BRITISH STANDARD

BS EN 15852:2010

Ambient air quality — Standard method for the determination of total gaseous mercury

ICS 13.040.20

British Standards

National foreword

This British Standard is the UK implementation of EN 15852:2010.

The UK participation in its preparation was entrusted to Technical Committee EH/2/3, Ambient atmospheres.

A list of organizations represented on this committee can be obtained on request to its secretary.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 June 2010

ISBN 978 0 580 61501 6

Amendments/corrigenda issued since publication

Date	Comments

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15852

June 2010

ICS 13.040.20

English Version

Ambient air quality - Standard method for the determination of total gaseous mercury

Qualité de l'air ambiant - Méthode normalisée pour la détermination du mercure gazeux total

Außenluftbeschaffenheit - Standardisiertes Verfahren zur Bestimmung des gesamten gasförmigen Quecksilbers

This European Standard was approved by CEN on 5 May 2010.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

© 2010 CEN All rights of exploitation in any form and by any means reserved worldwide for CEN national Members.

Ref. No. EN 15852:2010: E

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Contents

Page

Foreword

This document (EN 15852:2010) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by December 2010, and conflicting national standards shall be withdrawn at the latest by December 2010.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a standard method for determining total gaseous mercury (TGM) in ambient air using cold vapour atomic absorption spectrometry (CVAAS), or cold vapour atomic fluorescence spectrometry (CVAFS).

This European Standard is applicable to background sites that are in accordance with the requirements of Directive 2004/107/EC and to urban and industrial sites.

The performance characteristics of the method have been determined in comparative field validation tests carried out at four European locations: two background and two industrial sites. The method was tested for two months at each site over a period of twelve months using automated equipment currently used in Europe for determination of TGM in ambient air.

The working range of the method covers the range of ambient air concentrations from those found at background sites, typically less than 2 ng/m^3, up to those found at industrial sites where higher concentrations are expected. A maximum daily average up to 300 ng/m^3 was measured during the field trials.

Results are reported as the average mass of TGM per volume of air at 293,15 K and 101,325 kPa, measured over a specified time period, in nanograms per cubic metre.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ENV 13005, *Guide to the expression of uncertainty in measurement*

CR 14377, *Air quality — Approach to uncertainty estimation for ambient air reference measurement methods*

EN ISO 20988, *Air quality — Guidelines for estimating measurement uncertainty (ISO 20988:2007)*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of the trueness of a standard measurement method*

ISO 8573-1:2010, *Compressed air — Part 1: Contaminants and purity classes*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
ambient air
outdoor air in the troposphere, excluding workplace air

3.2
calibration
operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication

NOTE 1 A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty.

NOTE 2 Calibration should not be confused with adjustment of a measuring system, often mistakenly called "self-calibration", nor with verification of calibration.

NOTE 3 Often, the first step alone in the above definition is perceived as being calibration [ISO/IEC Guide 99:2007 (VIM)].

3.3
combined standard measurement uncertainty

standard measurement uncertainty that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model

NOTE In case of correlations of input quantities in a measurement model, covariances should also be taken into account when calculating the combined standard measurement uncertainty [ISO/IEC Guide 99:2007 (VIM)].

3.4
coverage factor

number larger than one by which a combined standard measurement uncertainty is multiplied to obtain an expanded measurement uncertainty

NOTE A coverage factor is usually symbolized k [ISO/IEC Guide 99:2007 (VIM)].

3.5
detection limit

measured quantity value for which the probability of falsely claiming the absence of a component in a material is β, given a probability α of falsