 + \left(\frac{C(g_s)\, V(g_s)}{p_d\, V(g_d)} \right)^2 u(p_s)^2 + \left(\frac{C(g_s)\, p_s}{p_d\, V(g_d)} \right)^2 u(V(g_s))^2 + \\ & \left(\frac{C(g_s)\, p_s V(g_s)}{p_d^{\,2}\, V(g_d)} \right)^2 u(p_d)^2 + \left(\frac{C(g_s)\, p_s V(g_s)}{p_d\, V(g_d)^2} \right)^2 u(V(g_d)^2 \end{aligned} \tag{3.21}$$

where $u(C(g_s))$, $u(p_s)$, $u(V(g_s))$, $u(p_d)$ and $u(V(g_d))$ are the standard uncertainties of the parent gas concentration $C(g_s)$ (pure gas or known concentration of CRM), the pressure of the parent gas p_s, the volume of the parent gas $V(g_s)$, the pressure of the static chamber at the end of filling p_d and the volume of the dilution gas at the end of the filling $V(g_d)$, respectively.

The next step is to define or to estimate each of the standard uncertainty components. The standard uncertainty of the pure gas component can be obtained from the certificate of the pure gas (which should include an impurity analysis and an uncertainty analysis). The standard uncertainty of the pressure measurements p_s and p_d can be found from the calibration certificate of the pressure meter. The standard uncertainty of the volume of the pure gas (syringe, sample loop etc.) can be got from the certificate of the syringe or can be defined, e.g., by defining the exact volume by weighing and calculating the standard uncertainty of the subsequent measurements. The standard uncertainty of the volume of the dilution gas is calculated from the uncertainty of the volume of the mixing chamber.

With all the standard uncertainties involved in Equation (3.21) solved, the expanded uncertainty of the binary gas mixture can be calculated. In Figure 3.9 the expanded uncertainty for carbon monoxide is presented as a function of the chamber pressure (dilution air) and the obtained concentration.

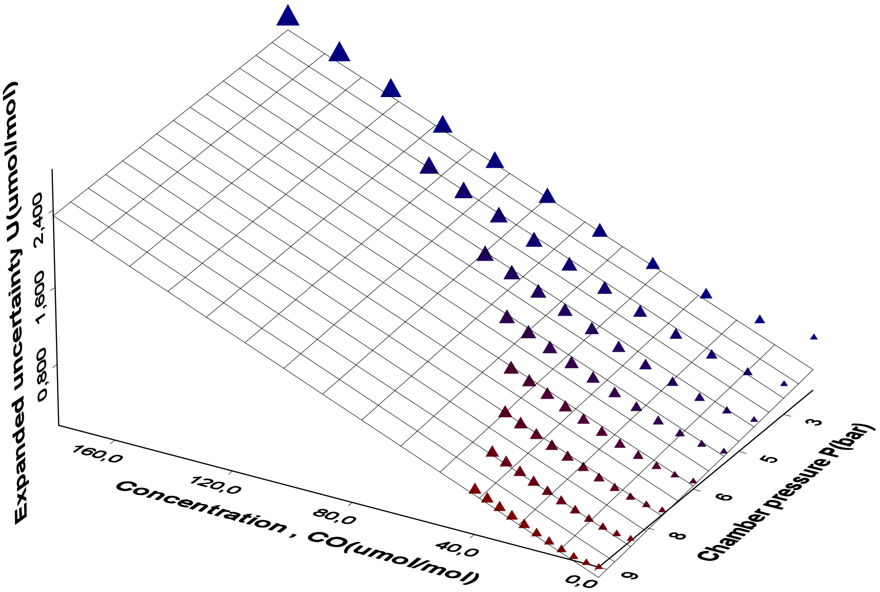


Figure 3.9. Expanded uncertainty for carbon monoxide as a function of concentration and the pressure of the chamber. The size of the triangle is proportional to the volume of the pure gas in the syringe at values of 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 ml.

An interesting application for static injection is the so-called exponential dilution method which has been used quite regularly for testing the linearity of the detectors used in gas chromatographs (Williams and Winefordner, 1966, Choi and Xiao, 1999). Continuous dilution of the gas concentration can be expressed by the well-known decay law of a radioactive isotope:

$$\frac{dC}{dt} = -\frac{F}{V \cdot t} \tag{3.22}$$

Integration of the Equation (3.22) with the initial condition of $C(t = t_o) = C_o$ would yield:

$$C(t) = C_o \cdot EXP(-F/V \cdot t) \tag{3.23}$$

where C_o is the initial concentration of the gas component, F is the dilution flow [ml/min], V is the volume of the reservoir [ml] and t is the time for dilution since the beginning. The mixing chamber in Figure 3.6 was used for testing the exponential dilution method for the gases carbon monoxide, sulphur dioxide and nitrogen monoxide. The response times of the analysers, t_f, were of the order of 30s to 60s, during which the change of concentration $C(t)$, according to Equation (3.23), needs to be of the same order as, or less than, the repeatability of the analyser. The other criterion for the method is that the dilution flow needs to be the same as, or larger than, the sampling flow rate of the analyser. These two criteria define the dilution flow F and the volume of the reservoir V, in order to guarantee that the change of the concentration $C(t)$ during the time $t = t_f$ is not too rapid. More details of the test set-up and the results are shown elsewhere (Walden et al., 2007).

3.4.4. UV-photometric method

In the previous chapter, several techniques are used for the production of gas mixtures for calibration purposes with a known expanded uncertainty and traceability chain to an SI have been discussed. The calibration methods were applicable to carbon monoxide, nitrogen dioxide, and nitrogen monoxide and sulphur dioxide. For ozone, the reference standard in a gas cylinder does not exist, because ozone is a highly oxidizing component and therefore difficult to store in any reservoir. For ozone a different approach is needed.

UV light is very effective in splitting oxygen molecules into oxygen atoms. These free oxygen atoms react rapidly with the oxygen molecules forming a three-atom molecule of oxygen, ozone. The reaction also takes place in the stratosphere, where the UV light from the sun creates the so-called ozone layer. The other technique is to use a high-voltage corona discharge to form oxygen atoms.

The basic measurement principle of the ozone instruments is the determination of the intensity of ultraviolet (UV) radiation at a specific wavelength absorbed by a sample of ozonized air. The source of the UV light is most often a mercury lamp. The lamp produces a very narrow but intensive (99.5 % of the total intensity of the lamp) peak at the wavelength of 253.7 nm where ozone has very strong absorption (Seinfeld, 1996 and EN-14625: 2005). Other wavelengths are removed with a quartz filter. From the transmittance of the radiation through the sample, the ozone content of the sample is determined by the application of the Beer-Lambert law:

$$\frac{I}{I_0} = e^{-\alpha L_{opt} C} \tag{3.24}$$

where

I = UV light intensity in the presence of ozone

I_o = UV light intensity without ozone in the sample

α = absorption coefficient of ozone [m^2 mol^{-1}] = N_A σ, where N_A is the Avogadro constant (= 6.023 10^{23} molecule/mol) and σ is the absorption cross-section of ozone [m^2 molecule^{-1}]

L_{opt} = optical path length of the absorption cell [m]

C = concentration of ozone by volume in the sample air [mol/m^3],

The concentration of ozone, C, can be expressed with the help of the ideal gas law (PV = nRT) as a mixing ratio by volume (Zucco et al. (2003) :

$$C = \frac{n_{o_3}}{V} = \frac{PV_{o_3}}{RTV} = \frac{cP}{RT} \tag{3.25}$$

where c is the ozone concentration as a mole fraction. The pressure P [Pa] and the temperature T [K] are at the ambient conditions and R is the gas constant [Nm mol^{-1} K^{-1}]. The gas constant R and the Avogadro number can be expressed with the help of Boltzman coefficient, k, in the form:

$$k = \frac{R}{N_A} = \frac{8.31451 \cdot [J/K \cdot mol]}{6.023 \cdot 10^{23} \cdot [1/mol]} = 1.3806503 \cdot 10^{-23} \cdot [J/K] \tag{3.26}$$

When Equation (3.25) is substituted into Equation (3.24) it can be expressed in the form:

$$\frac{I}{I_0} = e^{-\frac{-\alpha \cdot L_{opt} \cdot c \cdot P}{R \cdot T}} \Leftrightarrow \ln(\frac{I}{I_o}) = -\frac{N_A \cdot \sigma \cdot L_{opt} \cdot c \cdot P}{R \cdot T} \tag{3.27}$$

Finally the ozone concentration as a mole fraction can be expressed in the form:

$$c = \frac{-1}{\sigma \cdot L_{opt}} \cdot \frac{k \cdot T}{P} \cdot \ln(I/I_o) \tag{3.28}$$

One can see from Equation (3.28) that the ozone concentration is dependent on the transmittance of the UV light (i.e., the ratio I/I_o), the optical path length of the absorption cell, L_{opt}, the environmental pressure, P, the temperature of the absorption cell, T, the absorption cross-section of ozone, σ, and the Boltzman constant, k.

The accurate determination of the transmittance requires that care is taken to avoid errors caused by stray radiation and sample and light source variations during the measurement.

The National Institute of Standards and Technology has manufactured a photometer to measure the ozone concentration directly according to Equation (3.23) at a precise wavelength of 253.7 nm. The source of UV light must also be very stable and the light well-focused into the absorption cell. A more detailed description of the device can be found elsewhere (Paur et al, 2003). The Standard Reference Photometer (SRP) by NIST was established as a primary device for ground level ozone measurements. Over the last two decades NIST has made more than forty SRP units for the NMIs and different expert laboratories, working mostly in the field of air quality measurements.

The uncertainty budget for the SRP is calculated by identification of the sources of uncertainties as has proceeded in previous methods and proposed by ISO (GUM 1995). In Appendix 13 a detailed study of the uncertainty analysis is made, and in Figure 3.10 the expanded uncertainty of the SRP-37 is shown as a function of ozone concentration.

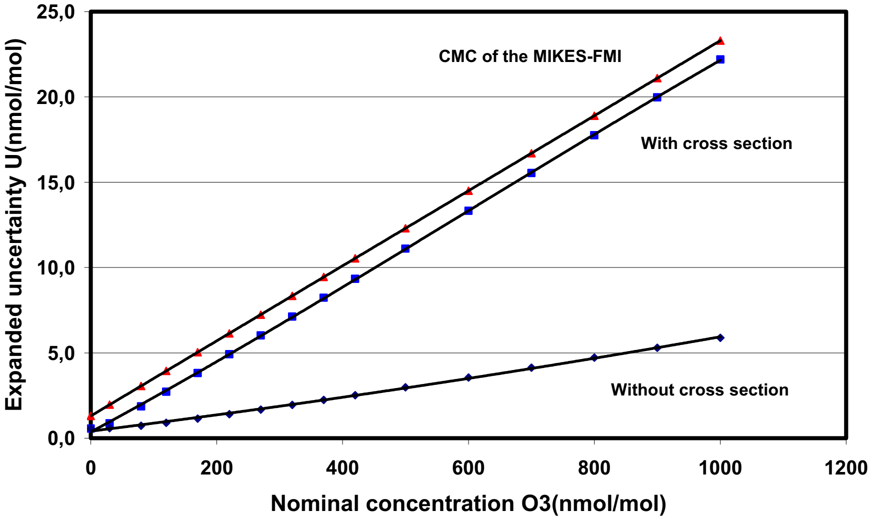


Figure 3.10. The expanded uncertainty of the SRP-37 is shown without the contribution of the absorption cross-section (lower line), with the absorption cross-section (middle line) and the CMC of the MIKES-FMI (upper line), see in Figure 5.17d.

The cross-section of ozone for absorption of UV light has been defined by a number of research groups (see in the Figure 3.11). The results were evaluated by the National Institute for Science and Technology, and the conclusion was reached that value of $\sigma = 1.147\ 10^{-21}\ m^2\ molecule^{-1}$ (or $\alpha = 30.4\ kPa^{-1}m^{-1} = 308.32\ atm^{-1}cm^{-1}$) was the best estimate for the absorption cross-section to be used with the SRP.

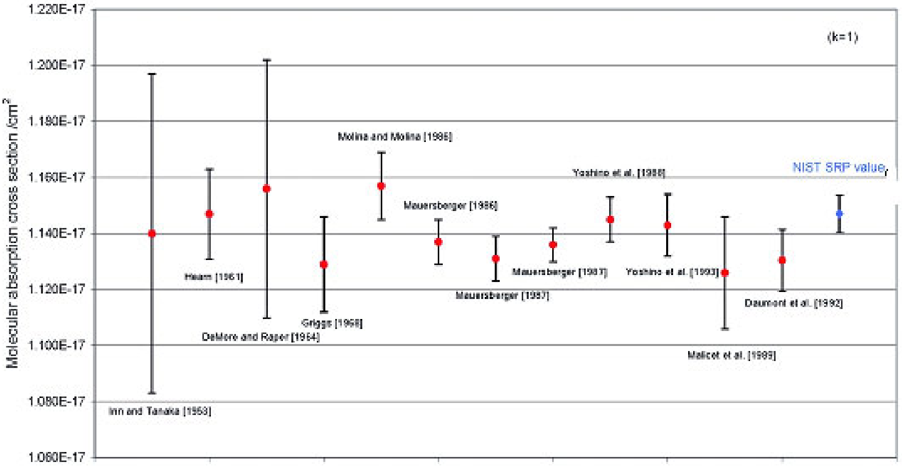


Figure 3.11. The absorption cross-section of ozone at a wavelength of 253.7 nm as found by various research groups. The value of 1.147 10^{-17} cm^2 by Hearn (1961) with a relative uncertainty of 1.5 % is used by NIST for the SRP. (The figure is presented here with the kind permission of Robert Wielgosz of the BIPM.)

Following the definition of the PMM, one can state that the SRP can be used as a PMM (BIPM, 1998; Woods, 2009). The operation of the SRP can be completely described by Equation (3.28), the complete uncertainty statement can be written down in terms of SI units, (see in Equation (A13.11) and Figure 3.10), and the performance characteristics of the device have thoroughly been tested (Klausen et al. 2003; Viallon et al., 2006). The absorption cross-section of ozone in Equation (3.28) and shown in Figure 3.11, is directly traceable to SI units (Hearn, 1961). As seen in the Figure 3.11, the difference between the results of the various research groups is within 3 %, which suggest a need to further study the determination of the cross section of ozone and/or to increase the uncertainty statement. There is also an alternative way of determining the concentration of ozone through a primary method, namely, by titration. A more detailed description of this is given in chapter 3.4.5.

3.4.5. Gas phase titration (GPT) method

The method described here is based on a titrimetric method, but instead of liquids (acid – alkali) gas is used. The term Gas Phase Titration (GPT) is used for the process. The laboratory's gas dilutor (Sonimix 6000 A1) is equipped with the components needed for performing the GPT. The titration is performed with NO and O_3, resulting in NO_2 and oxygen (O_2). The titration of nitrogen monoxide with ozone can be presented as:

$$NO + O_3 \rightarrow NO_2^* + O_2, \qquad \text{(R3-1)}$$

$$\rightarrow \qquad NO_2 \ \ \lambda\text{: } 600 \text{ nm} - 2400 \text{ nm}$$

The nitrogen dioxide formed in reaction (R3-1) can be in the exited state, NO_2^*, which decays to the ground state. The wave length, λ, of the transition energy occurs between 600 nm and 2400 nm, with an intensity peak at 1200 nm. This range overlaps with the sensitive spectral response function of the photomultiplier tube, making the detection of this transition feasible. The rate constant, $k_{R2\text{-}1}$, of the reaction (R3-1) has been studied quite intensively over a wide temperature range by a number of research groups. Here the value of $k_{R2\text{-}1} = (2.1 \pm 0.5) \times 10^{-14}$ at 298 K (Phillips et al., 1962) is used.

The phenomenon, in which the reaction product is in an exited state as a chemical reaction (e.g. in reaction (R3-1)) and decays to the ground state by emitting transition energy as light (and not as heat) is called chemiluminescence. The reaction (R3-1) is also an important reaction in the atmosphere, where nitrogen dioxide is dissociated into nitrogen monoxide and oxygen in the presence of sunlight; this is the most important photochemical reaction occurring in the atmosphere.

During the GPT, number of reactions with nitrogen dioxide and ozone may take place with the wall material of the reaction chamber. These reactions have been studied in the literature (Seinfeld, 1986). In order to avoid the other reactions than (R3-1) the reaction chamber and the tube materials in the Sonimix 6000 A1 dilutor have been made of inert materials, and a detectable loss of reactants has not been observed.

The reaction (R3-1) is allowed to proceed in an excess concentration of nitrogen monoxide compared to the concentration of ozone, in order to consume the ozone completely in the reaction. The reverse situation, ozone in excess of nitrogen monoxide, would leave ozone in the system. As a reactive molecule it would react again with the nitrogen monoxide after the NO_2–NO conversion causing nonlinear behaviour of the results.

From the conservation of nitrogen in the reaction (R3-1), the sum of nitrogen monoxide and nitrogen dioxide is a conservative quantity, i.e.,

$$[NO] + [NO_2] = [NO]_o + [NO_2]_o = [NO]_o \qquad (3.29)$$

On the right-hand side of the equation, an initial situation $[NO_2]_o = 0$ has been used. The reaction (R3-1) takes place in a stoichiometric condition, i.e., the changes in the ozone concentration equals the changes in the nitrogen monoxide concentration:

$$d[O_3] = [O_3]_o - [O_3] = [NO]_o - [NO] = d[NO] \qquad (3.30)$$

In the laboratory the titration takes place in a reaction chamber where the reaction time must be long enough to allow the titration reaction to go to completion. The rate constant of reaction (R3-1) is well-documented in the literature over a wide temperature range (Seinfeld, 1986). The rate of change of nitrogen monoxide in reaction (R3-1) using the condition of Equation (3.30) can be calculated according to:

$$-\frac{d[NO]}{dt} = k[NO][O_3] = k[NO]\left([O_3]_0 - ([NO]_0 - [NO])\right) \qquad (3.31)$$

Integration of Equation (3.31) with the initial condition of Equation (3.29) yields

$$t = \frac{1}{k \cdot ([O_3]_0 - [NO]_0)} \ln\left(\frac{[NO]_0([O_3]_0 - [NO]_0 + [NO])}{[NO][O_3]_0} \right) \tag{3.32}$$

where

$[O_3]_o$ = initial O_3 concentration (in nmol/mol)
$[NO]_o$ = initial NO concentration (in nmol/mol)
[NO] = final NO concentration (in nmol/mol)
k = rate constant (nmol/mol^{-1} min^{-1})
t = time of reaction (min)

By defining the value of the initial concentrations of nitrogen monoxide and ozone, the reaction time for the complete reaction can be calculated.

An important aspect of the GPT method with nitrogen monoxide is that the amount of ozone introduced into the system can be calculated from the change in nitrogen monoxide. This gives the possibility of tracing the ozone concentration to a reference standard of nitrogen monoxide made by a gravimetric method. However, there are some problems along the way. First, the reaction (R3-1) has to go to completion with respect to ozone. The materials of the GPT system have to be inert to ozone as well as to nitrogen compounds, in order to prevent the loss of reactants with the wall and tube materials. The best way is to build a very compact system of inert material and use high concentrations of both gas components to minimize the required delay time according to Equation (3.32 for the complete reaction (R3-1).

Laboratory studies have been performed to demonstrate GPT as a method to trace the ozone reference standard to a gravimetrically-prepared nitrogen monoxide standard. In order to reach a complete reaction (R3-1), an empirical parameter, the so-called dynamic parameter (EPA-600, 1975) is used. This parameter, P_R, is a product of the concentration of nitrogen monoxide and the residence time, t_R, of the reactants in the reaction chamber. It should fulfil the criteria:

$$P_P = [\mathrm{NO}]_{\mathrm{RC}} \cdot t_{\mathrm{R}} = [\mathrm{NO}]_{\mathrm{RC}} \cdot \frac{V_{\mathrm{RC}}}{f_{\mathrm{ozone}} + f_{\mathrm{NO}}} > 2.75 \mu mol / mol \cdot \mathrm{min} \tag{3.33}$$

where V_{RC} is the volume of the vessel (reaction chamber), and f_{ozone} and f_{NO} are the flows of the ozone and the nitrogen monoxide, respectively. The volume of the reaction chamber is designed in such a way that $t_R > t$, where the reaction time, t, is calculated from Equation (3.32). The dilutor is designed in such a way that the concentration of nitrogen monoxide in the reaction vessel, $[NO]_{RC} = [NO]_{STD}$, i.e., no dilution with zero air takes place before the reaction with ozone. When the concentration of NO is high, the reaction time is short enough to make the reaction (R3-1) complete with ozone. Note that the dilution of the reactants takes place after the reactions in the dilution chamber. The flow rate of ozone is f_{ozone} = 50 ml/min and f_{NO} varies depending on the dilution rate, being from 3 to 20 ml/min. The size of the reaction chamber is about 7 cm^3 and the concentration of the gas standard of nitrogen monoxide is 100 ppm. The dynamic parameter, P_R is thus from 10 to 13.5 [µmol/mol·min], fulfilling the criterion of Equation (3.33).

Dilution of the nitrogen dioxide produced, is made soon after the completed reaction; the concentration of the nitrogen dioxide produced can be calculated with the help of Equations (3.29) and (3.30):

$$[\mathrm{NO_2}]_{\mathrm{prod}} = [\mathrm{NO}]_o - [\mathrm{NO}] = [\mathrm{O_3}]_o - [\mathrm{O_3}] = \frac{[\mathrm{O_3}]_{\mathrm{STD}} \cdot f_{\mathrm{ozone}}}{f_{\mathrm{ozone}} + f_{\mathrm{dil}}} \tag{3.34}$$

where on the right-hand side of Equation (3.34) $[O_3]_{STD}$ is the ozone concentration produced by the ozone source (UV-lamp) of the dilutor and f_{ozone} and f_{dil} are the flow rate through the ozone source and the dilution flow, respectively.

The reaction scheme of the (R3-1) with an excess of nitrogen monoxide compared to the ozone calculated from the Equation (3.32) with the criterion of Equation (3.33) is presented in Figure 3.12.

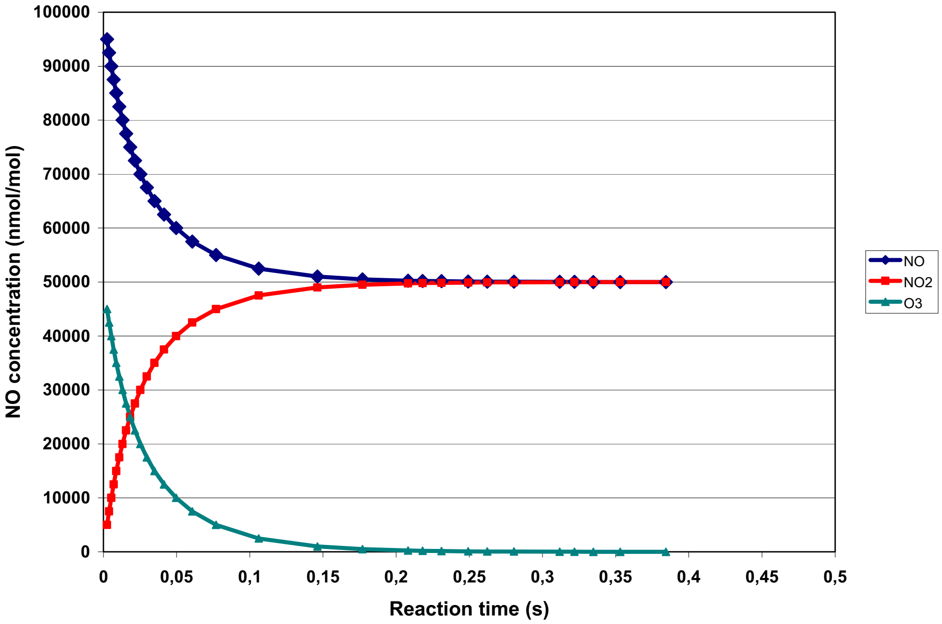


Figure 3.12. The reaction scheme of the titration reaction of nitrogen monoxide (NO) with ozone (O_3) producing nitrogen dioxide (NO_2), presented as a function of reaction time t(s).

From Figure 3.12 it is evident that the time for complete reaction is reached in less than 0.5 s; according to Equation (3.32) the delay time for the reaction in the dilutor is 6 s. Therefore the reaction has completed before dilution. When the dilution of NO takes place before the adding of ozone, the reaction time can be longer, order of several seconds to tens of seconds, as has been shown by Esler et al. (2005).

The uncertainty of the concentration of nitrogen dioxide produced by the GPT method is calculated in Appendix 14. The right-hand side of Equation (3.34) is similar to that of Equation (3.5), and the same approach is used as in chapter 3.2 in the case of mass flow controllers. If the effect of impurity in the zero gas in Equation (3.5) is neglected, the variance of the standard uncertainty of Equation (3.34) can be expressed in a simplified form:

$$u_c^2(C_{[NO_2]_{prod}}) = \sum_{i=1}^{N} \left(\frac{\partial E}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

$$= \left(\frac{[O_3]_{STD} f_{dil}}{\left(f_{span} + f_{dil}\right)^2} \right)^2 \cdot u^2(f_{ozone}) + \left(\frac{[O_3]_{STD} f_{dil}}{\left(f_{span} + f_{dil}\right)^2} \right)^2 \cdot u^2(f_{dil}) + \left(\frac{[O_3]_{STD} f_{dil}}{\left(f_{span} + f_{dil}\right)^2} \right)^2 \cdot u^2(C_{ozone})^2$$

((3.35))

where the first and second terms on the right-hand side of Equation (3.35) include the variances of the ozone flow rate and the dilution flow, respectively, while the third term includes the variance of the ozone source measured by the ozone photometer of the laboratory, (see chapter 3.4). Using the values of the flow rates of the Sonimix 6000 A1 dilutor in chapter 3.2 and the values of the ozone measurements in chapter 3.4, the expanded uncertainty of the gas phase titration based on ozone measurements can be calculated. This is shown in Figure 3.13.

Next the expanded uncertainty of nitrogen monoxide needs to be calculated. The first equality in Equation (3.34) is the difference in concentration between the nitrogen monoxide at the beginning of the GPT and after injection of ozone into the system. As an initial situation a known concentration of nitrogen monoxide is produced through the calibration system of the laboratory, and the final concentration is the result after the injection of ozone. Due to the excess of nitrogen monoxide with respect to ozone, the final concentration of ozone is zero, while the concentrations of nitrogen monoxide and nitrogen dioxide are measured with an NO- NO_x-analyser. The variance of the standard uncertainty of nitrogen monoxide can be now expressed as:

$$u_c^2(NO) = u_c^2([C_{NO}]_0) + u_c^2([C_{NO}]) = 2 \cdot u_c^2([C_{NO}]_0)(1 + u_c^2(C_{anal}))$$

(3.36)

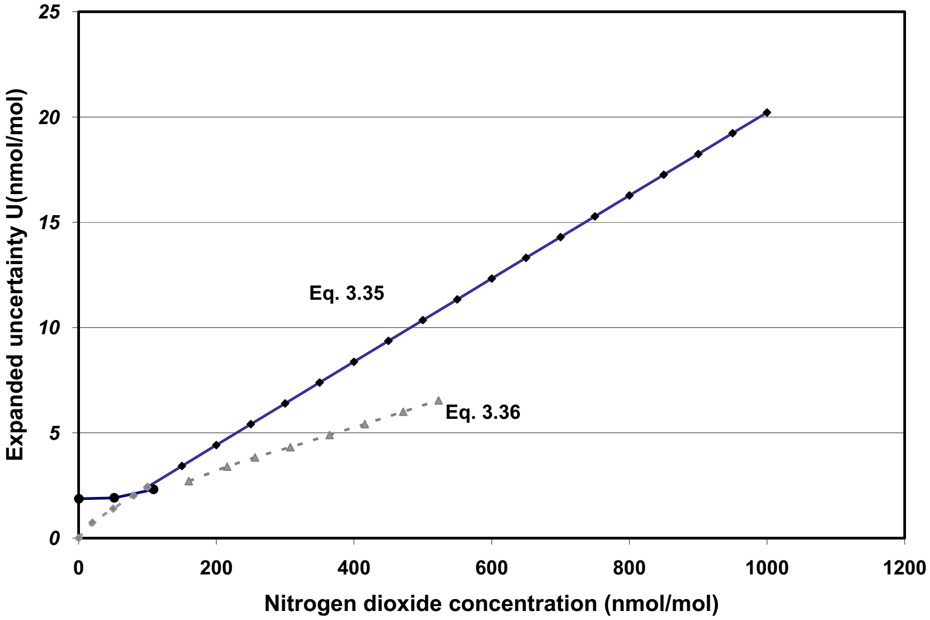


Figure 3.13. The expanded uncertainty of the gas phase titration method according to the Equation (3.35), U=2·$u_c(C_{[NO2]prod})$, and Equation (3.36), U=2·u_c(NO).

where $u_c^2([C_{NO}]_o)$ and $u_c^2([C_{NO}]_o)$ are the variances of the standard uncertainties of the concentrations of $[NO]_o$ and [NO] respectively, and $u_c^2(C_{anal})$ is the uncertainty component due to the analysis of the nitrogen monoxide.

The uncertainty components from Equations (3.35) and (3.36) need to be compared. This is done in Figure 3.13. The expanded uncertainty according to Equation (3.35) is calculated based on the uncertainty components of the gas dilutor (Sonimix 6000 A1, see Appendix 8). The expanded uncertainty according to Equation (3.36) is calculated with the help of the uncertainty components of the gas dilutor (see Appendix 8) and with the help of the uncertainty components of the NO-NO_x analyser (see Appendix 14). From Figure 3.13 one can see that the expanded uncertainty based on Equation (3.36) is preferable better at lower concentrations (up to 100 nmol/mol) while the expanded uncertainty based on Equation (3.36) gives a more conservative estimate at concentrations higher than 100 nmol/mol.

3.5. Analysis of the gas concentration

The concentrations of gas mixtures produced with the calibration methods used by the laboratory are analysed with the reference methods described by the EN standards for the specific gas components. Nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are expressed as oxides of nitrogen (NO_x) and measured by the chemiluminescence method (SFS-EN 14211). Sulphur dioxide is measured by the UV-fluorescence method (SFS-EN 14212), ozone is measured by the UV-absorption method (SFS-EN 14625) and carbon monoxide is measured by the non-dispersive IR method (SFS-EN 14626). The reference methods described above have been defined for use in air quality measurements by European air quality directives (Council directive, 2008). The International Standardization Organization has also prepared standards for the determination of sulphur dioxide by the UV-fluorescence method (ISO 10498: 2004), for oxides of nitrogen by the chemiluminescence method (ISO 7996:1985), for carbon monoxide by the non-dispersive infrared method (ISO 4224: 2000) and for ozone by the UV-photometric method (ISO-13964, 1998).

The major differences between the ISO standards and the EN standards are that the former describe the method itself. The latter, on the other hand, are more complete guides for fulfilling the data quality objectives (DQO) of the directives for air quality measurements. The EN standards include the performance characteristics of the reference method, the test procedure for type approval of the instruments, field operation and ongoing quality control procedures and also provide guidance for the uncertainty calculation of field measurements at limit values.

Considering the measurement of calibration gas mixtures in the laboratory, the following performance characteristics of the analysers are taken into account:

- Response time
- Linearity of the analyser (lack of linearity)
- Short-term drift (12 hours) of the analyser at zero and span level
- Repeatability of the analyser
- Interference due to humidity
- Dependence on sample gas pressure, sample gas temperature, environment temperature, and line voltage

Interference other than that due to water vapour is not included, because the CRMs and the SRMs are tested against the impurities by the NMI. The pure gas components that are used for the static injection system were tested for impurities at the VSL (The Netherlands). The quality of the dilution air prepared in the laboratory is tested against synthetic air with the supplier's highest purity. Additionally, the dilution air is analysed with the gas chromatograph for certain organic gas components (benzene, toluene, ethyl benzene, o-xylene and m/p-xylene) in order to check if these impurities are being passed through the scrubbers. However, the contribution of the impurity in the dilution air is added into the uncertainty budget (see in Ch 3.4). The effect of water vapour is negligible because the air is cooled down to – 40 ºC.

The performance characteristics that are defined in the EN standards but not included here are those that influence field measurements. In addition, the averaging effect is not relevant because the concentration must be stabilised before the measurement takes place. The response time of an analyser is determined to check that the rise and fall times do not differ by more than 5 % from each other. However, the response time is not included in the uncertainty budget. A more detailed description of the test procedures for the performance characteristics of the analysers is found in Appendix 15.

Following the EN standards (SFS-EN 14211, SFS-EN 14212, SFS-EN 14625 and SFS-EN 14626), the combined standard uncertainty of the most important performance characteristics of the analysers used in laboratory measurements can be expressed in the form:

$$u_{c,a} = \sqrt{u_l^2 + u_{drift}^2 + u_{rep,z}^2 + u_{rep,s}^2 + u_{\text{int}}^2 + u_p^2 + u_{stemp}^2 + u_{envtemp}^2} \tag{3.37}$$

Where ,

$u_{c,a}$ = combined standard uncertainty of the analyser

u_l = standard uncertainty of the linearity

u_{drift} = standard uncertainty of the short-term drift

$u_{rep,z}$ = standard uncertainty of the repeatability at zero concentration

$u_{rep,s}$ = standard uncertainty of the repeatability at a known concentration

u_{int} = standard uncertainty of the interference (moisture)

u_p = standard uncertainty of the sample pressure

u_{stemp} = standard uncertainty of the sample temperature

$u_{envtemp}$ = standard uncertainty of the environment temperature

The values for each of the standard uncertainties of the analysers used are shown in Appendix 15. When the analyser is used with the laboratory calibration methods to measure the output concentration of the prepared gas mixture, the expanded uncertainty of the measured concentration can be calculated according to Equation (3.38):

$$U = 2 \cdot \sqrt{u_{cal}^2 + u_{c,a}^2} \tag{3.38}$$

where u_{cal} is the standard uncertainty of the calibration method used and $u_{c,a}$ is the standard uncertainty of the analyser used.

3.6. Realisation of the unit of the amount of substance and dissemination of the traceability

In chapter 3.3 the traceability chain of the reference and the working standards of the laboratory were discussed. The calibration methods and the reference methods for the analysis of the gas compounds were discussed in chapters 3.4 and 3.5, respectively. This chapter reviews the ways in which the unit of the amount of substance, the *mole*, is realised in the laboratory. One should also keep in mind the definition of PMM from chapter 2.4 (BIPM 1998), and that the measurand for expressing the output of the calibration methods of the laboratory is concentration (the amount of substance fraction). The realisation of the *mole* is not based on the definition of the *mole* itself, the intention here is rather to demonstrate that the concentration and its uncertainty relating to the gas mixtures prepared by the calibration methods can be expressed in SI, more precisely in *mole fraction* (e.g., nmol/mol of NO in air).

In the case of gas mixtures prepared by PMM, i.e., gravimetric gas standards, the traceability chain starts with a primary realisation of the mole fraction for a specified chemical entity.

$$y_B = \frac{n_B}{\sum n_i} = \frac{\frac{m_B}{M_B}}{\sum \frac{m_i}{M_i}} \tag{3.39}$$

where n_B is the amount of substance of entity B [*mol*], m_B is the mass of substance B [*kg*], M_B is the molecular weight of substance B [*kg/mol*], and the unit of the measurand y_B is the concentration of entity B as a mole fraction [*mol/mol*]. Here the traceability of the weight of the mass m_B is linked to the primary standard of mass (artifact of the kg). When the CRM is prepared, the value of the CRM (e.g., PRM standard) is defined by direct comparison with the gravimetric standard (Holland et al, 2000). In this case the traceability of the CRM is linked to gravimetrically-prepared gas standards having the same unit as the gravimetric standard.

In the case in which the value of the CRM is based on a chemical measurement, the unit of the result may be expressed as a volume fraction. The difference between the volume fraction and the mole fraction arises with gas compounds that differ from an ideal gas. In the case of real gases, the compressibility factor has been calculated using the basic thermodynamic equations for gases together with the values of the parameters from CODATA (Mohr and Taylor, 1998, Mohr et al 2007).

In Figure 3.14 the compressibility factors for specific gas compounds are presented as a function of pressure. From the Figure 3.14 one can see that, the effect of the compressibility factor for other compounds than benzene is negligible. For benzene and for other similar aromatic hydrocarbons, the compressibility factor is taken into account when expressing the results as a mole fraction or as a volume fraction.

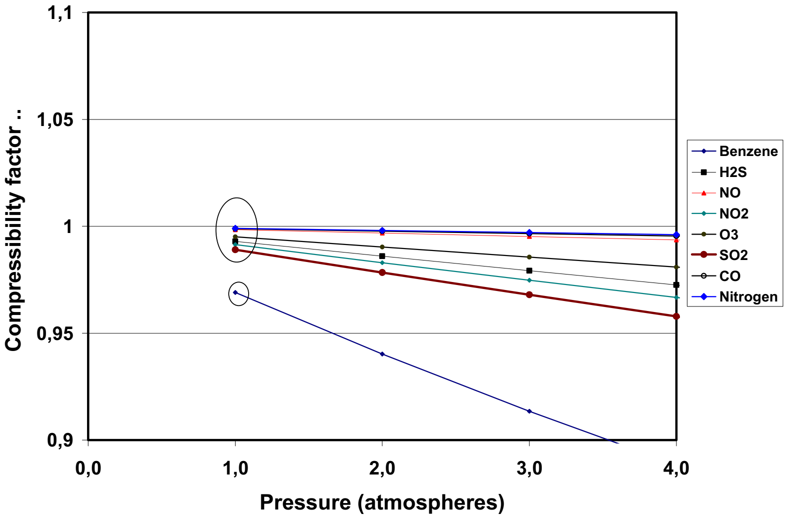


Figure 3.14. The compressibility factors for specific gas compounds as a function of pressure. The temperature is fixed at 273.15 K. For an ideal gas the compressibility is one.

The traceability chain for the value of the concentration (mol/m^3) of a gas mixture of component B, prepared by the dynamic dilution method from the CRM, starts with a primary realisation of the gas component, B:

$$C_B = \frac{n_B}{V} = \frac{m_B}{M_B V} \qquad (3.40)$$

where C_B is the concentration of the gas B, and V is the volume of the dilution gas. The unit of the concentration of the gas mixtures prepared in the laboratory is realised by the dynamic dilution method, the permeation method, and the static volumetric method. The characteristics of the gas compound (e.g., compressibility) and the external conditions (pressure and temperature) affect the dilution process, and must be taken into account to correct the results or to compensate the effect (see chapter 3.4.1).

The uncertainty of the gas concentration prepared by the calibration methods of the laboratory is expressed directly as a molar fraction or a volume fraction. The molar fraction is obtained by the dynamic dilution method, Equation (3.6), the permeation method Equation (3.17), the static volumetric method, Equation (3.21), and by the GPT-method using Equations (3.35) and (3.36). The unit of amount of substance by volume fraction is obtained by the static volumetric method, Equation (3.18), and by the UV-photometric method, Equation (3.28). The unit of amount of substance by volume fraction can be converted into the molar fraction directly keeping, in mind the compressibility factor from Figure 3.15.

In the following the unit that is realised by the analysis of the gas mixtures is examined. The value obtained in the detection of the oxides of nitrogen by the chemiluminescence method is proportional to the number of molecules in the reaction chamber. The calibration gas mixture is expressed as a mole fraction and so too is the unit of the analyser. In the case of other analysers (SO_2-, CO-, and O_3-analysers) a beam of light from the light source goes through the sample cuvette or the sample cell causing either an excitation or absorption effect on the molecules in question in the sample. The value obtained from the measurement method is thus proportional to the density of the gas compound in the sample, and is therefore proportional to the mass rather than to the volume. The mole fraction is the correct unit for the measurement signal for these types of analysers.

The value of the concentration prepared by the different calibration methods at the laboratory is disseminated to the customer by a direct calibration procedure. The calibration may be performed against the customer's analyser, calibration device or the whole calibration system. The calibration procedure has been conducted through the preparation of gas mixtures of known concentration values for the device under calibration, with mixtures of three to six different concentrations being used. The exact concentration values with their expanded uncertainty (Equation 2.7) are calculated for each of the gas mixtures used in the calibration. In addition, a linear regression function can be applied to the data and an equation describing the response of the analyser to the calibration concentration can be used for correcting the respond. The valid range of the equation and the figure of showing the expanded uncertainty are provided for the customer. The procedure of ordinary least squares or the generalized least squares is used for regression analysis (Smith and Onakunle, 2007; ISO 6143: 2001). The contribution of the instrument under calibration is included in the uncertainty budget and is described in the calibration certificate. Not only calibration instruments, which may include a gas standard as part of the facility, but also single gas standards themselves are calibrated at the laboratory. In this case it is not a question of the certification of the standard but of the calibration of the concentration of the given gas mixture. Therefore in accordance with ISO Guide 35 no date of expiration is given in the calibration certificate.

3.7. Cross-checks of the calibration methods

Even when the quality system of the laboratory is built to achieve and to maintain the stated accuracy and good quality of the calibration service, malfunctioning or drift in the calibration system can occur. The malfunctioning of the calibration devices is somewhat easier to detect, although the reason may be difficult to identify. Instead, a drift in the output concentration can occur, e.g., from an unstable gas source (gas cylinder, permeation source), a drift of the flow measurement device (mass flow controllers) or a drift of the analyser. The cause of the drift can be difficult to identify, but the influence of the drift on the calibration results can be seen by comparison with previous results. Also the laboratory maintains practices to cross-check the calibration results by other methods. The difficulty of this kind of cross-check is to find a method independent of the method to be checked given that the uncertainties of the methods should be the same.

As discussed in chapter 3.4.1, the most accurate method in laboratory for obtaining gas mixtures for calibration purposes is the dynamic dilution method using the highest quality of gas standard. The calibration ranges with the best measurement capability for all other gas components except ozone, and shown in the scope of accreditation of the laboratory, refer to the dynamic dilution method. In the gas dilution system, components that can drift away from their expected values are, e.g., the content of the gas standard, impurity of the dilution gas, drift of the flow devices (mass flow controller or critical orifices), the pressure inside the gas line (input/output line/exhaust line), and a sudden pressure change in the environment. The variation of all the items above is included into the uncertainty budget. The working scenario at the laboratory is constructed at three different levels, to obtain

1. The best operation of the laboratory
2. Normal operation of the laboratory (routine work)
3. Acceptable operation of the laboratory

The philosophy behind the categories is that the first category is the best that the laboratory can achieve. This means that all equipment is calibrated and checked prior to the measurements being made. This is the case, e.g., in comparison projects (key comparisons). The second category is the normal operation in the laboratory, in which the equipment is not calibrated prior to the measurements, but calibration has been done within the allowed time-scale, and the mean values for the allowed drift of all the components are used in the uncertainty calculations. The third category is the same as category two, but the maximum allowable drift for each of the uncertainty components associated with the calibration method is used.

The methods that are applicable for cross-check studies depend on the gas compounds. The way to do the cross-checks is to calibrate the analyser for the specific gas compounds with methods that have been checked. The gas components that can be cross-checked with various different methods are shown in Table 3.2.

Table 3.2. The gas compounds that are applicable for use against the different calibration methods of the laboratory.

Calibration method	Dynamic dilution	Permeation	Static injection	GPT	SRP-37
Dynamic dilution	NO, CO, SO_2	SO_2,	NO, CO	NO	_
Permeation	SO_2	SO_2, NO_2	_	NO_2	_
Static injection	NO, CO	_	CO, NO	NO	_
GPT	NO	NO_2	NO	NO, NO_2, O_3	O_3
SRP-37	_	_	_	O_3	O_3

As one can see from Table 3.2, the dynamic dilution method can be checked against the permeation method, the static volumetric method and the GPT. The permeation method can be check against the dynamic dilution method and the GPT method. The static volumetric method can be checked against the dynamic dilution method and GPT method. The GPT method can be checked against every other method, while and the SRP-37 device can only be checked against the GPT and in addition against the ozone analyser/calibrator. However the limitation of the usable gas compounds for different methods may be a more serious problem than finding the applicable calibration method.

4. KEY COMPARISON PROJECTS, AND CALIBRATION AND MEASUREMENT CAPABILITIES

4.1. Key comparison projects

The most important way of evaluating the consistency of the quality system is participation in comparison exercises. There are a number of organizers that are capable of organizing comparison events for laboratories, but a clear distinction between the organizers is made on how the reference value of the comparison is reached. Terminology used for comparison events varies, terms as intercomparison, interlaboratory comparisons, proficiency testing and comparison projects, have been used. The last term is used here for comparisons organized by metrology community (RMO, CCQM, BIPM). Laboratories that have been accredited to organising comparison events according to the scheme of proficiency testing (ISO Guide 43, 1997 and ISO 13528, 2005) are able to provide intercomparison events that the participants can rely on. The reference value that is most often assigned is the median value of the results of participating laboratories, according to the analysis described by ISO guide 43 (ISO Guide 43, 1997). The KC is an exception in comparison projects, because the exact reference value is traceable to SI with a known uncertainty, and is defined by the organizer (pilot laboratory) of the KC. In this case also the reference value can be a consensus value from the results of the participants (e.g. median or weighted median). In both cases, however, the reference value will be the most reliable.

The MIKES-FMI Standard Laboratory as a DI has the right and the duty, consequent on its membership of CIPM MRA, to participate in the Key Comparison Projects organized by the BIPM, or the CCQM, or in regional comparisons organized by EURAMET to validate its CMC entries.

The reference value of a KC project is an important issue that the key comparison project can provide to the participants with, especially in the field of chemical metrology. In addition, the statement for the “How Far The Light Shines”, HFTLS, is important, since the meaning of this statement is to provide the range over which the laboratories can use the result of the KC to support the range of the CMC of the laboratory. The HFTLS statement for each KC is defined in the approved protocol provided by the organizer or the pilot laboratory of the KC.

The MIKES-FMI Calibration Laboratory has participated in key and pilot comparison projects organized by the CCQM or by EURAMET, as well as in intercomparison exercises organized by the European Reference Laboratory for Atmospheric Pollution (ERLAP) of the EC/Joint Research Centre (JRC). The gas compounds covered by the regional comparison, key comparison, or pilot comparison are sulphur dioxide (EUROMET-430, CCQM-K26b), nitrogen monoxide (EUROMET-430, EUROMET.QM-K1c and CCQM-K26a), nitrogen dioxide (EUROMET-430), ozone (EUROMET-414, CCQM-P28 and BIPM.QM-K1) and carbon monoxide (EUROMET-430 and CCQM-K51). The key comparison for carbon monoxide (CCQM-K51), was conducted in July 2008 at the MIKES-FMI Standards Laboratory.

4.2. Presentation of the KC results

The data analysis of a key comparison is based on the agreement that has been established by the CIPM. As a result of this agreement, the guidelines and the technical protocols for the analysis of the results of a CIPM key comparison have been prepared (Guidelines for CIPM key comparison, 1999). The guidelines state that the reference value, or more precisely, the key comparison reference value (KCRV) is a close, but not necessary the best, approximation to the value traceable to SI (Alink, 2000). The pilot laboratory defines the reference value based on the result of the primary method of measurements. Therefore, by definition, the key comparison reference value is consistent with that of the other laboratories using the same PMM. The deviation of the result from the KCRV is expressed as the degree of equivalence, including the uncertainty of the deviation (expanded uncertainty with a coverage factor of k = 2), i.e.,

$$D_{ij} = x_i - x_j \tag{4.1}$$

where degree of equivalence, (D_{ij}), is the difference between the results of the pilot laboratory (x_i) and the participating laboratory (x_j).

The laboratories (NMIs or DIs) participating in the key comparison projects define their expanded uncertainties to the measurements. Following the procedure described in chapters 2 and 3, the combined standard uncertainty of the degree of equivalence can be expressed as

$$u(D_{ij}) = \sqrt{u(x_i)^2 + u(x_j)^2} \tag{4.2}$$

where $u(x_i)$ and $u(x_j)$ are the combined standard uncertainties of the KCRV (*i*) and the laboratory (*j*), respectively. The covariance terms between the laboratories x_i and x_j have been neglected (see in Equation 2.6). The degree of equivalence can now be expressed with the expanded uncertainty as

$$E_n = \frac{D_{ij}}{U(D_{ij})} = \frac{x_i - x_j}{2 \cdot \sqrt{u(x_i)^2 + u(x_j)^2}} \tag{4.3}$$

The KCRV can be defined by the pilot laboratory based on the use of a PMM, but it can also be defined as a consensus value by the participating laboratories (Workshop held at BIPM 16.4.2007). The consensus value that is accepted is the mean of the results of the participating laboratories. The WG for the KCRV has not so far reached a conclusion for the definition of the KCRV if this is not based on the value obtained by the primary method.

In the case of several reference values, a regression model can be used. The ordinary linear regression model is traditional, but it cannot accept uncertainty of the measurements for both of the axes (independent and dependent parameters). Therefore other techniques, e.g., generalized least squares (El Shaarawi and Posch, 2002; Smith and Onakunle, 2007), that take into account the uncertainty of the results in both of the quantities, can be used. An example of generalized linear models is the orthogonal linear relation (OLR) (Heidam, 1980; Bremser, 1998) which turns into an ordinary regression model through the transformation of the coordinate axes. The OLR has been used in intercomparison studies of sulphur dioxide analysers (Walden et al, 1987) and at the key comparison pilot study of national ozone photometers (Viallon et al, 2006). Other techniques that are more robust than regression analysis have been used for analysis of the results between two different analysers used to measure the concentration of particulate matter in ambient air (R. Beier, 2007).

4.3. Calibration and measurement capabilities, CMC

In chapter 2.4 the concept of calibration and measurement capabilities (CMC) was described and connected to the CIPM MRA. CMC claims are important for laboratories in order for them to show their capabilities for obtaining reliable measurement results, but also to provide CRMs. As stated previously, participation in key comparison projects under the CIPM or the RMO (e.g., EURAMET) is the way for a laboratory to support its CMC claims. In addition, the laboratory may also indicate its wish to participate in a key comparison project as a pilot study in order to gain evidence for the NMI regarding the capability of the laboratory. This is usually part of the process for a laboratory seeking designation by the NMI.

The MIKES-FMI Standard Laboratory submitted its CMCs via MIKES to the Gas Working Group (GWG) of MetChem for evaluation. The procedure started in the year 2000 initially within the EUROMET forum (EUROMET-512, project) by filling in a questionnaire provided by EUROMET and by filling in the CMC Table. In Appendix 17, the EUROMET questionnaire for reviewing CMC is presented, and in Appendix 18 the content of the CMC claims of the laboratory are shown. The evaluation of the CMC Tables of the NMIs and the designated laboratories in Europe was conducted by the GWG of the MetChem (Woods, 2000) for the first cycle in September 2000. The evaluation of the FMI was made by the NMIs of Slovakia (SMU) and Poland (GUM). The acceptance of the CMC was approved by EUROMET in 2001, and approval by the other RMOs took place in 2002. Finally the CMC tables of the laboratory, after its being designated as an NSL, were included in the database of the BIPM in 2002 (www.bipm.org).

The entries of the calibration and measurement capabilities of the laboratory were based on the uncertainty analysis that had been prepared for the calibration and measurement methods according to the Chapters 3.4.1, 3.4.2, and 3.4.4. The supporting evidence for the CMC entries were obtained from three comparison projects: EUROMET 430, EUROMET.QM-K1c and EUROMET 414 projects. The EUROMET 430 project, “Harmonisation of air quality measurements in Europe, HAMAQ” (Bell et al 2000), was conducted during 1997 – 2000, and included the gas components NO, NO_2, SO_2, CO and benzene (C_6H_6). Secondly, participation in the EUROMET.QM-K1c-project for the “Comparison of measurements of nitrogen monoxide in nitrogen” (Van der Veen at al. 2004) was to obtain supporting evidence for the NO entries in the laboratory’s CMC. Finally ozone, which was the last component to be added to the CMCs of the calibration laboratory, was supported by the EUROMET 414-project, conducted in 2001 (Sweeney et al, 2002). Since then, further support for the CMC entries has been obtained from participation in key comparison projects (see next chapter).

5. RESULTS

5.1 Key comparison results

5.1.1 EUROMET 430 project

The first KC project that the FMI-Calibration Laboratory took part in was in the EUROMET arena (EUROMET 430), originally Research and Development Programme IV (Standards, measurements and technology, SMT), funded by the European Commission, EC. The name of the project was “Harmonization of air quality measurements in Europe, HAMAQ” (Bell et al 2000). The gas components included in the project were benzene (C_6H_6), carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO_2), and sulphur dioxide (SO_2). The project was established to support the aims of the European air quality directives (Council directive 1999) and to determine the capabilities of the European air quality national reference laboratories and metrological institutes to prepare and to analyse these gas compounds at the required level of uncertainty. The overall aim of the HAMAQ project was to improve the consistency of air quality measurements made by EU member states, particularly the key measurements associated with the EC’s Air Quality Directives (Bell et al. 2000).

During the first comparison, only the core laboratories, shown in Appendix 16, analysed the samples in order to check the coherency of the results. The results of the first comparison were not, however, very good. The target value for the relative difference of the results between the value assigned value by the pilot laboratory and the result gained by the participating laboratory was 1%. As this was only reached in the case of carbon monoxide, more work was done at the laboratories for improving both the analysis and the preparation of the samples (Bell et al. 2000). In Tables 5.1a to d the subsequent results for the different compounds analysed by the FMI is shown.

Table 5.1a. The results for carbon monoxide (CO Circulation Cylinder, number 5701201) during the second intercomparison round of the HAMAQ project with the laboratories that analysed the same gas standard.

Laboratory	**Date Measured**	**Derived concentration/ppm**	**Uncertainty (for 95% confidence limit)**	**% difference from pilot laboratory NPL = ½ (NPL_1 + NPL_2)**
NPL (initial measurement: NPL_1)	13.1, 3.2, 5.2.98	20.37	0.06	0.0
LNE	2.3, 3.3, 4.3.98	20.00	0.43	-1.8
NMi	25.5.98	20.33	0.06	-0.2
VTT/FMI	30.8.98	20.52	0.23	+0.8
UBA	16.9.98	20.30	0.27	-0.3
NPL (final measurement: NPL_2)	11.12.98	20.36	0.09	0.0

Table 5.1.b. The results for nitrogen monoxide (NO Circulation Cylinder, number 9642) during the second intercomparison round of the HAMAQ-project with the laboratories that analysed the same gas standard.

Laboratory	**Date Measured**	**Derived Concentration/nmol /mol**	**Uncertainty (for 95% confidence limit)**	**% difference from pilot laboratory LNE = ½ x (LNE_1 + LNE_2)**
LNE (initial measurements: LNE_1)	17.12.97	194.1	1.9	-0.1
VTT/FMI	29.1.98	195.5	3.8	+0.6
JRC	4.3.98	193.5	3.0	-0.4
ISCIII	15.6.98-21.7.98	194.1	11.3	-0.1
NPL	15.9.98	192.7	1.9	-0.8
UBA	22.10.98	197.0	2.2	+1.4
NMi	11.11.98	190.4	3.8	-2.0
LNE (final measurements: LNE_2)	24.11.98	194.4	1.9	+0.1

Table 5.1.c. The results of sulphur dioxide (SO_2 Circulation Cylinder, number 5791F) during the second intercomparison round of the HAMAQ-project with the laboratories that analysed the same gas standard.

Laboratory	**Date Measured**	**Derived concentration/nmol/mol**	**Uncertainty (for 95% confidence limit)**	**% difference from pilot laboratory JRC = ½ x (JRC_1 + JRC_2)**
JRC (initial measurement: JRC_1)	10.03.	183.4	4.0	+1.0
NPL	04.06., 09.06., 15.06.	181.4	1.5	-0.1
NMi	23.07., 27.07., 28.07.	179.0	0.4	-1.4
VTT/FMI	08.09., 10.09., 11.09.	179,0	7.2	-1.4
JRC (final measurement: JRC_2)	09.11., 10.11., 01.12.	179.7	3.9	-1.0

Table 5.1.d. The results of nitrogen dioxide (NO_2 Circulation Cylinder (number 9817) during the second intercomparison round of the HAMAQ-project with the laboratories that analysed the same gas standard.

Laboratory	**Date Measured**	**Derived concentration/nmol/mol**	**Uncertainty (for 95% confidence limit)**	**% difference from pilot laboratory UBA = ½ (UBA_1 + UBA_2)**
UBA (initial measurement: UBA_1)	7.2.98	219.3	2.8	-2.08
VTT/FMI	18.3.98	226.1	5.0	+0.96
LNE	6.4.98	222.3	3.7	-0.74
ISCIII	23-26.11.98	229.4	13.7	+2.43
NMI	24.12.98	237.6	5.9	+6.10
UBA (final measurement: UBA_2)	7.7.99	228.6	3.7	+2.08

In general, the FMI Calibration Laboratory successfully managed to take part in this first comparison project and the results obtained in the project were good. The target value for the relative difference of the results between the assigned value and that of the participating laboratory was achieved with all the gas compounds except sulphur dioxide. As can be seen from Tables 5.1c and 5.1d, there seems to have been some drift between the initial and final values of the standard for sulphur dioxide and nitrogen dioxide. The project gave good experience, as well as motivation to improve operations at the calibration laboratory.

5.1.3 EUROMET 414 project

The EUROMET 414 project was a supplementary project, carried out to determine the accuracy and uniformity of the primary ozone calibration standards held at NMIs and NRLs in fifteen countries across Europe. Two European national metrology institutes acted as pilot laboratories, and these transported photometric ozone transfer standards to all the participants (Sweeney et al, 2002). The pilot laboratories were the Physikalisch-Technischen Bundesanstalt, PTB, Germany and the National Physical Laboratory, NPL, in the United Kingdom. Both laboratories were using a Standard Reference Photometer by NIST as a primary ozone photometer, and the comparison was conducted with a transfer standard that was checked against the SRP.

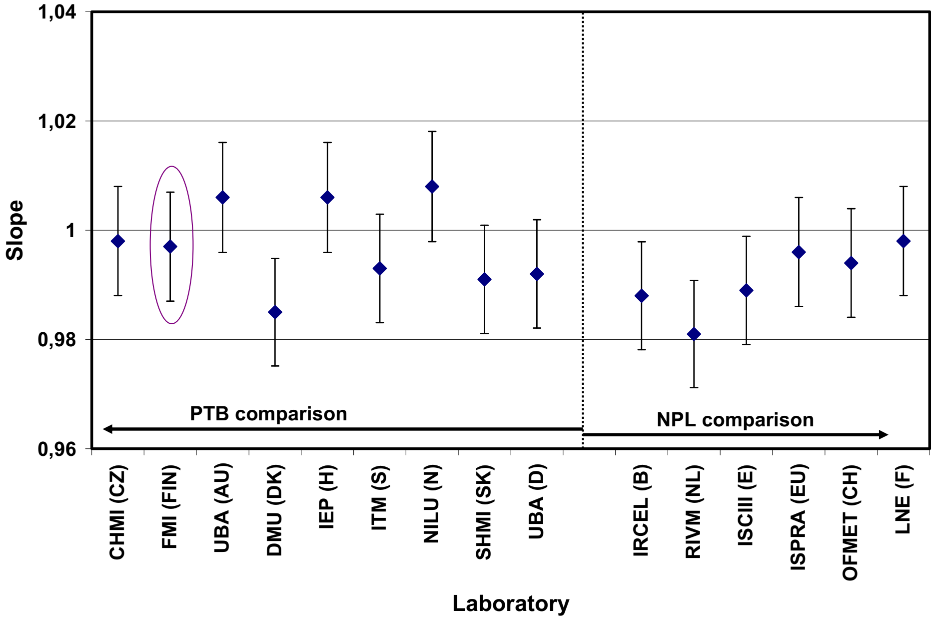


Figure 5.1. The slope of the ozone photometer of the participating NMIs and NRLs against the SRP of the pilot laboratories is shown, together with the relative target uncertainty of 1 %.

The comparison was conducted at the FMI in 2000 by the transfer standard of the PTB,. A summary of the results of the comparison is presented in Figure 5.1, in which the slope is that of the linear regression line between the national ozone photometer of the participant laboratory (as the y-axis) against the SRP of the pilot laboratory (x-axis). Also shown is the target uncertainty of 1 % for the slope. The uncertainty estimations for each of the participants and each of the concentrations were performed in the same way for all of the participants. The traceability of the Finnish national ozone photometer, TEI 49CPS by Thermo Electron Inc, USA, was to SRP-15 at the Swiss Federal Laboratories for Materials Testing and Research (EMPA). The result of the MIKES-FMI Standard Laboratory was very good. A more detailed analysis can be found in the final report (Sweeney et al. 2002).

5.1.4 EUROMET 638 project (EUROMET QM-K1c)

The first key comparison project of CCQM (CCQM-K1.a-g) was launched in 1995, and the final report was prepared in 1999 (Alink, 2000). The group of gas mixtures included in the project comprised carbon monoxide, carbon dioxide, nitrogen monoxide, sulphur dioxide and natural gas. The natural gas included nitrogen, carbon dioxide, ethane, propane, butane and methane. The activities of the gas working group within MetChem have increased considerably since then, and it was decided to conduct a regional key comparison, CCQM-K1c, but conduct the project only with nitrogen monoxide. The objective of EUROMET QM-K1-project was the same as CCQM-K1c: to compare the measurement capabilities of National Metrology Institutes in measuring the amount of substance fraction in nitrogen monoxide in nitrogen. The list of participants and the calibration methods is shown in Table A16.6 in Appendix 16.

The degrees of equivalence, together with the uncertainty of the results (see in Equation 5.3), are shown in Figure 5.2. The degree of equivalence of the MIKES-FMI Standard Laboratory is -0.4 % which is well within the relative expanded uncertainty of the laboratory. The expanded uncertainty of the reference gas standard used in this comparison by the laboratory was ± 1 %. Most of the contribution to the uncertainty budget of the laboratory (± 1.5 %, see in Figure 5.2)) comes from the uncertainty of the gas standard; the result is good, and shows that by purchasing more accurate gas standards the uncertainty of the measurements can be decreased. The other environmental laboratory, CMI/CHMI, also succeeded very well, having almost the same results as the MIKES-FMI Standard Laboratory.

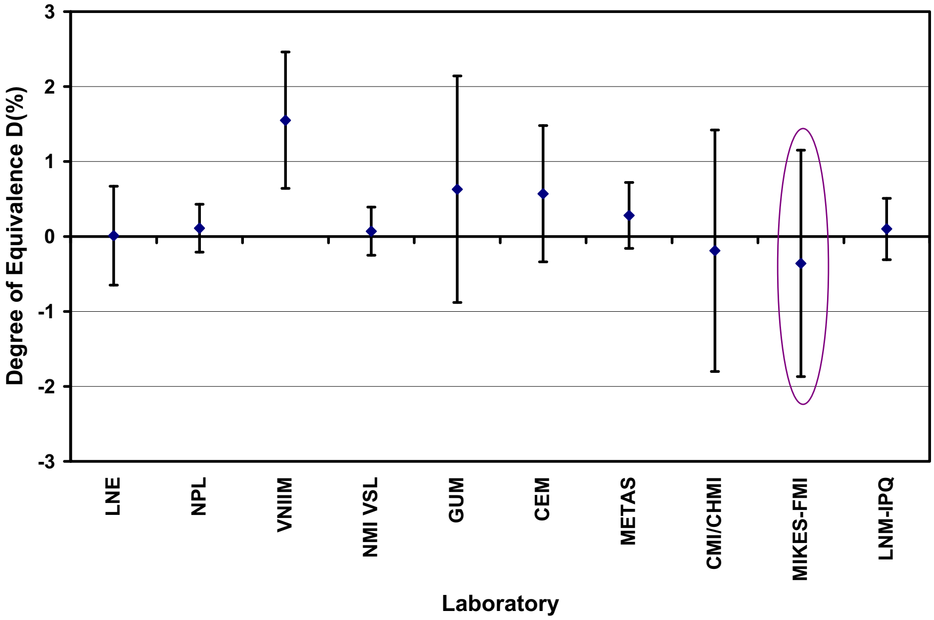


Figure 5.2. Degrees of equivalence with the expanded uncertainty for nitrogen monoxide of the EUROMET K1 project by the participating laboratories.

5.1.5 CCQM-P28 project

This pilot project was aimed at evaluating the comparability of ozone reference standards that are maintained as national standards, or as primary standards within international networks for ambient ozone measurements. The project was organized by the Consultative Committee for Amount of Substance (CCQM). Laboratories that held national ozone standards were invited to join the project by a questionnaire that was sent out by the chemical sector of the BIPM in 2002. The study was a prelude to an on-going key comparison. The comparisons of the national ozone standards of participating laboratories were conducted at the BIPM during the period from July 2003 to February 2005 (Viallon et al., 2006). Comparisons were performed at the BIPM following two protocols: a direct comparison with a national standard (protocol A), or by means of the transfer standard (protocol B). In the latter case the comparison of the transfer standard and the national standard should have been made by the participating laboratory. The comparison was made by introducing zero and ten different concentrations of ozone into the national ozone photometer and the reference photometer covering the range of 0 to 500 nmol/mol of ozone. The FMI followed the protocol A with traceability to the Standard Reference Photometer no 24 of the Laboratoire National D'Essais (LNE, France). The participating laboratories, with the protocol followed (A or B) and the traceability of the measurements, are listed in Appendix 16 (Table A16.8).

The results shown in Figure 5.3 are the slope between the SRP-27 and the national ozone photometer. The uncertainty estimate for the photometers varies, depending on whether there is a direct link to an SRP, or there is traceability to the SRP of another country (see Table A16.8). In the case of laboratories that support an SRP, the uncertainty of the cross-section for ozone has been neglected (see in Figure 5.3). Laboratories without an SRP have included the uncertainty due to the traceability chain in their uncertainty budget, but not that of the cross-section. This was the case with the FMI, which participated with the then national ozone photometer by Thermo Environment Ltd, model TEI 49CPS. The calibration of the TEI 48CPS was conducted at the French NMI (LNE laboratory) a few days prior to the comparison at the BIPM.

One should keep in mind that showing the slope of the national ozone photometer against the reference photometer (SRP-27) is not the conventional way of presenting the comparison results according to the CIPM MRA. It was therefore it was decided to use two concentrations from the comparison measurements, 80 nmol/mol and 420 nmol/mol , to be used as the reference values for the comparison. The degree of equivalence for both of the reference values and the uncertainties were calculated. For more details of the results, the reader is referred to the final report of this pilot study (Viallon et al., 2006).

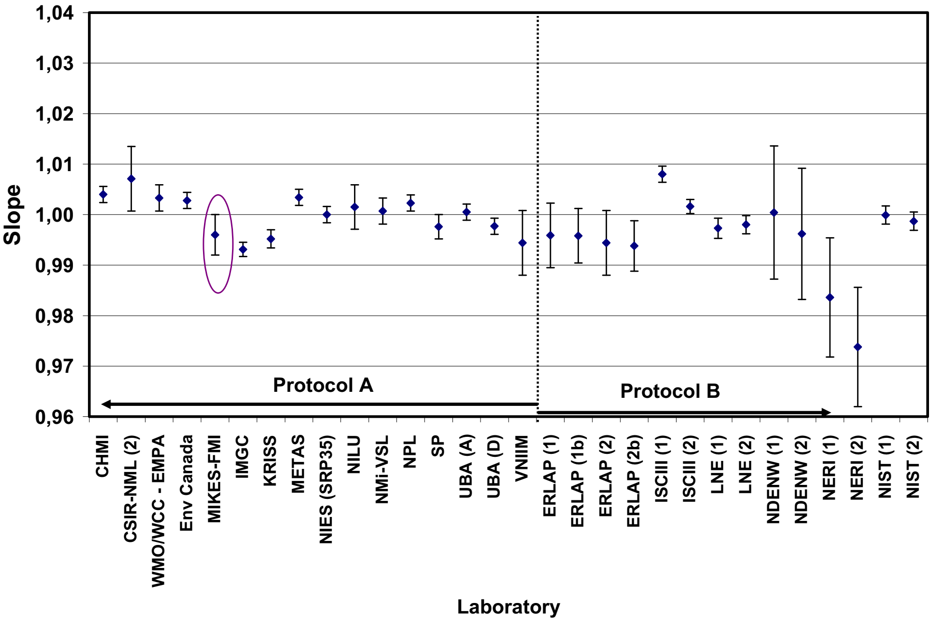


Figure 5.3. Slopes of the national ozone photometers against the SRP-27 of BIPM (analyzed by a generalized least-squares model) are presented by the participating laboratories following the protocol A or B (Viallon et al., 2006).

5.1.6 CCQM-K26a and b key comparison project

This project was focused on supporting the monitoring requirements of European air quality legislation. The limit values (LV) or maximum allowed concentrations of sulphur dioxide and nitrogen dioxide in ambient air are regulated by almost every country, and therefore the project interested a number of metrological laboratories around the world. Even though an LV air quality standard is set for nitrogen dioxide, nitrogen monoxide was chosen as the gas compound in the CCQM-K26a-comparison project. This was because the reference method for measurements of nitrogen dioxide within the EU is the chemiluminescence method, which measures nitrogen monoxide according to reaction (R3-1). Manufacturers that have built continuously-working analysers on this principle measure nitrogen dioxide by converting it into nitrogen monoxide as described in chapter

3.5. Finally, it is somewhat easier to prepare a stable gas standard of nitrogen monoxide at low levels of concentration than that for nitrogen dioxide.

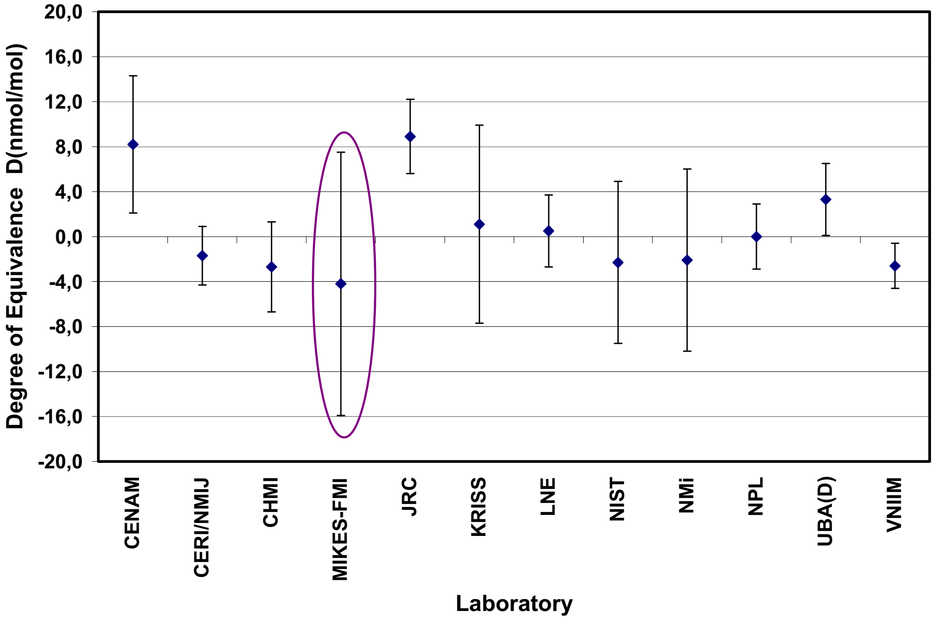


Figure 5.4. Degrees of equivalence of the laboratories participating in the CCQM K26a project, nitrogen monoxide (NO) in nitrogen (N_2).

NO mixtures prepared for the project have a balance gas of nitrogen, to minimise the oxidation of NO into NO_2, while SO_2 mixtures have a balance gas of synthetic air.

The concentrations involved in these comparisons have been chosen as those likely to be used for field calibrations within the appropriate European standards.

The protocol for this key comparison was initiated by NPL at the EUROMET Gas Analysis Working Group. Subsequently, laboratories from outside the EUROMET group expressed an interest in participation, and the proposal was submitted to the CCQM Gas Working Group as a key comparison. The proposal was ratified by the CCQM in April

2002 (Protocol of the CCQM-K26a and b-projects), and the measurements were conducted in 2005.

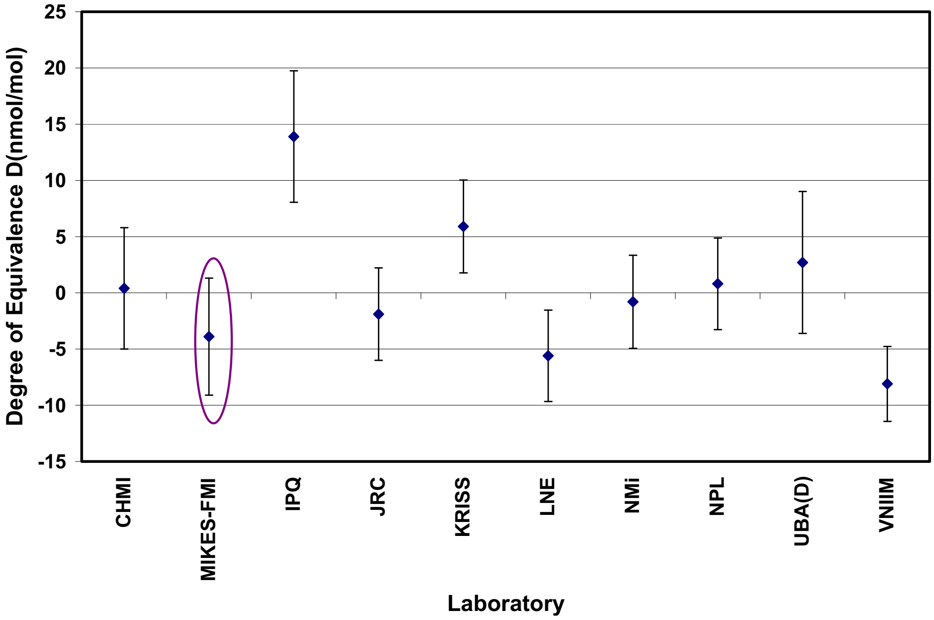


Figure 5.5. Degrees of equivalence of the laboratories participating in the CCQM K26b project, sulphur dioxide (SO_2) in synthetic air.

The results of the projects are shown in Figures 5.4 and 5.5. Both of the results shows that the FMI managed to achieve results within the uncertainty statement of the laboratory (Maruyama et al. 2007, Perez et al 2007). There seems to be some evidence of underestimation of the reference value in both of the key comparisons. The measurements were conducted at the laboratory in close proximity to each other using the same dilution coefficients for both of the measurements (see in Figure 3.3a). The correction factor for correcting the dilution stages was 0.47 %, which was less than the 1 % agreed for the quality system of the laboratory (Equation 3.32). The results were not corrected based on the calibration, and this might be a cause for underestimation in the results. In spite of this, the laboratory showed consistent results, and succeeded very well in both of the projects.

5.1.7 BIPM.QM-K1 project

The project was initiated as an ongoing key comparison project after CCQM-28P, which was a pilot project. The BIPM.QM-K1 project is aimed at evaluating the level of comparability of ozone reference standards that are maintained as national standards, or as primary standards within international networks for ambient ozone measurements (BIPM.QM-K1, 2007). Two different protocols exist, depending on the comparison instrument: national ozone photometer or transfer ozone photometer. At this time the FMI participated with the SRP-37 at the BIPM where the comparison was conducted against the SRP-27. Three reports of the project have so far been published (Viallon et al, 2008a, 2008b, 2008c). The list of participants is not available, but it is most likely that the same laboratories that participated in CCQM-P28 are also participating in this project.

In Table 5.2 the results are given of the comparison between the SRP-37 (Finnish National Standard) and the SRP-27 (BIPM Reference Standard). Results are not yet final.

Table 5.2. The results of the BIPM.QM-K1 key comparison project for ozone photometers. The Reference Standard is the SRP-27 of the BIPM and the National Standard is the SRP-37 of the MIKES-FMI Standards laboratory. Parameters x_{RS} and s_{RS} are the mean value over ten stable readings from the instruments and the standard deviation of the mean, while $u(x_{RS})$ and $u(x_{NS})$ are the standard uncertainties of the Reference Standard and the National Standard, respectively. The degrees of equivalence D_i, and the uncertainty components of $u(D_i)$ and $U(D_i)$ are presented on the right-hand side of the columns.

	Measurement results								
	Reference Standard (RS)			National standard (NS)			Degrees of Equivalence		
Nominal value	x_{RS} nmol/mol	s_{RS} nmol/mol	$u(x_{RS})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	Di (nmol/mol)	u(Di) (nmol/mol)	U(Di) (nmol/mol)
0	0,04	0,16	0,28	-0,16	0,23	0,28	-0,20	0,40	0,79
220	223,85	0,21	0,70	222,68	0,27	0,70	-1,17	0,99	1,98
80	80,37	0,27	0,36	80,20	0,25	0,36	-0,17	0,52	1,03
420	420,49	0,18	1,26	418,92	0,28	1,26	-1,57	1,78	3,56
120	123,33	0,12	0,45	122,93	0,18	0,45	-0,41	0,63	1,27
320	320,52	0,32	0,98	319,23	0,21	0,98	-1,29	1,38	2,76
30	33,96	0,23	0,29	33,78	0,25	0,29	-0,18	0,41	0,83
370	372,47	0,20	1,12	370,89	0,37	1,12	-1,58	1,58	3,16
170	171,22	0,27	0,57	170,68	0,24	0,57	-0,54	0,81	1,61
500	497,25	0,21	1,49	495,52	0,22	1,49	-1,74	2,10	4,20
270	273,73	0,28	0,84	272,64	0,35	0,84	-1,09	1,18	2,37
0	-0,06	0,32	0,28	-0,04	0,15	0,28	0,01	0,40	0,79

From Table 5.2 one can see that $u(x_{RS})$ and $u(x_{NS})$ are the same and that the degree of equivalence, D_i, is less than the expanded uncertainty of the degree of equivalence. Still there is some systematic behaviour ($D_i < 0$, for all i) seen in the result of the degree of equivalence.

The comparison of the reference standard and the national standards were performed at 12 nominal ozone concentrations (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270 and 0). The evaluation of the degrees of equivalence was chosen to be performed at concentrations of 80 and 420 nmol/mol. In Figure 5.6 the degrees of equivalence at both of these concentrations are shown for the case of the MIKES-FMI Standards Laboratory. The results from the CCQM-P28 and BIPM.QM-K1 projects are both shown for comparison.

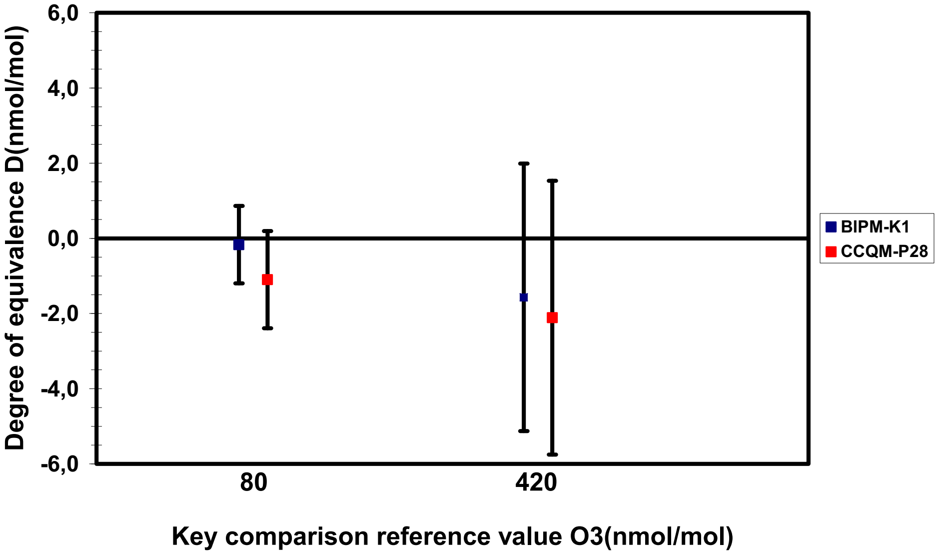


Figure 5.6. Degrees of equivalences at the nominal concentrations of 80 and 420 nmol/mol for the MIKES-FMI Standard Laboratory in the CCQM-P28 and BIPM.QM-K1 projects.

In Figure 5.6 one should keep in mind that, in the case of project CCQM-P28, the measurements were conducted with the TEI-49 CPS as the Finnish national standard and the traceability chain was connected to SRP-24 (see chapter 5.1.5). The comparison at the BIPM at that time was conducted against the SRP-27, as was also the case in BIPM.QM-K1. The uncertainty of the results of the MIKES-FMI Standards Laboratory has decreased only to a small extent, even though the national photometer has been changed from the TEI-49 CPS to the SRP-37. The discrepancy between the SRP-27 and SRP-37 would be expected to be smaller, but these discrepancies are well within the uncertainty limit (see in Appendix 13).

5.1.8 CCQM-K51 project

Carbon monoxide was one of the gas compounds used in the first key comparison projects CCQM-K1a (Alink, 2000). The FMI did not participate in the project, since at the time it was launched (1994 – 95) the FMI was not designated as a metrology laboratory. When the FMI submitted its CMCs in 2000, carbon monoxide was included. The CO entry was supported by the EUROMET 430 project (chapter 5.1.2). CCQM-K51 was launched in 2008 and the MIKES-FMI Standards Laboratory took part in the project. The nominal concentration was 5 µmol/mol in nitrogen. The HFTLS statement of the project supports the CMC claims for carbon monoxide of 5 µmol/mol and higher. One point of clarification is needed, since the balance gas is nitrogen and not synthetic air as stated in the CMC entry. To overcome this problem, the MIKES-FMI Standards Laboratory has made comparisons between nitrogen and synthetic air as the dilution gas, and no clear evidence for any difference between them has been found. However, evidence regarding the sensitivity of the analyser based on the NDIR method between nitrogen and synthetic air as balance gases in the gas standards (gas cylinder) was reported by Bell et al. (2000).

The list of participants is shown in Appendix 16 (Table A16.10). The uncertainty budget for the measurements at the MIKES-FMI Standards Laboratory was constructed including the uncertainty components of the gas standards for the calibration of the analyser and the performance characteristics of the analyser (see Appendix 15 and 16).

In Table 5.3 the key comparison results, including the uncertainty components of the KCRV and of the MIKES-FMI Standards laboratory is shown (CCQM-K51, 2008). Since at the present time only the Draft A-report of the CCQM-K51 project has been prepared for the participants, the results are not complete, and the results of the other participating laboratories are not shown here.

Table 5.3. The key comparison reference value, x_{KCRV}; standard uncertainty of the preparation, u_{prep}; standard uncertainty of verification, u_{ver}; expanded uncertainty of the KCRV, U_{KCRV} ; KC-result of the MIKES-FMI Standards Laboratory, $x_{\mathrm{MIKES\text{-}FMI}}$; expanded uncertainty of the MIKES-FMI Standards Laboratory, $U_{\mathrm{MIKES\text{-}FMI}}$; degree of equivalence, $D_{\mathrm{MIKES\text{-}FMI}}$; expanded uncertainty of the degree of equivalence, $U(D)$; coverage factor, k; relative degree of equivalence, $U(D)/D_{\mathrm{MIKES\text{-}FMI}}$; and relative expanded uncertainty of the degree of equivalence $U(\%)$.

Parameter	Value (µmol/mol) or %
x_{KCRV}	5.0258
u_{prep}	0.0112
u_{ver}	0.0126
U_{KCRV}	0.0337
$x_{\mathrm{MIKES\text{-}FMI}}$	5.0200
$U_{\mathrm{MIKES\text{-}FMI}}$	0.0540
$D_{\mathrm{MIKES\text{-}FMI}}$	-0.00577
$U(D)$	0.064476
k	2
$U(D)/D_{\mathrm{MIKES\text{-}FMI}}$	-0.11%
$U(\%)$	1.28%

As can be seen from Table 5.3, the relative degree of equivalence of the MIKES-FMI Standards Laboratory (= -0.11 %) is well within the relative expanded uncertainty of the degree of equivalence (=1.28 %).

5.2 Results from the cross-checks of the calibration methods

5.2.1 Dynamic dilution method

Over the years the Sonimix 6000 A1 dilutor has been calibrated at the laboratory based on the calibrated CO analyser. The slope of the dilution stages has been defined at the calibrations of the dilutor and is shown in Figure 5.8. In the figure are shown the slope, the average of the slope, the upper and lower alarm lines (= median ±2σ), and the upper and lower control lines (= median ±3σ) since 2002. As one can see from the Figure 5.8, the slope has mostly been within 2 % except just at the beginning of the time series. The reason was that at that time the pressure of the dilution line was not monitored and could change due to changes in the compressed air system of the laboratory. After installing a pressure meter on the gas and dilution lines of the Sonimix 6000 A1, one could monitor whether the input pressure was constant, or changing as a function of ambient pressure, only. The Sonimix was also calibrated for mass flow through each of the dilution stage at the LNE in February, 2002 and in October, 2007. Based on the calibration results no changes to the mass flow rate were observed over the 5 year period. On the other hand there is a clear change at the slope in November, 2007. Most likely the change is associated with the change of the gas standard than the change of the output of the mass flow rate of the each of the dilution stage.

In Figure 5.9 one can see the effect of the pressure of the input line both on the dilution line and on the calibration gas line.

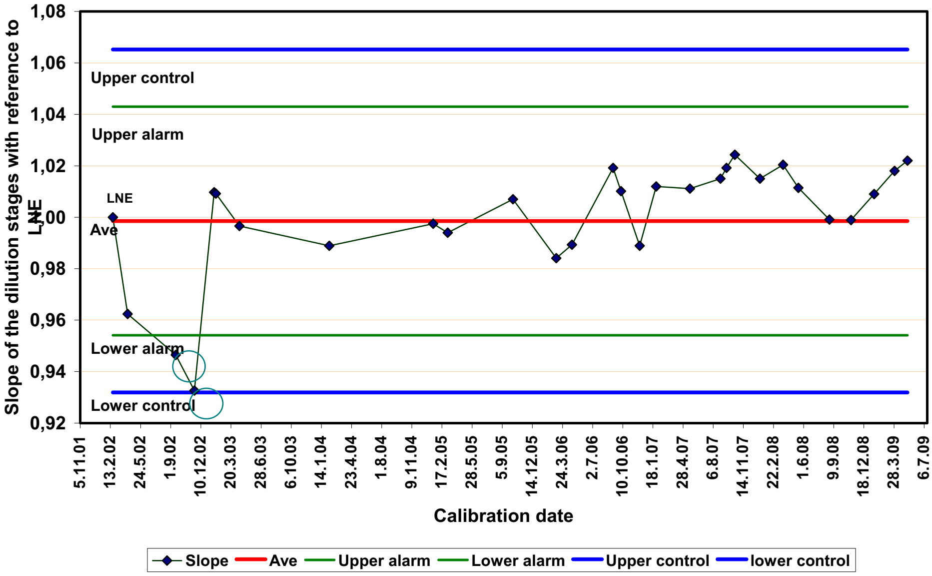


Figure 5.8. The slope of the dilution stages of the Sonimix 6000 A1 dilutor as obtained from different calibrations with progression of time. Ave is the average of the slope over the whole period. The alarm and control lines (upper and lower) are the average ±2σ and average ±3σ, respectively, where *σ* is the standard deviation of the slopes.

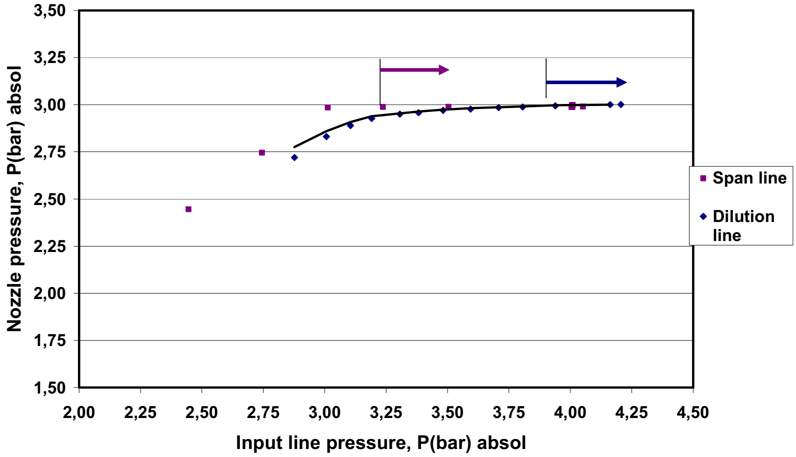


Figure 5.9. The upstream pressure to the nozzles of the Sonimix 6000 A1 as a function of the input line pressure for the dilution line and the span gas line. The arrows indicate the lowest level of input pressure that maintains the nozzle pressure constant for the span and dilutions lines.

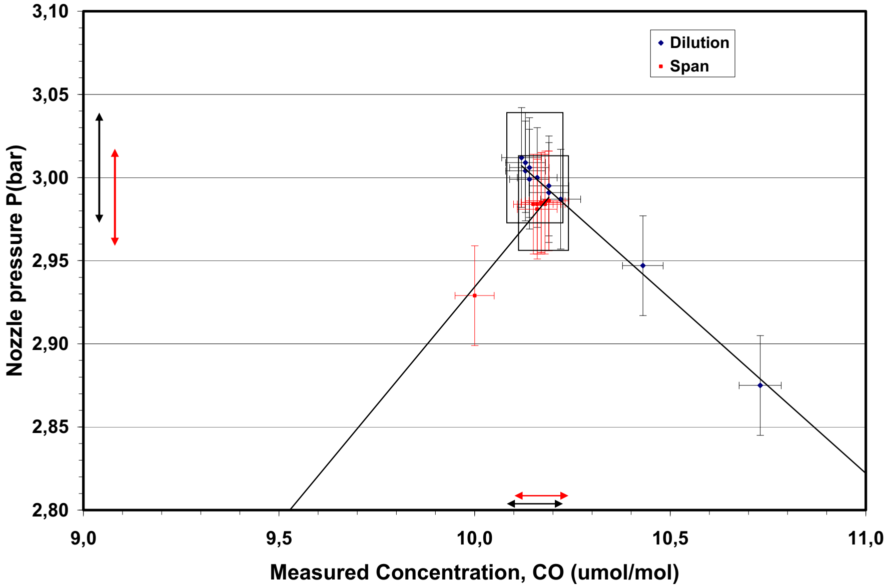


Figure 5.10. The upstream nozzle pressure for the gas flow and the dilution flow is presented as a function of the measured concentration. The coloureds areas covers the range of nozzle pressures, inside which the output concentration (measured concentration) found to be constant within 0.5 %. The straight lines on the span and dilution lines are the regression lines of the nozzle pressure as a function of concentration.

From Figure 5.9 one can see that close to and above an input pressure of 3 bar, the nozzle pressure is constant for the span line, but for the dilution line the input pressure needs to be higher than about 4 bar. The difference between the input pressure ranges arises from the fact that the flow rates of the nozzles are 4 to 10 ml/min in the span line but as high as 3500 ml/min in dilution line. Still the pressure regulation for both lines is set to about 2 bar as relative pressure above the ambient pressure. The stable output concentration is limited to the ability to maintain a stable nozzle pressure. When the nozzle pressure decreases in the dilution line, the concentration increases linearly, as is seen in the Figure 5.10 (on the right-hand side of the figure). On the other hand when the nozzle pressure decreases in the span line, the concentration decreases as well. The range of stable output with the concentration varying within the 0.5 % of the concentration can be achieved if the nozzle pressure is from 2.98 *bar* to 3.04 *bar* in the span line and from 2.96 *bar* to 3.02 *bar* in the dilution line.

The temperature has also an effect to the mass flow through the sonic orifice, as can be seen in Equation (3.1). However, the dependence of the temperature on the mass flow is proportional to the one over the square root of temperature ($T^{-1/2}$). It is therefore much too weaker dependence than that of the pressure.

5.2.2 Permeation method

The permeation method has been used mainly for testing the instruments and to cross-check another calibration method if there is some evidence of a drift in the results gained with that method.

The cross-check of the permeation method against the dynamic dilution method (Sonimix 6000 A1) is presented in Figure 5.11 for sulphur dioxide. The gas obtained from the permeation tube was diluted to a lower concentration with the dilution device (Environnement MG 101), and injected into the analyser. The mass flow controllers of the dilution device were calibrated against the reference flow meter of the laboratory. The temperature and the pressure of the dilution gas were measured during the calibration in order to correct the flow to the reference conditions of the flow meter. The flow meter, the temperature and the pressure meters are calibrated at the NMI annually (see Appendix 4). In Figure 5.11 the expanded uncertainties of both of the methods are shown as error bars; these were calculated according to Equations (3.14) and (3.17) for the dynamic dilution method and the permeation method, respectively.

The gas mixtures prepared by both of the methods were analysed by the same gas analysers. The contribution of the analyser is thus not included in the expanded uncertainty calculated for either of the calibration methods.

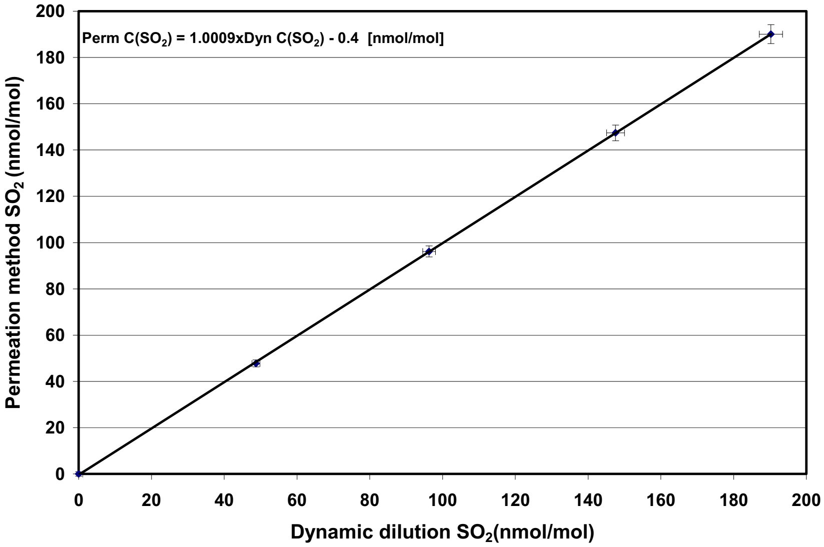


Figure 5.11. The cross checks of dynamic dilution method versus the permeation method for sulphur dioxide. The expanded uncertainty of both of the methods is indicated in the figure as bars.

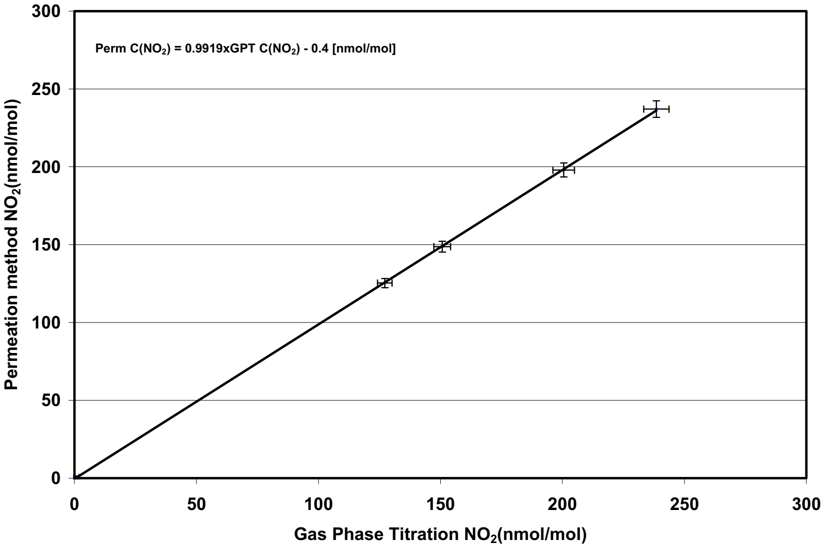


Figure 5.12. The nitrogen dioxide concentration obtained by the permeation method (y-axis) is compared to that obtained by the GPT method (x-axis). The error bars are the expanded uncertainty components associated with both of the methods at the measured concentrations.

The cross-checks of the permeation method against the GPT method (Sonimix 6000 A1) is presented in Figure 5.12 for nitrogen dioxide.

From Figure 5.11 one can see that the agreement between the dynamic and permeation methods with sulphur dioxide is extremely good. The same is true for the Gas Phase Titration method and the permeation method with nitrogen dioxide. Many of the NMI have reported their experience that the performance of the preparation of gas mixtures of sulphur dioxide by the permeation method is fairly good. This is also the case at the FMI, the operation of the permeation method with sulphur dioxide works very reliably. In the case of nitrogen dioxide, the key issue is that the flush flow (see in Figure 3.4) through the permeation oven must be very dry. Recently diffusion technique has been under more detailed study at some of the NMIs in parallel or replacement of the permeation method.

One should keep in mind that when performing the GPT, the converter efficiency of the NO-NO_x analyser needs to be known, and a correction to the results based on the defined converter efficiency be made. The expanded uncertainty between the permeation method (Equation 3.21) and the GPT method (Equations (3.37 and 3.38) are fairly close to each other. The regression equation shown in the two figures describes the relationship between the two methods. The regression line has not been forced through zero, but in both cases the intercept is within the uncertainty of the concentration for pure dilution gas.

5.2.3 Static volumetric dilution

The results from the comparison of a dynamically-diluted high concentration gas standard and the gas concentration prepared by the static injection system with a single injection of a volume of 4 ml of carbon monoxide is shown in Figure 5.13.

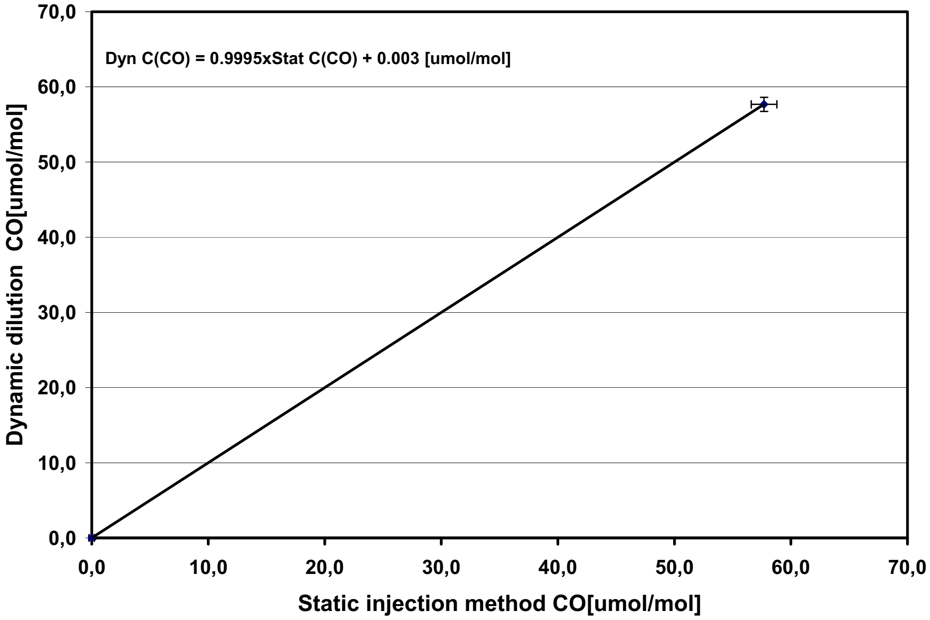


Figure 5.13. The comparison of the concentration of carbon monoxide prepared by the static volumetric method and by the dynamic dilution method. The error bars are the expanded uncertainties of both of the methods. The regression equation is shown at the top of the figure.

The concentration of the gas mixture prepared by the static volumetric method in Figure 5.13 is calculated according to Equation (3.14a or 3.14b), and is plotted on the x-axis. The prepared gas mixture is measured with the analyser calibrated by the dynamic dilution method and is plotted on the y-axis. The agreement between both of the methods is fairly good. The error bars shown in the figure are obtained from the uncertainty analyses of the dynamic dilution method and the static volumetric method according to Equations (3.14) and (3.21), respectively. One can see that the uncertainty of the static volumetric method is slightly larger than that of the dynamic dilution method. A problem arises when nitrogen monoxide is used instead of carbon monoxide. A certain amount of nitrogen dioxide is formed when synthetic air is used as the dilution gas. In addition, a certain quantity of the oxides of nitrogen has decreased, indicating some wall effect either for nitrogen monoxide or nitrogen dioxide.

5.2.4 Titration of nitrogen monoxide with ozone

The Sonimix 6000 A1 dilutor has an inbuilt function for performing the gas phase titration of nitrogen monoxide by ozone. As described in chapter 2.5.5, the common practice when using the GPT is to use an excess of nitrogen monoxide compared to ozone content. The method is used for defining the efficiency of the NO_2 – NO converter in the NO/NO_x analysers, and also to compare the consistency between the photometric method and dynamically-diluted gas standards that are traceable to the gravimetric method. The reverse method, in which the gas phase titration is made with an excess of ozone, can be used to calibrate ozone analysers.

During the GPT-measurements, the ozone and the NO/NO_x analysers are installed in the output line of the Sonimix 6000 A1 dilutor having an excess flow into the exhaust system. The exhaust system operates at ambient air pressure to ensure the correct operation of the analyser and the Sonimix 6000 A1. The gas phase reaction takes place during a sequence of functions that are clearly distinguishable from each other. The first step is to calibrate both of the analysers according to the SOP of the laboratory. The NO/NOx analyser is calibrated with the dilution method, using the high quality of the gas standard from the NMI. The ozone analyser is calibrated against the SRP-37. The next step is to pass pure dilution gas to both of the analysers. This will confirm the base level of the analysers. The next step is to produce a nitrogen monoxide concentration only. This will give the initial concentration level of the nitrogen monoxide. After this, the selected concentration of ozone (fulfilling the criteria of the Equation 3. 36) is created with the UV-lamp of the Sonimix 6000 A1. Recording the concentration value with the ozone analyser, the amount of ozone injected into the system will be known. During the next step, the reaction of the nitrogen monoxide at the initial concentration (Step 2) and the ozone concentration prepared at the previous concentration takes place according to reaction R2-1. At the high concentration in the Sonimix 6000 A1, the reaction takes place very rapidly (see Figure 3.12), after which dilution takes place. In Figure 5.14 are shown the steps in the procedure for performing the GPT by the Sonimix 6000 A1.

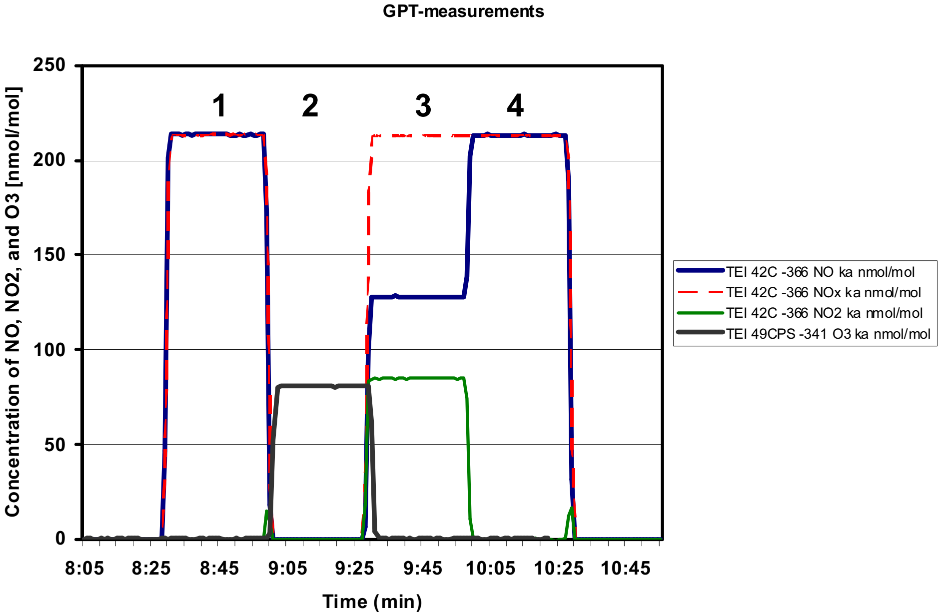


Figure 5.14. The sequences of the gas phase titration method using the Sonimix 6000 A1.

The sequence of the GPT (see Figure 5.14) can be repeated at different concentrations of nitrogen monoxide and varying concentrations of ozone as long as the criterion of Equation (3.33). In Figure 5.15 the results of the gas phase titration is shown. The x-axis of Figure 5.15 shows the concentration of nitrogen monoxide consumed by the reaction (R3-1); this is the difference between the initial condition at step 1 and that at step 3 in Figure 5.14. On the y-axis of figure is shown the ozone concentration measured at step 2 in Figure 5.14. At step 3, the amount of ozone consumed by the nitrogen monoxide is given by reaction (R3-1). The data points in Figure 5.15 are the results of the repeated sequences of the GPT at different concentrations of nitrogen monoxide and ozone. The error bars at each measurement point, both on the x-axis and y-axis, are the expanded uncertainties of the calibration method and the analyser (Equation 3.40). The regression equation, shown at the top left of the Figure 5.15, shows that the discrepancy between the two methods is about 2.8 % .

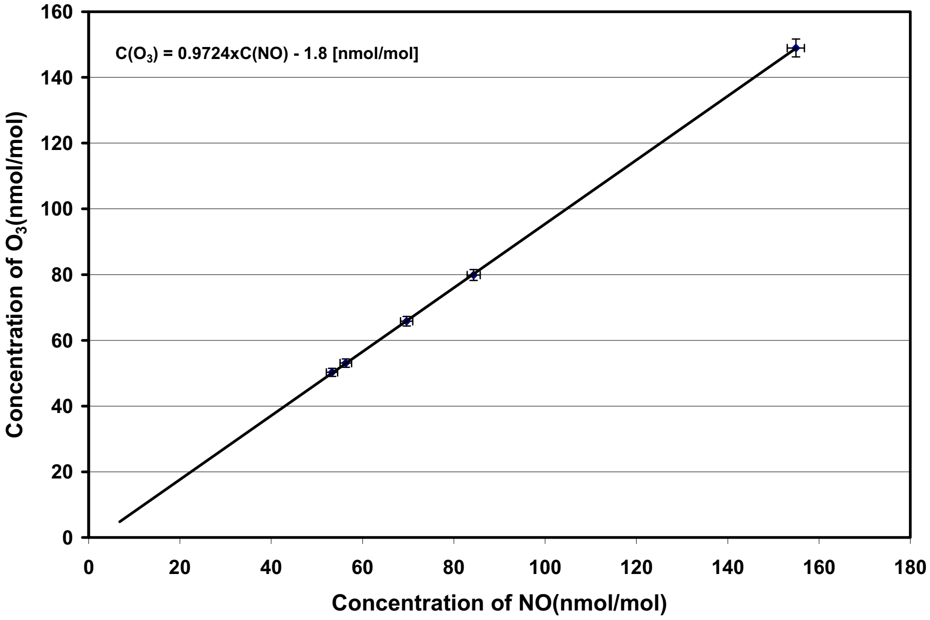


Figure 5.15. The results of the gas phase titration between the nitrogen monoxide and the ozone with an excess of nitrogen monoxide.

The degree of equivalence was calculated according to Equation (4.1), keeping the concentration of nitrogen monoxide as the reference value and the ozone concentration as the depended value. In addition, the uncertainty of the degree of equivalence was calculated according to Equation (4.3) with the help of Equations (3.14), (3.35), (3.36), and (3.37), and is plotted in Figure 5.16. Since the discrepancies between the two methods are more than the expanded uncertainty, the conclusion can be drawn that there is a systematic difference (bias) between the two methods. This result supports those obtained by the Japanese group (Tanimoto et al. 2005) and reported by BIPM (Viallon et al., 2006a).

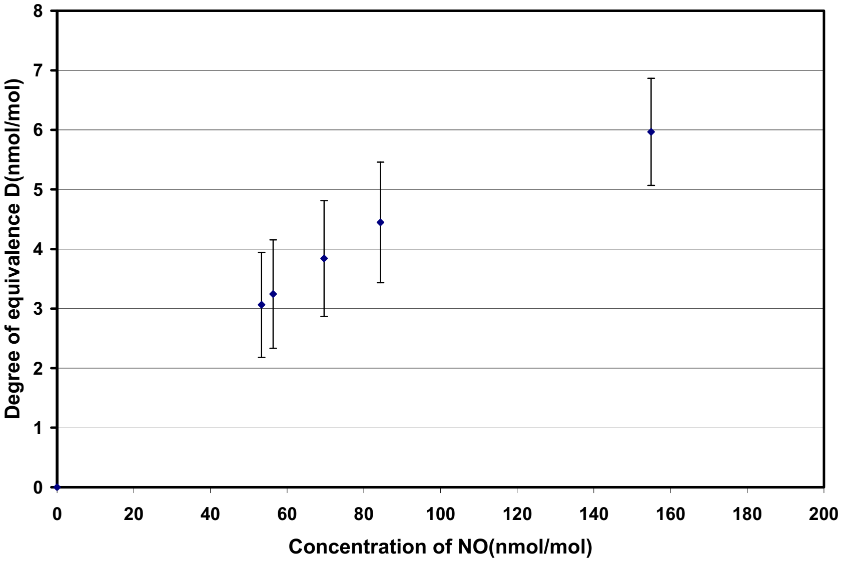
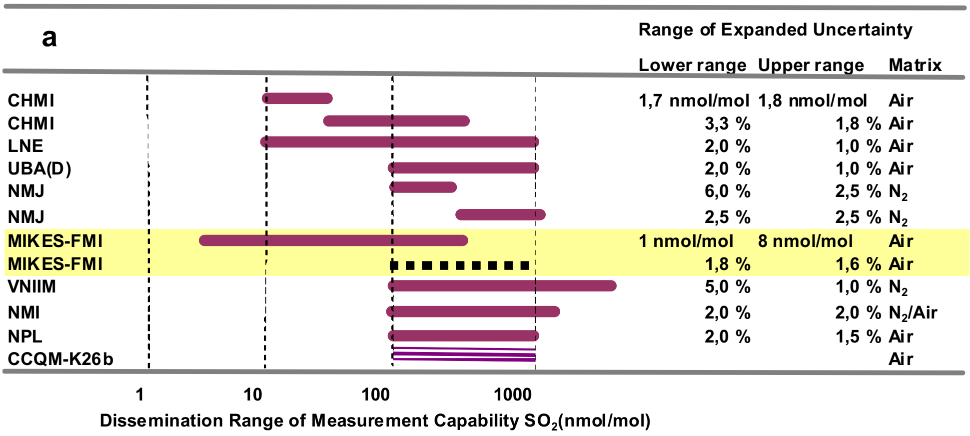


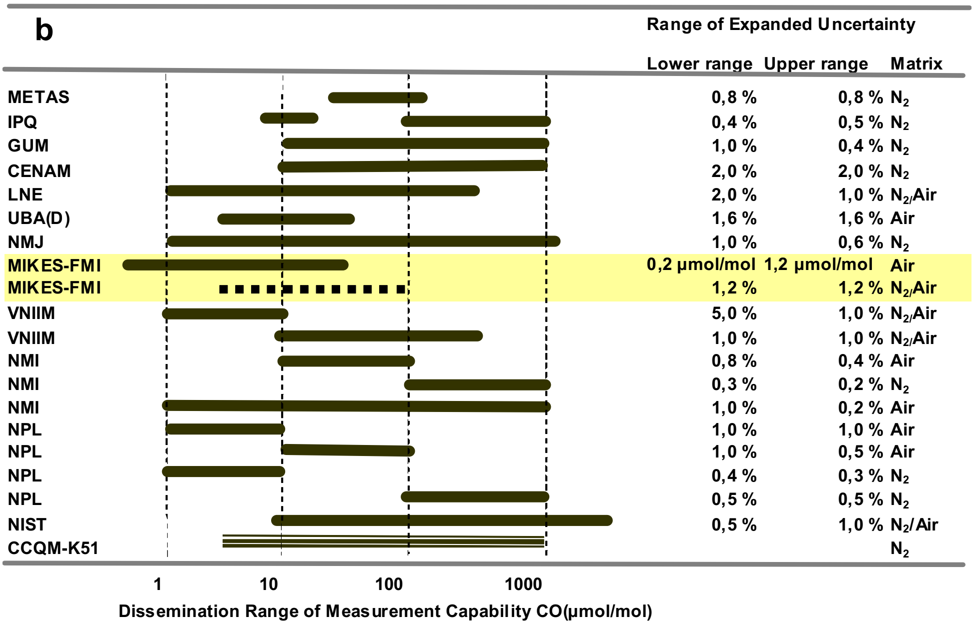
Figure 5.16. Degree of equivalence of the gravimetric method and the photometric method with the expanded uncertainty during the GPT method. The concentration of nitrogen monoxide is taken as the reference value.

5.3. CMC entries of the laboratory

The measurement and calibration capability of the laboratory was created based on the uncertainty budget of the calibration methods, as shown in chapter 3 and the questionnaire provided by the EUROMET project (EUROMET 512). The CMC entries of the laboratory taken from the BIPM database (www.bipm.org) are given in Appendix 16.

The CMC entries of the various laboratories are presented in Figures 5.17a-d for sulphur dioxide, carbon monoxide, nitrogen monoxide, and for ozone in the Environmental sub-category of the measurement service.


a
Range of Expanded Uncertainty
Lower range Upper range Matrix
CHMI 1,7 nmol/mol 1,8 nmol/mol Air
CHMI 3,3 % 1,8 % Air
LNE 2,0 % 1,0 % Air
UBA(D) 2,0 % 1,0 % Air
NMJ 6,0 % 2,5 % N_2
NMJ 2,5 % 2,5 % N_2
MIKES-FMI 1 nmol/mol 8 nmol/mol Air
MIKES-FMI 1,8 % 1,6 % Air
VNIIM 5,0 % 1,0 % N_2
NMI 2,0 % 2,0 % N_2/Air
NPL 2,0 % 1,5 % Air
CCQM-K26b Air
1
10
100
1000
Dissemination Range of Measurement Capability SO_2(nmol/mol)


b
Range of Expanded Uncertainty
Lower range Upper range Matrix
METAS 0,8 % 0,8 % N_2
IPQ 0,4 % 0,5 % N_2
GUM 1,0 % 0,4 % N_2
CENAM 2,0 % 2,0 % N_2
LNE 2,0 % 1,0 % N_2/Air
UBA(D) 1,6 % 1,6 % Air
NMJ 1,0 % 0,6 % N_2
MIKES-FMI 0,2 µmol/mol 1,2 µmol/mol Air
MIKES-FMI 1,2 % 1,2 % N_2/Air
VNIIM 5,0 % 1,0 % N_2/Air
VNIIM 1,0 % 1,0 % N_2/Air
NMI 0,8 % 0,4 % Air
NMI 0,3 % 0,2 % N_2
NMI 1,0 % 0,2 % Air
NPL 1,0 % 1,0 % Air
NPL 1,0 % 0,5 % Air
NPL 0,4 % 0,3 % N_2
NPL 0,5 % 0,5 % N_2
NIST 0,5 % 1,0 % N_2/Air
CCQM-K51 N_2
1
10
100
1000
Dissemination Range of Measurement Capability CO(µmol/mol)

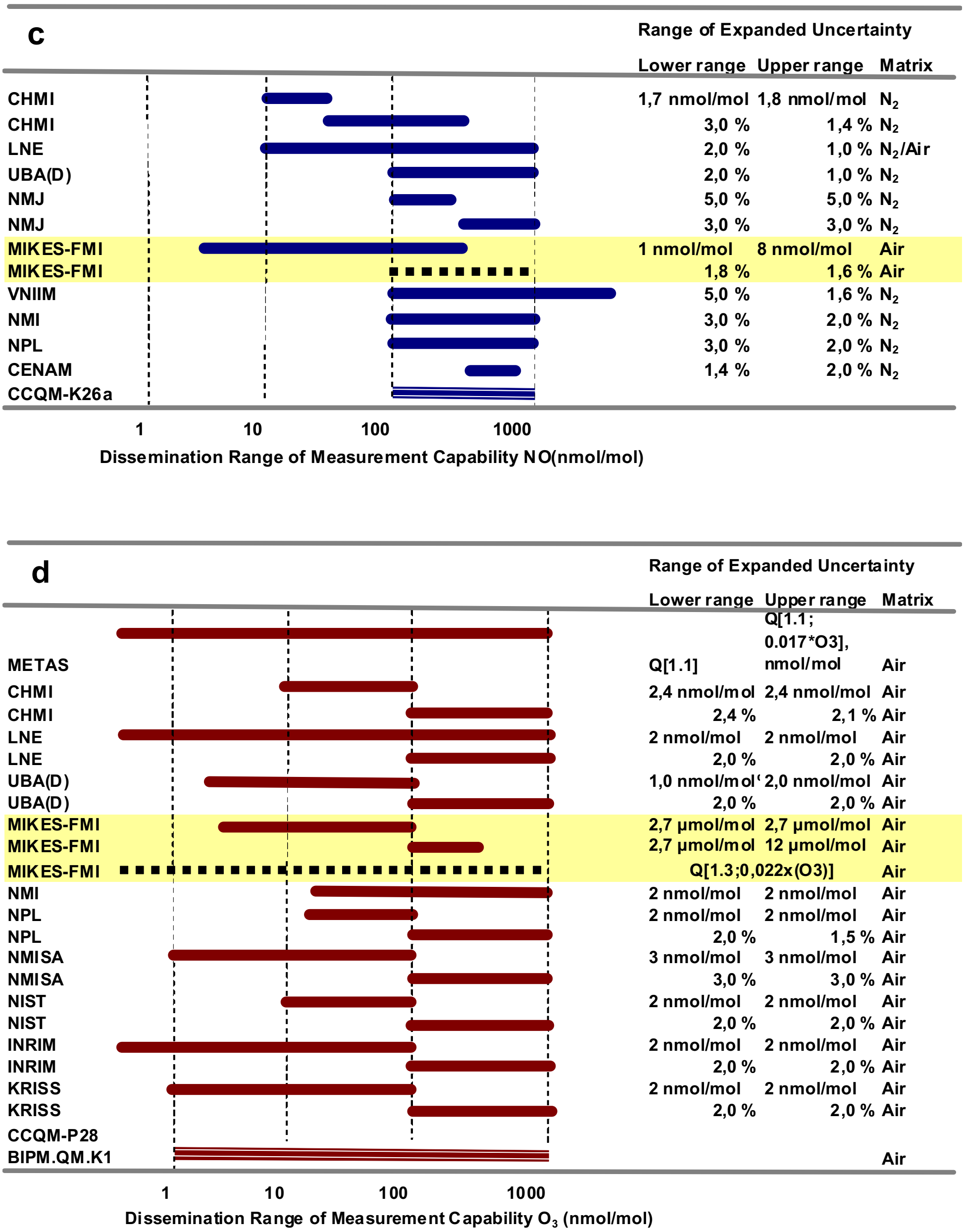


Figure 5.17a to d. The range of measurement capability and the range of expanded uncertainty of SO_2 (Figure 5.17a), CO (Figure 5.17b), NO (Figure 5.17c), and O_3 (Figure 5.17d) are reported for laboratories claiming CMCs in the BIPM database (www.bipm.org). The background of the CMC lines for MIKES-FMI is coloured. The

continuous lines of MIKES-FMI for each of the gas compounds in Figures 5.16a to d, are the present CMC (cycle IX), while the dashed lines are the reviewed CMCs for cycle X in 2009. The diluent gas stated as matrix is Air (Synthetic air). The statements of "How Far the Light Shines" supported by the CCQM K26b project, the CCQM K51 project, the CCQM K26a project and the BIPM.QM.K1 project for the gas compounds of sulphur dioxide, carbon monoxide, nitrogen monoxide and ozone, respectively, are shown on the lowest line of each table.

As can be seen from the Figures 5.17a to d, the CMC ranges start at lower concentrations than the HFTLS statement supported by the key comparison projects for each of the gas compounds. In the case of MIKES-FMI, the CMC range starts at 5 nmol/mol for sulphur dioxide and nitrogen monoxide; these need to be supported up to 100 nmol/mol by other documents than the CCQM-K26 a and b projects. In the case of carbon monoxide, the measurement capability of MIKES-FMI starts from 0.2 µmol/mol which is the lowest value of any of the laboratories. The reason for this is that the FMI takes part of the Global Atmosphere Watch (GAW) program, organized by the World Meteorological Organization (WMO) in which the measurement range for carbon monoxide is from 90 to 230 nmol/mol. However the update the MIKES-FMI CMCs is under way for cycle X. The proposed new CMCs (dashed lines in Figures 5.19a to d) have been evaluated and approved by the GW of MetChem. The process towards the gaining of final acceptance of the CMCs follows that described in chapter 4.3.

In the case of ozone, both the range and uncertainty of measurement differ from those of the other compounds. The range of measurements starts from zero, and the uncertainty statement is expressed in the form of the equation: $U(\text{nmol/mol}) = 1.3 + 0.023 \cdot C(O_3)$, where $C(O_3)$ is the ozone concentration in [nmol/mol]. This format has already been accepted for METAS, and a few other laboratories have submitted their CMC claims for ozone in a similar way (www.bipm.org). The fact that the measurement range starts at zero and not from certain ozone concentration value (e.g. from the lower level of detection of the SRPs) has raised questions of the validity of the range. According to the equation shown in Figure 5.17d the expanded uncertainty is 1.3 nmol/mol at concentration of $C = 0$. The standard uncertainty of the zero concentration from Figure

3.10 or from Equation (A13.1) gives a value of 0.3 nmol/mol for SRP. The decision of the MetChem gas working group as well as the Gas Analysis Working Group of CCQM was quite extraordinary and can raise further discussion before final acceptance of the CMCs by the JCRB.

In general the CMCs do not differ very much between the different laboratories, even though many of them prepare gas standards by gravimetric methods having relative uncertainties from 0.1 to 0.5 %. Clearly laboratories claim their measurement capabilities in a conservative way.

For comparison, the expanded uncertainty of the gas mixtures prepared by the FMI for various purposes is presented for nitrogen monoxide in Figure 5.18.

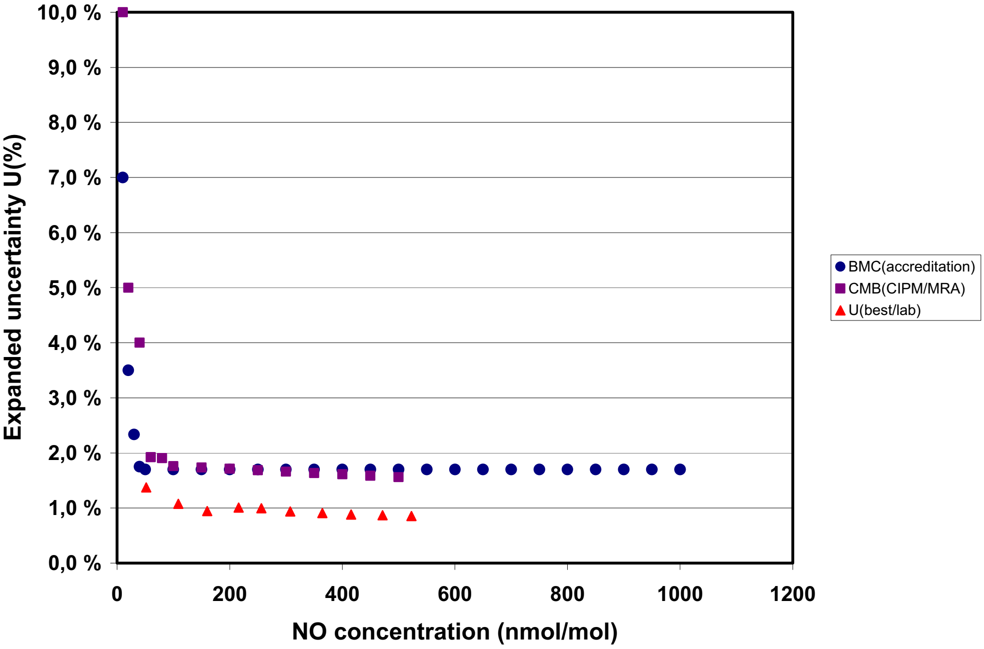


Figure 5.18. The expanded uncertainty for the calibration concentration prepared in the laboratory for nitrogen monoxide based on the scope of accreditation (spheres), on the CMC entries (squares) and on the best laboratory calibration method (triangles).

The fact that the performance characteristics for the calibration capabilities of the laboratory can vary depending on the purpose of use is not abnormal. There have been discussions that the CMCs and the BMCs based on the scope of accreditation should be the same to avoid confusion. However, changes to the scope of accreditation can be made based solely on supporting evidence by the laboratory and do not entail international evaluation. Besides, changing the entries in the CMC Tables is a much longer process than the changing the scope of accreditation. However, as can be seen from Figure 5.18, the differences between the CMCs and the BMC are relatively small. The clear difference is that the range for the CMC is up to 500 nmol/mol while in case of the BMC the range is up to 1000 nmol/mol.

6. CONLUSIONS

The structure and organization of the MIKES-FMI Standards Laboratory in the field of gas metrology, with emphasis on air quality measurements in Finland, has been described. The structure, in which the NMI delegates the task of realisation of the SI to an expert laboratory in its own field, has proven to function well. The same structure has also been used in other countries, especially in Europe. The process for the designation of the Finnish Meteorological Institute as the National Standard Laboratory for gas metrology followed international practices, and was conducted by the Centre for Metrology and Accreditation. By this designation Finland was brought into the CIPM MRA in gas metrology in the sub-field of amount of substance. The power of the CIPM MRA lies in the common principle “once measured – accepted everywhere”.

The comparability and the mutual recognition of the calibration results were sought through participation in high-level comparison projects, i.e., key comparison projects. The results of those key comparison projects showed that the laboratory, within the calculated uncertainty, has succeeded very well. The results have been consistently in line with the uncertainty statements as well as with other NMIs. Based on the results of the key comparison projects, the CMCs of the laboratory are slightly conservative.

The traceability of the measurement results is organized in the laboratory by establishing an unbroken chain of calibrations of the reference standards associated with the measurements or the concentrations of the gas mixtures prepared in the laboratory to SI. The fraction of amount of substance, *mole/mole*, is the SI unit used for the concentration of the gas standard. In spite of the fact that both the *kg* and the *mole* are subject to redefinition, no changes are foreseen to the traceability chart of the gas mixtures and measurements in the laboratory.

The quality system of the laboratory has been built up according to the SFS-EN-ISO/IEC 17025:2005 standard. The scope of the accreditation covers the most essential part of activities at the moment. The developments of the quality system have been conducted over the years, focussing primarily on the tasks of the laboratory.

The services provided to air quality measurements have become established and work very well at the moment. In the near future, more effort will be put into providing calibration services emission measurements, where applicable. For improving the accuracy of the calibration service, analysis of the impurities in the dilution gas and also in the gas standards is needed. The most powerful way to proceed is by using spectroscopic methods (Fourier Transform Infrared spectroscopy). The operation of the static volumetric method and the magnetic suspension method will be improved to reach the “highest metrological qualities”, as required from a PMM. The advantages of the CIPM MRA have already been apparent for the operation of the laboratory, and it is foreseen that activities within international projects can be increased on the basis of that agreement.

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Appendix 1 : SI base units and their definitions

Quantity	***Unit***	***Apprevia tion***	***Definition***
Length	metre	*m*	The metre is the length of the path travelled by light in a vacuum during a time interval of 1/299 792 458 of a second.
Mass	kilogram	*kg*	The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
Time	second	*s*	The second is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium 133 atom.
Electric current	ampere	*A*	The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in a vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per metre of length
Thermodynamic temperature	kelvin	*K*	The Kelvin, the unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water
Amount of substance	mole	*mol*	1. The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12. 2. When the mole is used, the elementary entities must be specified: these may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Luminous intensity	candela	*cd*	The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

Appendix 2. Task of the National Reference Laboratory in the field of Air Quality

Article 3 of the DIRECTIVE 2008/50/EC:

Member States shall designate at the appropriate levels the competent authorities and bodies responsible for the following:

(a) assessment of ambient air quality;

(b) approval of measurement systems (methods, equipment, networks and laboratories);

(c) ensuring the accuracy of measurements;

(d) analysis of assessment methods;

(e) coordination on their territory if Community-wide quality assurance programmes are being organized by the Commission;

(f) cooperation with the other Member States and the Commission. Where relevant, the competent authorities and bodies shall comply with Section C of Annex I.

The scope of the Finnish reference laboratory for the atmospheric pollutants

- To produce and maintain a traceable calibration service for air quality measurements
- sampling
- Testing of analyser and measurement systems
- To organize and arrange intercomparison exercises for local air quality networks
- To ensure the accuracy of measurement of its own measuring devices and to check the maintenance of such accuracy by those devices, in particular by internal quality controls carried out in accordance, inter alia, with the requirements of European quality assurance standards (2008/50/EC, Article 3/(c))
- To participate in intercomparison exercises organized by the EU

- To coordinate on its territory of Community-wide quality assurance programmes organized by the Commission (2008/50/EC, Article 3/(e))
- To develop measurement techniques for air quality
- To provide assistance to the authorities
- To participate in the development of new CEN standards
- To organize training for local air quality networks in the field of quality assurance
- To promote the exchange of information between local air quality networks and the reference laboratory
- To participate in international cooperation in this field of expertise

Note: Items (a), (b) and (e) of the Article 3 are not the responsibility of the FMI Calibration laboratory, but are made case by case basis by the FMI.

Appendix 3. The scope of accreditation of the calibration laboratory

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K043/M05/2006 *Appendix 1*
03.03.2006 *Date of decision*
22.08.2009 *date of expiry*

ACCREDITED CALIBRATION LABORATORY

FINNISH METEOROLOGICAL INSTITUTE

AIRQUALITY
MEASUREMENT TECHNOLOGY RESEARCH

K043 (EN ISO/IEC 17025)

Code	*Laboratory*	*Address*	*Tel./fax/e-mail/www*
K043	***Finnish Meteorological Institute AirQuality Measurement Technology Research***	***(Erik Palménin aukio 1) P.O.BOX 503 FI-00101 HELSINKI FINLAND***	***Phone int.:+358 9 192 91 Fax int.:+358 9 1929 5403 E-mail: forename.surename@fmi.fi www.fmi.fi***

Manager:	***Fields of calibration***
Jari Waldén	***Chemical analyses; reference materials: gas mixtures***

SCOPE OF ACCREDITATION

Quantity		***Measured range***	***Best measurement capability (±)***
Gas mixtures			
SO_2 *in air*		5 - 50 nmol/mol	0,7 nmol/mol
		50 - 1000 nmol/mol	1,3 % (rel.) nmol/mol
NO in air		5 - 50 nmol/mol	0,7 nmol/mol
		50 - 1000 nmol/mol	1,3 % (rel.) nmol/mol
NO_2 *in air*		5 - 50 nmol/mol	1,5 nmol/mol
		50 - 1000 nmol/mol	2,0 % (rel.) nmol/mol
CO in air		0,2 - 10 μ mol/mol	0,09 μ mol/mol
		10 - 100 μ mol/mol	1,5 % (rel.) μ mol/mol
O_3 *in air*		5 - 100 nmol/mol	2,0 nmol/mol
		100 - 1000 nmol/mol	2,0 % (rel.) nmol/mol
Benzene in air	C_6H_6	0,1 – 6 nmol/mol	0,1 nmol/mol
		6 – 25 nmol/mol	3 % (rel.)
Toluene in air	C_7H_8	0,1 – 6 nmol/mol	0,2 nmol/mol
		6 – 25 nmol/mol	4 % (rel.)

Ethylbenzene in air	C_8H_{10}	0,1 – 6 nmol/mol	0,2 nmol/mol
		6 – 25 nmol/mol	4 % (rel.)
Xylene (o, m + p) in air	C_8H_{10}	0,1 – 6 nmol/mol	0,3 nmol/mol
		6 -25 nmol/mol	6 % (rel.)

Appendix 4. Traceability and hierarchy of the reference standards of the laboratory

Table A4.1. Traceability chart of the reference standards of the MIKES-FMI Calibration laboratory

NMI Primary method SI-unit	Direct link	Reference standards of the laboratory
Key comparison BIPM-QM.K1 - Mole fraction of ozone - SRP-27 (SRP-2)		Ozone (O_3) , - Mole fraction - Reference method; Standard Reference Photometer, SRP-37
Realization of mole fraction by gravimetry: kg	NPL: PRM NMi: PSM	CO-, NO-, and SO_2 gas standards - Mole fraction - Certified reference material, CRM
Primary method: titrimetry Realization of mole fraction by gravimetry: kg	NPL: PRM NMi: PSM	NO_2 gas standards - Mole fraction -Gas Phase Titration Method, GPT
BNM:LNE - kg/s	MIKES: National standard	Gas flow rate (mg/min, ml/min) - Nitrogen
BNM:LNE - Pa (Not an SI unit)	MIKES: National standard	Pressure (Pascal, Pa)
Primary standard , ITS-90	MIKES: National standard	Temperature (Celsius)

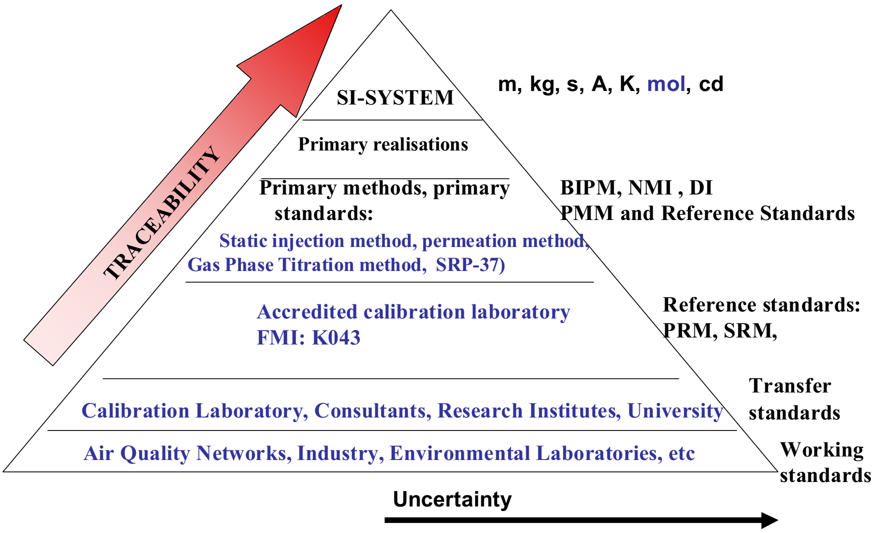


Figure A4.1 Dissemination of traceability of the measurement results through the MIKES-FMI Calibration Laboratory (traceability pyramid).

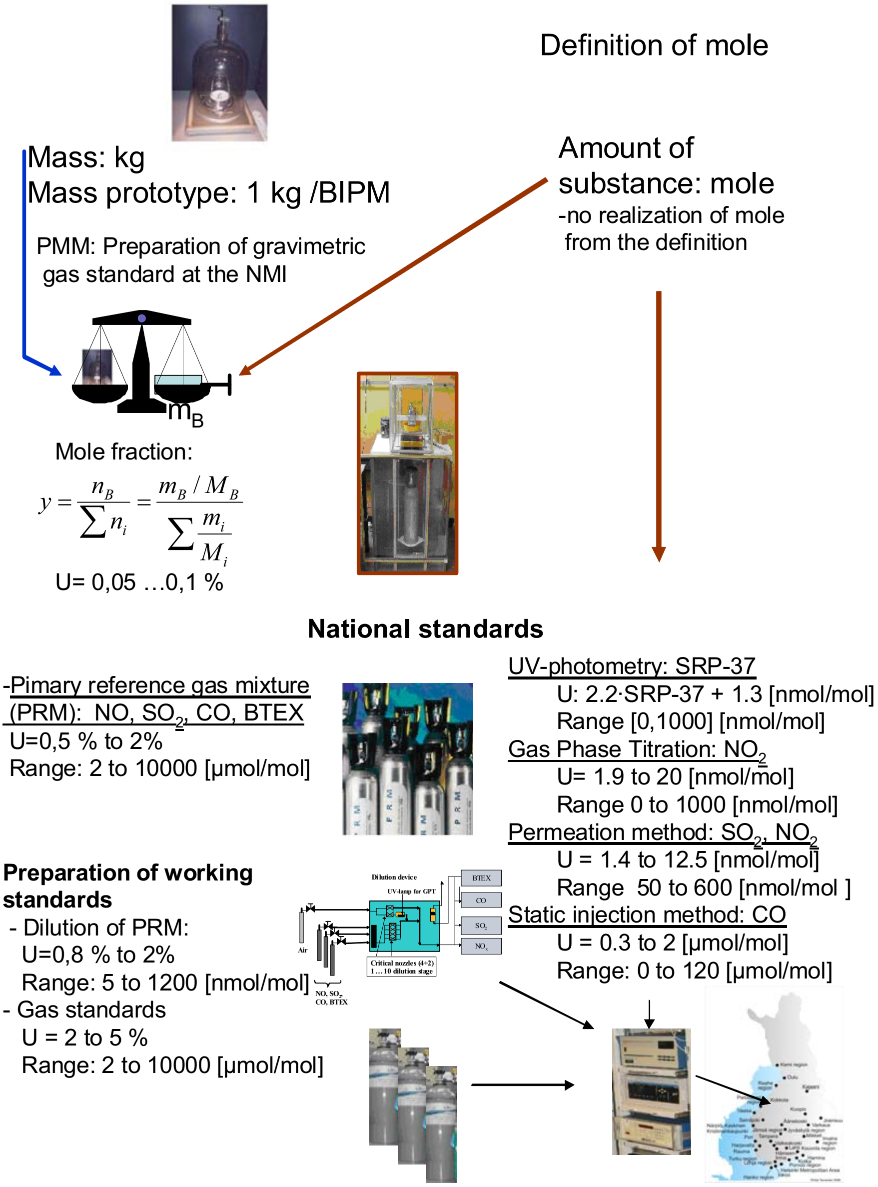
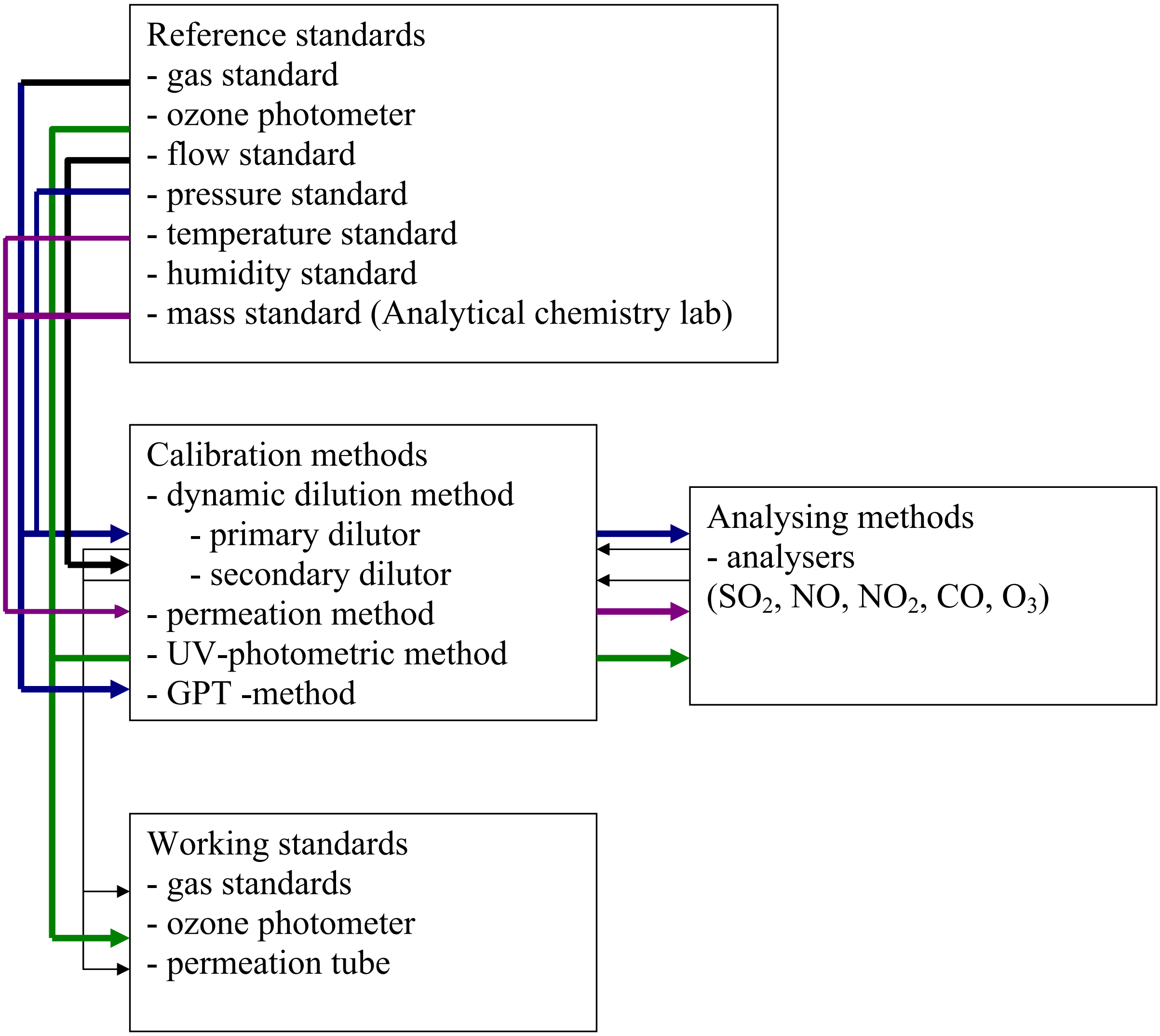


Figure A4.2. The hierarchy of the gas standards at national level in Finland

Appendix 5. Use of reference standard for calibration of working standards



Appendix 6. Partial derivatives for the uncertainty calculations of the Environnement MG 101 gas dilutor

The uncertainty calculations for the commercial dilutor, the Environnement MGC 101 based on mass flow controllers is presented. The relevant sources of uncertainty caused by the dilution are taken into account. Important contributors are the accuracy of the calibration gas concentration, the uncertainty of the zero air, and the uncertainty of the mass flow controllers.

The concentration of the gas mixture produced by the Environnement MGC 101 can be presented in the form:

$$C(x_i) = \frac{f_{span} \cdot C_s}{f_{span} + f_{dil}} + \frac{f_{dil} \cdot C_0}{f_{span} + f_{dil}} \qquad \text{(A6.1)}$$

where C_s is the concentration of the reference gas standard, C_0 is the zero gas concentration, f_{dil} is the flow used in the dilution and f_{span} is the flow of the gas standard (span gas). The uncertainty of the concentration of the gas mixture according to Equation (A6.1) can be calculated following Equation (2.1). The combined standard uncertainty component for the gas concentration prepared by the dynamic dilution device (Environnement MGC 101) is calculated as follows:

The standard uncertainty components of the concentration of the gas mixture prepared by the dilution method of mass flow controllers can be calculated from the following

$$\frac{\partial C}{\partial f_{span}}=\frac{\left(f_{span}+f_{dil}\right)\cdot c_s-f_{span}\cdot c_s\cdot 1}{\left(f_{span}+f_{dil}\right)^2}+\frac{\left(f_{span}+f_{dil}\right)\cdot 0-f_{dil}\cdot c_0\cdot 1}{\left(f_{span}+f_{dil}\right)^2}= \\ \frac{f_{dil}\cdot c_s}{\left(f_{span}+f_{dil}\right)^2}-\frac{f_{dil}\cdot c_0}{\left(f_{span}+f_{dil}\right)^2} \qquad \text{(A6.2)}$$

$$\frac{\partial C}{\partial f_{dil}}=\frac{\left(f_{span}+f_{dil}\right)\cdot 0-f_{span}\cdot c_s\cdot 1}{\left(f_{span}+f_{dil}\right)^2}+\frac{\left(f_{span}+f_{dil}\right)\cdot c_0-f_{dil}\cdot c_0\cdot 1}{\left(f_{span}+f_{dil}\right)^2}= \\ -\frac{f_{span}\cdot c_s}{\left(f_{span}+f_{dil}\right)^2}+\frac{f_{span}\cdot c_0}{\left(f_{span}+f_{dil}\right)^2} \qquad \text{(A6.3)}$$

$$\frac{\partial C}{\partial c_s}=\frac{f_{span}}{f_{span}+f_{dil}} \qquad \text{(A6.4)}$$

$$\frac{\partial C}{\partial c_0}=\frac{f_{dil}}{f_{span}+f_{dil}} \qquad \text{(A6.5)}$$

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial C}{\partial x_i} \right)^2 \cdot u^2(x_i) =$$

$$\left(\frac{f_{dil} \cdot C_s}{\left(f_{span} + f_{dil}\right)^2} \right)^2 \cdot u^2(f_{span}) + \left(\frac{-f_{span} \cdot C_s}{\left(f_{span} + f_{dil}\right)^2} \right)^2 \cdot u^2(f_{dil}) + \left(\frac{f_{span}}{f_{span} + f_{dil}} \right)^2 \cdot u^2(C_s) +$$

$$\left(\frac{-f_{dil} \cdot C_0}{\left(f_{span} + f_{dil}\right)^2} \right)^2 \cdot u^2(f_{span}) + \left(\frac{f_{span} \cdot C_0}{\left(f_{span} + f_{dil}\right)^2} \right)^2 \cdot u^2(f_{dil}) + \left(\frac{f_{dil}}{f_{span} + f_{dil}} \right)^2 \cdot u^2(C_0) \tag{A6.6}$$

where the standard uncertainties of u(C_s), u(C_0), u(f_{dil}) and u(f_{span}) are associated with their quantities, i.e., the standard uncertainty of the gas standard, the impurity of the dilution gas and the uncertainties of the mass flow controllers of the dilutor. The individual standard uncertainty components are presented in Appendix 7.

Appendix 7. The uncertainty factors used in the calculations (NO, SO_2, CO)

Standard uncertainty component	Description of the effect	Standard uncertainty
$u(f_{span})$	Median of flow calibrations made to the mass flow controller MF2.	0.5 %
$u(f_{dil})$	Median of flow calibrations made to the mass flow controller MF1.	0.5 %
$u(C_s)$	Uncertainty of the gas standard. The concentration is determined by the Sonimix 6000 A1 dilutor.	1 %
$u(C_0)$	Uncertainty of the zero gas.	CO: 0.05 ppm SO_2: 0.5 nmol/mol NO: 0.5 nmol/mol
$u(f_{f.norm.})$	Uncertainty of the flow standard. 0.5 ml/min << the total flows used.	0.5 ml/min

The expanded uncertainty of the calibration concentrations produced by the Environnement MGC 101 is shown in the Figure A7.1 calculated according to Equation (A6.6). The gas standards used in the calculations are carbon monoxide (CO), sulphur dioxide (SO_2) and nitrogen monoxide (NO). Three different scenarios are used: the best measurement capability, the mean measurement capability and the worst measurement capability.

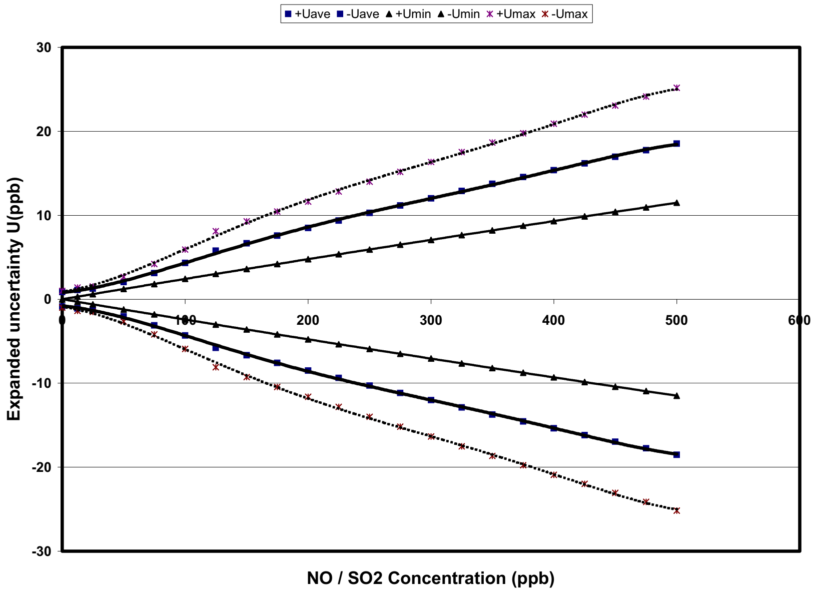


Figure A7.1-a. Expanded uncertainties of the SO_2 and NO calibration concentrations. The expanded uncertainty of the secondary standard is 2 %. $\pm U_{min}$ describes the best measuring capability of the laboratory, and $\pm U_{max}$ the worst measuring capability with the applied method and standard.

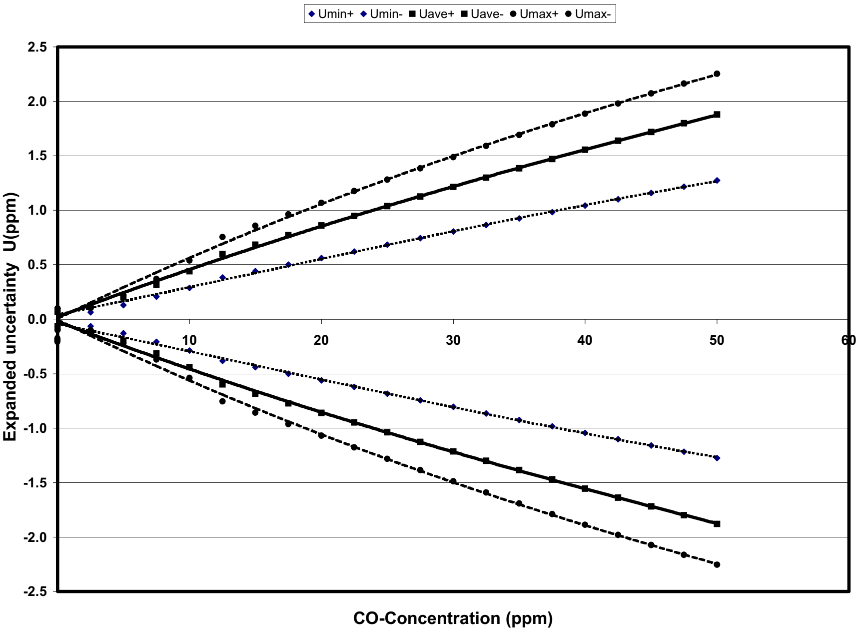


Figure A7.1b. Expanded uncertainties of the CO calibration concentrations. The expanded uncertainty of the secondary standard is 2 %. ±U_{min} describes the best measuring capability of the laboratory and ±U_{max} the worst measuring capability with the applied method and standard. The best measurement capability is obtained by using the highest quality of reference standards of the laboratory fit for the purpose. The average measurement capability means that the highest quality of the reference standards are used but that the calibration of all the necessary equipment and standards is not made just prior to the measurements. The worst measurement capability means that working standards can be used for the measurements and that the calibration of all the necessary equipment and standards is not made just prior the measurements.

Appendix 8. Calibration concentration of the Sonimix 6000 A1:

The calibration concentration produced by the Sonimix 6000 A1dilutor can be expressed with the help of the truth Table and Equation (3.5):

$$\begin{aligned}
C(1) &= \frac{f(bs4)}{f(bs4)+f(bs5)+f(bs6)+f(bs7)+f(bs1)+f(bs2)} C_{ST} \\
&+ \frac{f(bs5)+f(bs6)+f(bs7)+f(bs1)+f(bs2)}{f(bs4)+f(bs5)+f(bs6)+f(bs7)+f(bs1)+f(bs2)} C_{dil} \\
&\approx \frac{f(bs4)}{f(bs1)+f(bs2)} C_{ST} + \frac{f(bs1)+f(bs2}{f(bs1)+f(bs2)} C_{dil} = \frac{f(bs4)}{f(bs1)+f(bs2)} C_{ST} + C_{dil}
\end{aligned} \tag{A8.1}$$

where the right-hand side of the equation is obtained by an estimation of:
$f(bs1), f(bs2) >> f(bs4), f(bs5), f(bs6), f(bs7)$.

A similar expression can be made to the other dilution stages C(2), …, C(10).

Since the equation for calculating the concentration value for each dilution stage is known, the partial derivates for the concentration of C(1) from Equation (A8.1) with respect to all the quantities can be obtained:

$$\frac{\partial C(1)}{\partial f(bs4)} = \frac{C_{ST}}{f(bs1)+f(bs2)} \tag{A8.2}$$

$$\frac{\partial C(1)}{\partial f(bs1)} = -\frac{f(bs4) \cdot C_{ST}}{(f(bs1)+f(bs2))^2} \tag{A8.3}$$

$$\frac{\partial C(1)}{\partial f(bs2)} = -\frac{f(bs4) \cdot C_{ST}}{(f(bs1)+f(bs2))^2} \tag{A8.4}$$

$$\frac{\partial C(1)}{\partial C_{ST}} = \frac{f(bs4)}{f(bs1)+f(bs2)} \tag{A8.5}$$

$$\frac{\partial C(1)}{\partial C_{dil}} = 1 \tag{A8.6}$$

$$u(C(1))^2 = \left(\frac{C_{ST}}{f(bs1)+f(bs2)}\right)^2 u(bs4)^2 + \left(\frac{f(bs4)\cdot C_{ST}}{(f(bs1)+f(bs2))^2}\right)^2 (u(bs1)^2 + u(bs2)^2) + \left(\frac{f(bs4)}{f(bs1)+f(bs2)}\right)^2 u(C_{ST})^2 + u(C_{dil})^2 \tag{A8.7}$$

Similar equations can be found for all the other dilution stages (P1, …, P10) of the Sonimix 6000 A1 dilutor. The standard uncertainties *u(bs1) – u(bs4*) associated with the sonic orifices can be defined from the calibration of the individual orifices. The standard uncertainty of the calibration gas standard (primary or secondary reference material) is stated in the certificate provided by the Metrological Institute. The standard uncertainty due to the impurities in the dilution gas is defined by the laboratory. All the standard uncertainty components shown in Equation (A8.7) are listed in Table A8.1.

Table A8.1. The individual components of the standard uncertainties for the dynamic dilution method by the Sonimix 6000 A1 dilutor.

Standard uncertainty component	Description of the effect	Standard uncertainty
$u_{bs1} \ldots u_{bs7}$	The uncertainty of the flow through individual sonic orifices. The standard uncertainty is obtained from the operating manual of the Sonimix 6000 A1 dilutor for each of the sonic orifices.	0.3 … 0.5 % of the flow of the sonic orifice
$u(C)_{ST}$	Standard uncertainty of the gas standard used.	0.25 … 1.0 % of the certified concentration.
$u(C)_{dil}$	The standard uncertainty of the impurity of the zero gas.	0 - 0.5 nmol/mol

Appendix 9. The uncertainty calculation of the permeation method and the standard uncertainties of all relevant parameters associated with the permeation method using the Kin-Tek 491M

$$\boldsymbol{C} = \frac{\boldsymbol{E} \cdot \boldsymbol{K_o}}{\boldsymbol{F}} + \boldsymbol{C_o}$$

The standard uncertainty components of the concentration of the gas mixture prepared by the permeation method can be calculated as follows:

$$\frac{\partial C}{\partial E} = \frac{K_o}{F} \tag{A10.1}$$

$$\frac{\partial C}{\partial K_o} = \frac{E}{F} \cdot 0 = 0 \tag{A10.2}$$

$$\frac{\partial C}{\partial F} = -\frac{E \cdot K_o}{F^2} \tag{A10.3}$$

$$\frac{\partial C}{\partial C_o} = 1 \tag{A10.4}$$

The combined standard uncertainty for the permeation can be presented in the form:

$$\begin{aligned} u_p^2(C) &= \sum_{i=1}^{N} \left(\frac{\partial C}{\partial x_i} \right)^2 \cdot u^2(x_i) \\ &= \left(\frac{K_o}{F} \right)^2 \cdot u^2(E) + \left(-\frac{E \cdot K_o}{F^2} \right)^2 \cdot u^2(F) + \cdot u^2(C_o) \qquad \text{(A10.5)} \\ &= \left(\frac{K_o}{F} \right)^2 \cdot u^2(E) + \left(\frac{E \cdot K_o}{F^2} \right)^2 \cdot (u^2(F_s) + u^2(Fd)) + \cdot u^2(C_o) \end{aligned}$$

The permeation rate, E, can be measured by weighing the permeation tube after a certain time lag:

$$E = \frac{\Delta m}{\Delta t} = \frac{m_{pg} + m_{pi} + m_{buo}}{\Delta t} \tag{A10.6}$$

The standard uncertainty of the output of the permeation tube (u_E) can be calculated from:

$$\frac{\partial E}{\partial m_{pg}} = \frac{1}{\Delta t} \tag{A10.7}$$

$$\frac{\partial E}{\partial m_{pi}} = \frac{1}{\Delta t} \tag{A10.8}$$

$$\frac{\partial E}{\partial m_{buo}} = \frac{1}{\Delta t} \tag{A10.9}$$

$$\frac{\partial E}{\partial (\Delta t)} = -\frac{m_{pg} + m_{pi} + m_{buo}}{(\Delta t)^2} \tag{A10.10}$$

The variance of the combined standard uncertainty of the permeation rate can be expressed in the form:

$$u_E^2(y) = \sum_{i=1}^{N} \left(\frac{\partial E}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

$$= \left(\frac{1}{\Delta t} \right)^2 \cdot u^2(m_{pg}) + \left(\frac{1}{\Delta t} \right)^2 \cdot u^2(m_{pi}) + \left(\frac{1}{\Delta t} \right)^2 \cdot u^2(m_{buo}) + \left(\frac{m_{pg} + m_{pi} + m_{buo}}{(\Delta t)^2} \right)^2 \cdot u^2(\Delta t) \tag{A10.11}$$

Appendix 10. The compressibility of the air

The compressibility factor for moist air can be calculated using the second and third virial coefficients for dry air and water vapour, these are tabulated for various different values of relative humidity, temperature and pressure (Hyland, 1975). The Working Group of the CCM also provided a modelled equation for the compressibility factor that depends on the pressure (Pa), temperature (ºC), thermodynamic temperature (K) and mole fraction of water vapour. In Figure A10.1, the compressibility, Z, for air is presented using the modelled equation at a constant temperature of 25 ºC.

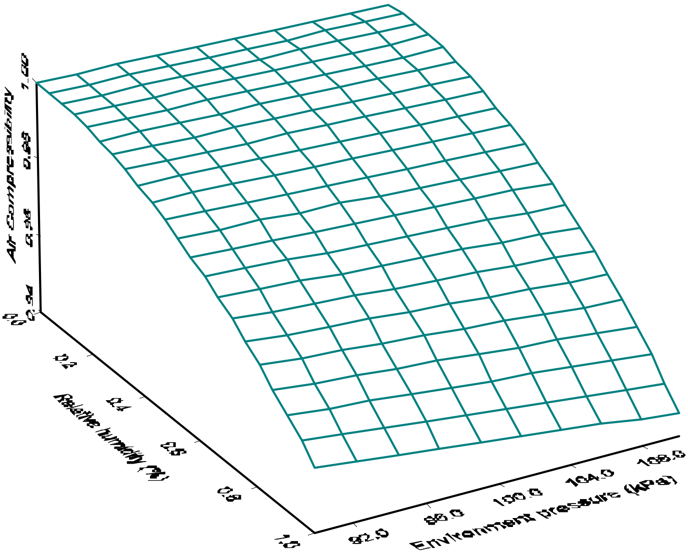


Figure A10.1. The compressibility of air is presented as a function of environment pressure (kPa), a mole fraction of water $x_v = 0.5$ and a constant temperature of 25 ºC. The plotted values for the compressibility are modelled by the CCM Working Group (Giacomo, 1982)

In Figure A10.2 the air density is presented as a function of temperature and pressure at a water content of 50%.

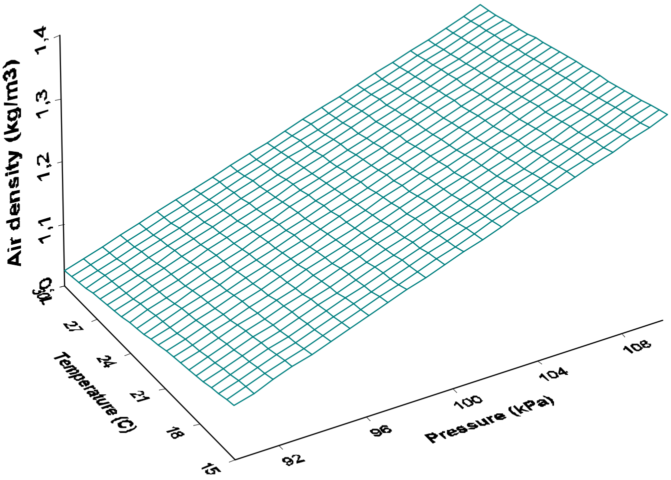


Figure A10.2. The dependence of air density on environment pressure and temperature at a mole fraction of water $x_v = 0.5$.

Appendix 11. The standard uncertainty components of all relevant parameters associated with the permeation method using the Kin-Tek 491M.

Parameter	Standard uncertainty, u	Value	Unit
The uncertainty of the permeation source:			
Deviation due to weighing:	$u(m_{pg})$=	0.1	Mg
Uncertainty of the time interval:	$u(\Delta t)$=	4	Min
Uncertainty of the buoyancy force	$u(m_{buo})$=	0.05	Mg
Uncertainty of the impurities	$u(m_{pi})$=	0.5	nmol/mol
The uncertainty of dilution			
Uncertainty of span flow	$u(F_s)$=	0.5	%
Uncertainty of dilution flow	$u(F_d)$=	0.5	%

Appendix 12. Expanded uncertainty of the SRP-37 for the photometric calibration of the ozone analysers

In case of SRP-37, the flow scheme is arranged in such a way that the sample is switched every 5 s between the two absorption cells. The intensities I_i and I_{jo} ($i = 1,2; j = 2,1$) are the intensities of the UV-light through the absorption cell *i* and *j*. The sample is switched in the next cycle between the tube *j* and *i* (see in Figure A12-1, solenoid valves 1 and 2). Equation (3.28) can be rewritten in the form (Paur et al., 2003):

$$c = -\frac{\ln(Tr)}{\alpha \cdot L_{opt}} = -\frac{\ln(Tr_1(cell1) \cdot Tr_2(cell2))}{\alpha \cdot L_{opt}} = \frac{-1}{2 \cdot \sigma \cdot L_{opt}} \cdot \frac{k \cdot T}{P} \cdot \ln(D) \qquad (3.28')$$

where Tr_i(cell*i*); ($i = 1,2$) is the transmittance (= I(cell i)/I_o(cell j)) for the half cycle of the sample flow scheme and D is the product of the transmittances of both of the cells (= $Tr_1 \cdot Tr_2$ = I(cell 1)/I_o(cell2)·I(cell 2)/I_o(cell 1)).

The standard uncertainty components of the concentration of the ozone photometer (SRP-37) can be calculated as follows

$$\frac{\partial c}{\partial \sigma} = \frac{1}{2 \cdot L_{opt} \sigma^2} \frac{kT}{P} \ln(D) = -\frac{c}{\sigma} \qquad (A12.1)$$

$$\frac{\partial c}{\partial L} = \frac{1}{2 \cdot \sigma \cdot L^2_{opt}} \frac{k \cdot T}{P} \ln(D) = -\frac{c}{L_{opt}} \qquad (A12.2)$$

$$\frac{\partial c}{\partial T} = -\frac{1}{\sigma \cdot L_{opt}} \frac{k}{P} \ln(D) = \frac{c}{T} \qquad (A12.3)$$

$$\frac{\partial c}{\partial P} = \frac{1}{\sigma \cdot L_{opt}} \frac{kT}{P^2} \ln(D) = -\frac{c}{P} \qquad (A12.4)$$

$$\frac{\partial c}{\partial D} = -\frac{1}{\sigma \cdot L_{opt}} \frac{k \cdot T}{P} \frac{\partial}{\partial D}(\ln(D)) = -\frac{1}{\sigma \cdot L_{opt}} \frac{k \cdot T}{P} \frac{1}{D} \qquad \text{(A12.5)}$$

The quadratic terms of Equations (A12.1 – 5)) can now be calculated

$$(\frac{\partial c}{\partial \sigma} u(\alpha))^2 = (\frac{c}{\sigma} u(\sigma))^2 \qquad \text{(A12.6)}$$

$$(\frac{\partial c}{\partial L} u(L_{opt}))^2 = (\frac{c}{L_{opt}} u(L_{opt}))^2; \qquad \text{(A12.7)}$$

$$(\frac{\partial c}{\partial T} u(T))^2 = (\frac{c}{T} u(T))^2; \qquad \text{(A12.8)}$$

$$(\frac{\partial c}{\partial P} u(P))^2 = (\frac{c}{P} u(P))^2; \qquad \text{(A12.9)}$$

$$(\frac{\partial c}{\partial D} u(D))^2 = (\frac{k \cdot T}{\sigma \cdot L_{opt} \cdot P \cdot D} u(D))^2; \qquad \text{(A12.10)}$$

Combining Equations (A12.6 to A12.10) with Equation (2.5):

$$u(x)^2 = (\frac{c}{\sigma} u(\sigma))^2 + (\frac{c}{L_{opt}} u(L_{opt}))^2) + (\frac{c}{T} u(T))^2 + (\frac{c}{P} u(P))^2 + (\frac{k \cdot T}{\sigma \cdot L_{opt} \cdot P \cdot D} u(D))^2 \qquad \text{(A12.11)}$$

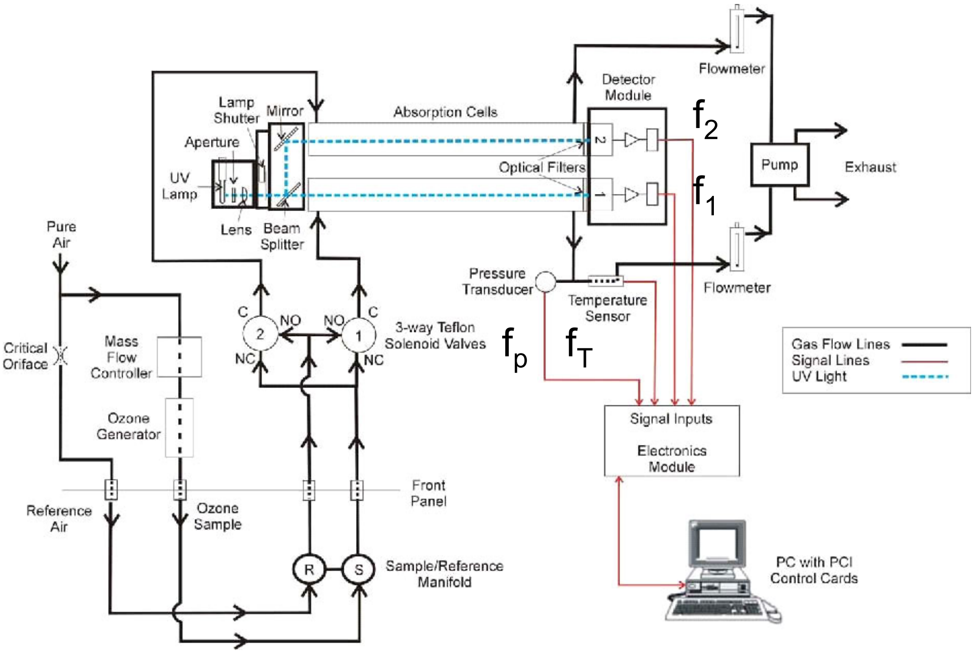


Figure A12-1. Schematic flow scheme and signals of the SRP. The frequencies f_1 and f_2 of the signals of the UV-light from the detectors 1 and 2 respectively are the integration values over 5 seconds as well as of the temperature and pressure transducers, f_T and f_p.

Appendix 13. Uncertainty components (standard uncertainties) of the SRP-37 for the photometric calibration of the ozone analysers

Table A13.1 The contribution of each of the standard uncertainties of the Equation (A12.11).

Pressure kPa **101**

Path lenght 89,8

Contribution of SRP

Component y	**Value**	**Standard uncertainty**		**Standard uncertainty**	**Comb stand uncertainty**	**Sensitivity coefficient** $c_i = \frac{\partial x}{\partial y}$	**Contribution to u(x) (nmol/mol) ci u(y) or ciu(y)x**
		Source	**Distribution**				
Optical path Length 2L cm	179,60	Measurement scale (cm)	Rect	0,002	0,52009999	$-\frac{x}{2L} = -\frac{x}{L_{opt}}$	
		Repeatability (cm)	Normal	0,01	0,5201		**2,896E-03**
		Bias (cm)	Rect	0,52			
Pressure kPa	101,21	Pressure gauge	Rect	0,029	0,034	$-\frac{x}{P}$	**3,321E-04**
kPa		Difference between cells	Rect	0,017			
Temperature, K	296,55	Temperature probe	Rect	0,03	0,065	$\frac{x}{T}$	**2,202E-04**
		Residual bias	Rect	0,058			
Ratio of intensities D	0,99	Scalers resolution	Rectancular	0,00	1,36E-05	$\frac{x}{D \cdot \ln(D)}$	**2,800E-01**
		Repeatability	Triang	0,000011			
Absorption Cross section α (cm^2/molecule	1,147E-17			1,227E-19		$-\frac{x}{\sigma}$	**1,07 %**
uncertainty of cross	1,070E-02						

$$x = \frac{-1}{2\alpha L} \cdot \frac{R}{N_a} \cdot \frac{T_{MEAS}}{P_{MEAS}} \ln(D) = B \ln(D)_o$$

Combining the standard uncertainties in Table A13.1 into the Equation (A13.11) one obtains:

$$u(c) = \sqrt{\{[(2{,}896 \cdot 10^{-3})^2 + (3{,}321 \cdot 10^{-4})^2 + (2{,}2 \cdot 10^{-4})^2] \cdot c^2 + (2{,}8 \cdot 10^{-1})^2\}}$$
$$= \sqrt{[(2{,}92 \cdot 10^{-3} \cdot c)^2 + (0{,}28)^2]} \tag{A13.1}$$

Appendix 14. Partial derivatives for the uncertainty calculations of the concentrations for the gas phase titration method (GPT)

$$[\boldsymbol{NO}_2]_{\boldsymbol{prod}} = [\boldsymbol{NO}]_{\boldsymbol{o}} - [\boldsymbol{NO}] = \frac{[\boldsymbol{O}_3]_{\boldsymbol{STD}} \cdot \boldsymbol{f}_{\boldsymbol{ozone}}}{\boldsymbol{f}_{\boldsymbol{ozone}} + \boldsymbol{f}_{\boldsymbol{dil}}}$$

The standard uncertainty components of the gas phase titration method can be calculated as follows

$$\frac{\partial C}{\partial f_{ozone}} = \frac{[O_3]_{STD} \cdot (f_{ozone} + f_{dil}) - [O_3]_{STD} f_{ozone}}{(f_{ozone} + f_{dil})^2} = \frac{[O_3]_{STD} f_{dil}}{\left(f_{span} + f_{dil}\right)^2} \qquad \text{(A14.1)}$$

$$\frac{\partial C}{\partial f_{dil}} = -\frac{[O_3]_{STD} \cdot f_{ozone}}{\left(f_{ozone} + f_{dil}\right)^2} \qquad \text{(A14.2)}$$

$$\frac{\partial C}{\partial c_{ozone}} = \frac{f_{ozone}}{f_{ozone} + f_{dil}} \qquad \text{(A14.3)}$$

The variance of the combined standard uncertainty of the concentration of the gas mixture prepared by the gas phase titration method can be calculated as follows

$$u_E^2(y) = \sum_{i=1}^{N} \left(\frac{\partial E}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

$$= \left(\frac{[O_3]_{STD} f_{dil}}{\left(f_{ozone} + f_{dil}\right)^2} \right)^2 \cdot u^2(f_{ozone}) + \left(\frac{[O_3]_{STD} f_{ozone}}{\left(f_{ozone} + f_{dil}\right)^2} \right)^2 \cdot u^2(f_{dil}) + \left(\frac{f_{ozone}}{\left(f_{ozone} + f_{dil}\right)} \right)^2 \cdot u^2(C_{ozone})^2$$

Appendix 15. Performance characteristics and the standard uncertainties of the gas analysers

The EN-standards (EN-14211, - 14212, - 14625, and -14626) defines the performance characteristics of the analysers and the procedure for calculating the standard uncertainties. The procedures described in the standards are applied to obtain the uncertainty budget of the analysers in the laboratory.

Table A15.1. The standard uncertainties of the performance characteristics for the sulphur dioxide and nitrogen monoxide analysers

		Test results		standard uncertainty u
Repeatability standard deviation at zero	$s_{r,z}$ =	**0,52**	**nmol/mol**	**0,07**
Repeatability standard deviation at concentration c_t	$s_{r,ct}$ =	**1**	**nmol/mol**	**0,01**
Lack of fit	X_l =	**1,0**	**% measured value**	**0,43**
Sensitivity coefficient of sample gas pressure	b_{gp} =	**0,2**	**nmol/mol/kPa**	**0,46**
Sensitivity coefficient of sample gas tenperature	b_{gt} =	**0,2**	**nmol/mol/K**	**0,25**
Sensitivity coefficient of surrounding temperature	b_{st} =	**0,25**	**nmol/mol/K**	**0,31**
Sensitivity coefficient of electrical voltage	b_v =	**0,1**	**nmol/mol/V**	**0,46**
Interferents at zero and concentration c_t				
H_2O concent. 19 nmol/mol	$X_{H2O,z}$ =	**-3**	**nmol/mol**	**0,97**
	$X_{H2O,ct}$ =	**-2,8**	**nmol/mol**	
Response time (rise)	t_r =	**57**	**s**	
Response time (fall)	t_f =	**58**	**s**	

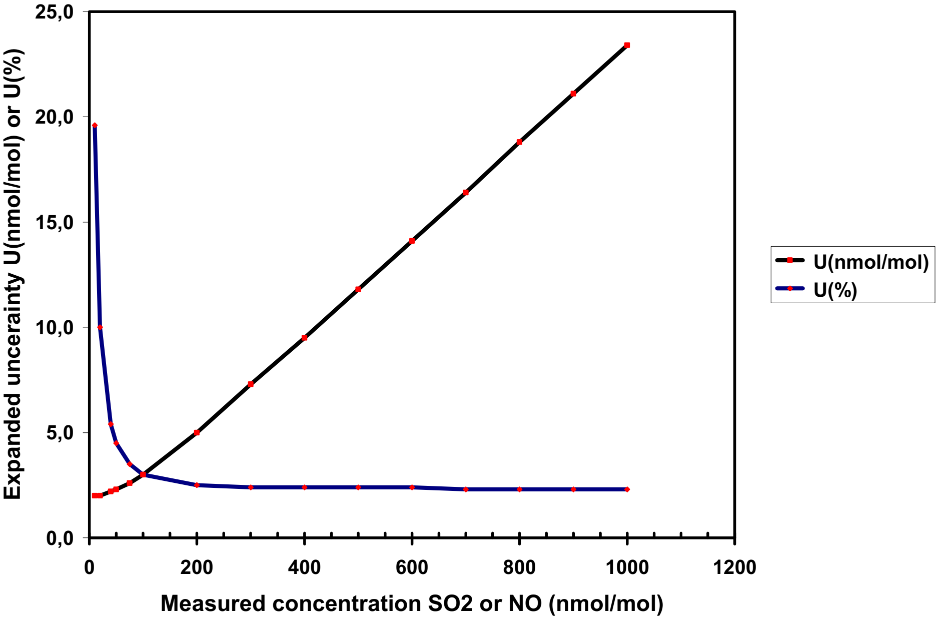


Figure A15.1. The expanded uncertainties, U(nmol/mol) and U(%) (both scales on the left) as a function of the measured concentration for the sulphur dioxide and nitrogen monoxide analysers.

Appendix 16. The key comparison projects

Table A16.1. The comparison projects or intercomparison exercises in which the calibration laboratory has participated.

Title of the comparison project	**Code of the project and the gas compound**	**Coordinating laboratory**	**Start of the project**	**Reporting status and the HFTLS**
Key comparison of nitrogen monoxide (NO) at ambient level	CCQM-K26a, Nitrogen monoxide (NO) in air	National Physical Laboratory (NPL), UK	2003	Final report completed, 2006 HFTLS: 100 – 1000 nmol/mol in air
Key comparison of sulphur dioxide (SO_2) at ambient level	CCQM-K26b, Sulphur dioxide (SO_2) in air	National Physical Laboratory (NPL), UK	2003	Final report completed, 2006 HFTLS: 100 – 1000 nmol/mol in air
Pilot comparison of ozone at ambient level	CCQM-P28, Ozone (O_3) in air	International Bureau of Weights and Measures (BIPM)	2003	Final report completed, 2006
Key comparison of ozone at ambient level	BIPM.QM-K1, Ozone (O_3) in air	International Bureau of Weights and Measures (BIPM)	2007	Draft report A HFTLS: 10 – 500 nmol/mol in air
Key comparison of carbon monoxide in nitrogen (5 µmol/mol)	CCQM-K51, Carbon monoxide (CO) in nitrogen	National Metrology Institute of South Africa (NMISA)	2008	Draft report HFTLS: 5 – 100 µmol/mol in nitrogen
Key comparison of nitrogen monoxide (NO)	EUROMET.QM-K1c, Nitrogen monoxide (NO) in nitrogen	Nederlands Meetinstitute, (NMi), Nl	2002	Final report completed, 2005
Regional comparison: National ozone photometers	EUROMET-414, Ozone in air	National Physical Laboratory (NPL), UK. Physikalisch-	1998	Final report completed, 2002

		Technischen Bundesanstalt (PTB), DE.		
Harmonization of air quality measurements in Europe, HAMAQ	EUROMET-430, CO in air, NO in air SO_2 in air NO_2 in air C_6H_6 in nitrogen	National Physical Laboratory (NPL)	1996	Final report completed, 2000
Intercomparison exercise for SO_2, CO, O_3, NO and NO_2	SO_2, CO, O_3, NO and NO_2	EC/Joint Research Centre, Ispra, Italy LUANW, Essen, Germany	1999, 2003 and 2007	Final report from 1999 Draft report from 2003 Draft report from 2007
First EC/JRC Aromatic (BTEX) compounds with automatic analysers.	Benzene, Toluene, Ethylbenzene, o-, p-, and m-Xylene	EC/Joint Research Centre, Ispra, Italy	2005	Draft report from 2006

EUROMET 430 project

The partnership assembled to address the specified aims and objectives comprised seven leading European metrology laboratories, and European and national reference laboratories. The Technical Research Centre (VTT) was the Finnish contractor with the FMI as a subcontractor. The responsibility of the FMI was to analyse the samples. The other participants in the project are listed in Table A16.2.

Table A16.2. The list of participants in the EUROMET 430 project

Country	**Abbreviation**	**Name of Institute**
EU	JRC, Ispra	European Commission, Joint Research Centre, Ispra
Finland	VTT-FMI	VTT Chemical Technology together with the Finnish Meteorological Institute
France	LNE	Laboratoire National D'Essais
Germany	UBA (D)	Umweltbundesamt Offenbach Pilotstation
Netherlands	RIVM	Rijksinstituut voor Volksgezondheid en Milieu
Spain	ISCIII	Instituto de Salud Carlos III
UK	NPL	National Physical Laboratory

The gas components, nominal concentration and pilot laboratories for each of the gas compounds in the HAMAQ project are listed in Table A16.3. The core participants were the metrological laboratories that took part in the project (at that time the FMI was not designated as a metrology laboratory).

Table A16.3. The list of gas components, nominal concentration, and pilot laboratories for each of the compounds together with the core participants.

Gas	**Concentration (nominal)**	**Pilot Laboratory**	**'Core' Participants involved in First Intercomparison**
CO	20 ppm	NPL	LNE, UBA
NO	200 nmol/mol	LNE	NPL, UBA
SO_2	200 nmol/mol	JRC	LNE, NMi, UBA
NO_2	200 nmol/mol	UBA	LNE, JRC
C_6H_6	20 nmol/mol	NMi	NPL, UBA

EUROMET 414 project

Table A16.4. The list of participants in the EUROMET 414 project

Country	Abbreviation	Name of Institute
Austria	UBA (A)	Umwelt Bundes Amt
Belgium	IRCEL	Interwestelijke Cel voor het Leefmilieu
Czech Republic	CHMI	Czech Hydro-Metrological Institute
Denmark	DMU	Danmarks Miljoundersogelser
EU	JRC, Ispra	European Commission, Joint Research Centre, Ispra
Finland	FMI	Finnish Meteorological Institute
France	LNE	Laboratoire National D'Essais
Germany	UBA (D)	Umwelt Bundes Amt
Germany	PTB	Physikalisch-Technischen Bundesanstalt
Hungary	IEP	Institute for Environmental Protection
Netherlands	RIVM	Rijksinstituut voor Volksgezondheid en Milieu
Norway	NILU	Norsk Instituut for Luftforskning
Slovakia	SHMI	Slovak Hydrometeorological Institute
Spain	ISCIII	Instituto de Salud Carlos III
Sweden	ITM	Institute of Applied Environmental Research
Switzerland	METAS	Metrologie und Akkreditierung Schweiz
UK	NPL	National Physical Laboratory

Table A16.5. The results of the comparison of ozone photometers by the FMI and the PTB.

summary data									zero	span
	lab standard				transfer standard			PTB correction	0.2	1.0101
	mean	Std	%std		Mean	std	%std	lab correction	0	1
1	256	n/a	n/a		256	n/a	n/a			
2	105	n/a	n/a		104	n/a	n/a			
3	64	n/a	n/a		64	n/a	n/a			
4	205	n/a	n/a		205	n/a	n/a			
5	0	n/a	n/a		0	n/a	n/a			
6	406	n/a	n/a		407	n/a	n/a			
7	34	n/a	n/a		34	n/a	n/a			
8	155	n/a	n/a		155	n/a	n/a			
9	491	n/a	n/a		492	n/a	n/a			
10	306	n/a	n/a		307	n/a	n/a			
Slope	0.997	0.000								
Offset	0.473	0.092								

EUROMET 638 project (EUROMET QM-K1c)

Table A16.6. List of participants in EUROMET.QM.K1, the measurement and calibration method that obtained the results, and the traceability of the measurements.

Laboratory	Measurement method	Calibration method	Traceability
NMi Van Swinden Laboratorium B.V.	ND-UV	Polynomial regression (8 points), weighted	NMi Gravimetric PSMs
METAS Metrologie und Akkreditierung Schweiz	Chemiluminescence	Linear regression (6 points)	METAS Certified Gas Mixtures
VNIIM D.I. Mendeleyev Institute for Metrology	UV absorption	Linear regression (6 points)	VNIIM Gravimetric PSM's
CMI-CHMI Czech Hydrometerological Institute	Chemiluminescence	manometric static injection	Diluted NMi PRM
LNE Laboratoire National D'Essais	Chemiluminescence	dynamic dilution + single point calibration	LNE Gravimetric PSM; dilution calibrated by LNE using gravimetry
NPL National Physical Laboratory	Chemiluminescence	bracketing with 4 pairs of cylinders	NPL Primary gravimetric Standards
IPQ	ND-IR	Linear regression (4 points)	NMi PRMs
FMI Finnish Meteorological Institute	Chemiluminescence	dynamic dilution + linear regression (6 points)	NPL Secondary Standard; dilutor calibrated by LNE
GUM Central Office of Measures, Physical Chemistry Division	Chemiluminescence	bracketing (2 points)	GUM Gravimetric PSMs
CEM Centro Espanol de Metrologia	Chemiluminescence	Linear regression (3 points)	NMi PRMs

Table A16.7. Results and degrees of equivalence for NO (µmol/mol) in the EUROMET 638 project. X_{grav} is the reference value of the gas standard, u_{gravR} is the relative standard uncertainty of the reference value, x_{lab} is the result reported by the participating laboratory, k_{lab} is the coverage factor, U_{lab} is the expanded uncertainty reported by the laboratory, D_i is the degree of equivalence and $U(D_i)$ is the uncertainty of the degree of equivalence.

Code	**Cylinder**	**x_{grav}**	**u_{gravR}**	**x_{lab}**	**k_{lab}**	**U_{lab}**	**D_i**	**$U(D_i)$**
LNE	153262	95.070	0.062	95.08	2	0.65	0.01	0.66
NPL	153673	95.094	0.062	95.2	2	0.3	0.11	0.32
VNIIM	153823	95.055	0.062	96.6	2	0.9	1.55	0.91
NMi VSL	152994	94.732	0.062	94.8	2	0.3	0.07	0.32
GUM	153596	95.172	0.062	95.8	2	1.5	0.63	1.51
CEM	153255	95.228	0.062	95.8	2	0.9	0.57	0.91
METAS	153181	94.843	0.062	95.12	2	0.42	0.28	0.44
CMI/CHMI	153418	95.064	0.062	94.87	2	1.6	-0.19	1.61
FMI	153038	95.158	0.062	94.8	2	1.5	-0.36	1.51
LNM-IPQ	153690	95.120	0.062	95.22	2	0.39	0.10	0.41

CCQM-P28 project

Table A16.8. List of the laboratories participating in the CCQM-P28 project.

Date of comparison	Institute	Country / organisation	National Standard model	Prot.	Transfer Standard model	Traceable to
July 2003	NIST National Institute for Standards and Technology	United States of America	SRP	B	SRP	
Sept 8-12, 2003	ISC III Institute de Salud Carlos III	Spain	SRP	B	TEI 49C	SRP2(NIST)
Sept 22-26, 2003	ERLAP (JRC) European Reference Laboratory of Air Pollution	European Community	UMEG	B	TEI 49CPS	
Oct 20-24, 2003	Environment Canada	Canada	SRP	A		
Nov 17-21, 2003	METAS Swiss Federal Office of Metrology and Accreditation	Switzerland	SRP	A/B	SRP	
Dec 1-5, 2003	KRISS Korean Research Institute of Standards and Science	Korea	O3-SRP	A		
Feb 2-6, 2004	VNIIM Mendeleyev Institute for Metrology	Russia	Dasibi 1008AH	A		
Mar 1 - 5, 2004	FMI Finnish Meteorological Institute	Finland	TEI 49CPS	A		SRP24(LNE)
Mar 15-19, 2004	WMO/WCC-EMPA World Calibration Center for Surface Ozone	World Meteorological Organisation	SRP	A		
Mar 29 Apr 2, 2004	UBA(A) Federal Environmental Agency	Austria	SRP	A		
May 3 – 7, 2004	SP Swedish National testing and Research Institute	Sweden	Environment SA 42M	A		SRP11(Univ of Stocholm)
May 24 - 28, 2004	NPL National Physical Laboratory	United Kingdom	SRP	A		
June 7 – 11, 2004	NDENW National Directorate for Environment, Nature and Water	Hungary	UMEG	B	TEI 49C	
June 21 – 25, 2004	UBA(D) Federal Environmental Agency	Germany	SRP	A		
July 26 – 30, 2004	NIES National Institute for Environmental Studies	Japan	SRP/GPT	A/B	SRP	
Sept 20 – 24, 2004	CHMI Czech Hydro Meteorological Institute	Czech Republic	SRP	A		
Sept 27 – oct 1, 2004 March 14 – 16, 2005	CSIR-NML National Metrology Institute	South Africa	API 401	A		SRP2 (NIST)
Nov 22 – 26, 2004	NERI National Environmental Research Institute	Denmark	UMEG	A	API 400A	
Nov 29 – Dec 3, 2004	NILU Norwegian Institute for Air Reseach	Norway	API 400E	A		SRP11 (Univ of Stocholm)
Jan 11-13, 2005	NMI-VSL, NMi van Swinden Laboratory	Nederland	UMEG	A		
Jan 24 – 26, 2005	INRIM Istituto Nazionale di Ricerca Metrologica	Italy	O3-SRP	A		
Feb 3, 2005	BIPM Bureau International des Poids et Mesures		GPT	B	TEI 49C	

Notes:

O3-SRP in Table A16.8 means that the traceability is to the SRP prepared by the Korean Research Institute of Standards and Sciences (KRISS). For others the traceability proceeds to the SRP by NIST or to SRP-11 (Univ of Stockholm).

CCQM-K51 project

Table A16.10. List of participants in the CCQM K51 project.

Laboratory code	**Calibration**	**Traceability**	**Matrix standards**	**Measurement technique**
NMIJ	ISO-6143			GC-FID
NMISA	ISO-6143			GC-FID
UBA-Germany	Bracketing			NDIR
VNIIM	ISO-6143			GC-FID
SMU	ISO-6143			GC-FID
NPL	Bracketing			GC-FID; NDIR
CERI	Ratio			Gas Filter CO correlation analyser
BAM				
CEM	ISO-6143			GC-HID
CENAM	ISO-6143			GC-FID
GUM	ISO-6143			NDIR
INMETRO	ISO-6143			GC-FID
IPQ	ISO-6143			NDIR
JRC-ERLAP	ISO-6143			NDIR
KRISS	ISO-6143			GC-FID
LNE	Ratio			CO Analyser (IR)
METAS	ISO-6143			GC-FID
NIM	ISO-6143			GC-FID; CO Analyser (IR)
NIMT	ISO-6143			NDIR
NIST	ISO-6143			GC-FID
NMi-VSL	ISO-6143			NDIR
NPL-India	Ratio			GC-FID
UBA-Austria	ISO-6143			NDIR
FMI	EN 14626			NDIR
NMIA	ISO-6143			FTIR (10m gas cell)

Appendix 17. The questionnaire for the review of EUROMET calibration and measurement capabilities of the calibration laboratory

QUESTIONNAIRE FOR THE REVIEW OF
EUROMET CALIBRATION AND MEASUREMENT CAPABILITIES

This questionnaire is to be filled in by the Rapporteur or any other person appointed by the Rapporteur in principle. Depending on the particular evidence used, questionnaire responses may be needed at the level of the whole Subject-Field, Sub-Field or even for individual CMC entries. This may either be done in the provided questionnaire form or, if the questions have to be answered individually, directly in the CMC Excel Tables (additional columns).

- Group 1 questions: One positive answer is sufficient, provided it is based on comparisons relevant for the claimed CMCs of the subject-field or sub-fields indicated or for a single CMC entries.
- Group 2 questions: At least two positive answers are needed. If the only positive answer in group 1 questions is 1.4, then all 4 questions in group 2 should have a positive answer.
- Group 3 questions: Either 3.1 and 3.2 need both to be answered positively or 3.3 needs a positive answer .
- Group 4 questions: If there are doubts which can be based on metrological evidence or/and the absence of enough positive answers for group 1-3 criteria at least one positive answer must result here.

Subject-Field MetChem.................................. **NMI** Centre for Metrology and Accreditation (MIKES)/

.... Finnish Meteorological Institute (IL)

Sub-Field(s) 4.2 Environmental 4.2.2. Ambient Air ....

CMC entry or entries PC-NO, PC-SO2, PC-CO, PTC-NO2, PC-O_3 ....

Code	*CMC review process*	Yes	No	Comments
1	Comparison results relevant to the claimed CMCs			
1.1	CIPM or EUROMET key comparisons?		X	
1.2	Supplementary comparisons?		X	
1.3	Past CIPM, EUROMET or other comparisons?	X		Harmonisation of Air Quality Measurements in Europe (HAMAQ), SMT4-CT)&-2094 (EUROMET 430). Final report: NPL Report COEM S31; Participation EUROMET 414 (intercomparison measuremet is scheduled on October 31, 2000)
1.4	Bilateral comparisons?	X		Intercomparison of the ozone transfer standards of the Finnish Meteorological Institute and the Transfer standard of the EMPA. EMPA report Helsinki, June, 1997. Calibrations of ozone transfer standard against NIST SRPs at Czech Hydrometeorological Institute and at University of Stockholm (ITM) Sweden.
2	Knowledge of the NMI's work and activities			
2.1	Activities of this NMI?	X		The activity of IL in metrology in chemistry started in 1995 by participation of the Advisory Commission for Metrology and by chairing the division of Metrology in Chemistry

Code	*CMC review process*	**Yes**	**No**	**Comments**
				since 1998.
2.2	Level of participation of this NMI in relevant projects?	X		Participation in EUROMET projects EUROMET-414 and EUROMET-430 and in addition laboratory has participated intercomparison exercises of CO, SO2, NO, NO2 and O3 by EU/JRC/ERLAP (10/99), EMEP intercomparison exercises of NO2 and O3(-95)
2.3	Scientific and technical qualification of the NMI staff?	X		The staff of the laboratory has been authors in scientific publications in international journals. The staff includes scientists, technician and assistant.
2.4	Knowledge of the measurement process and equipment?	X		The expertise of the laboratory staff on measurement equipments started 15 years ago.
3	*Quality system*			
3.1	Is the NMI accredited to ISO 17025 or equivalent for the subject-field or sub-fields?		X	Accreditation application according to ISO 17025 as a calibration laboratory was submitted to national body (FINAS) in spring 2000. The calibration capabilities under accreditation covers the claimed CMCs.
3.2	If the response is yes to 3.1, has the accreditation scope (quantities, range, uncertainties) been examined?		X	See 3.1. Technical inspection will be made on 5 of February 2001 by Dutch Accreditation Council (RvA)
3.3	Has the NMI another or a self-declared quality system	X		See 3.1

Code	***CMC review process***	**Yes**	**No**	**Comments**
	in place and does it cover the claimed CMCs?			
4	**Additional information**			
4.1	Has the NMI been visited? By whom and why?	X		The Centre for Metrology and Accreditation will examine the competence of the laboratory as a national reference laboratory through an external inspection.
4.2	Was other information used for the CMC review?		X	

Rapporteur's recommendation *) name: .... date: ....
*) or person appointed by the Rapporteur

☐ CMCs ok

☐ CMCs stay under review because ....

☐ Comments: ....

Chairman's decision name: .... date: ....

☐ CMCs are forwarded to JCRB

☐ CMCs stay under review within EUROMET

☐ Comments: ....

Additional columns and sample entries on CMC Excel Tables for individual CMC review

The codes used correspond to the ones in the questionnaire
Status "ok": CMC okay "rev": CMC stays under review

Review process (please enter review codes and comments as needed)							
1	2		3	4			Status
Comparison results	NMI's work and activities		Quality system	Additional information		Comments	Rapporteur's recommendation
1.1	2.1	2.3	3.1, 3.2			3.1: Accreditation body, Accr. No. xyz	
1.3	2.2	2.4	3.3			3.3: ISO Guide 25	
---	2.1	2.2	3.3			No comparison results available	
1.4	2.1, 2.2	2.3, 2.4	3.1, 3.2	4.2		4.2: published comparison data and refereed papers	

Appendix 16. The calibration and measurement capabilities of the MIKES-FMI Standards Laboratory

Verion to the Cycle 1, submitted in 2000

Centre for Metrology and Accreditation (MIKES) / Finnish Meteorological Institute (IL)

Country	NMI or Designated Service Provider	NMI Service Identifier	Measurement Service Category No.	Measurement Service Category	Matrix	Measurand	Dissemination Range of Measurement Capability		
							From	To	Unit
Finland	CMA/FMI	PC-O3	4,2	Environmental	synthetic air	Ozone	5	100	nmol/mol
Finland	CMA/FMI	PC-O3	4,2	Environmental	synthetic air	Ozone	100	500	nmol/mol
Finland	CMA/FMI	PC-SO2	4,2	Environmental	synthetic air	Sulphur dioxide	5	500	nmol/mol
Finland	CMA/FMI	PC-NO	4,2	Environmental	Nitrogen	Nitrogen monoxide	5	500	nmol/mol
Finland	CMA/FMI	PTC-NO2	4,2	Environmental	synthetic air	Nitrogen dioxide	50	600	nmol/mol
Finland	CMA/FMI	PC-CO	4,2	Environmental	Nitrogen	Carbon monoxide	0,2	50	μmol/mol
Finland	CMA/FMI	GCA-B	4,2	Environmental	Nitrogen	Benzene	2	20	nmol/mol

Range of Expanded Uncertainties for Certified Value					Mechanism(s) for Measurement Service Delivery	Source of Traceability	Measurement Technique(s) Used	Link(s) to Appendix B (Key Comp. Name)	Comment(s) of Service Provider	CCQM Services Administration	
From	To	Unit	Coverage factor	Level of confidence						Review Status	Review Comments
					Calibration	NIST SRP at ITM, CHMI, PTB	UV -Photometric	EUROMET 414	TEI 49C-PS, Calib uncertainty by NIST (cross section, temperature, pressure and transmittance)	OK	
					Calibration	ITM,CHMI, PTB	UV -Photometric	EUROMET 414	TEI 49C-PS, Calib uncertainty by NIST (cross section, temperature, pressure and transmittance)	OK	
					Calibration	NPL	UV fluorescence	EUROMET 430	TEI 43C; dynamic dilution	OK	
					Calibration	NPL	Chemiluminescence	EUROMET 430	TEI 42C; dynamic dilution	OK	
					Calibration	MIKES	Chemiluminescence	EUROMET 430	Perm facility: rate defined by weighing, traceable to MIKES. Purity analysis by manufacturer of the perm tube	OK	
					Calibration	NPL	NDIR	EUROMET 430	ML 8840; dynamic dilution	OK	
					Calibration /measurements	NPL	GC/FID	EUROMET 430		OK	

Finnish Meteorological Institute Contributions

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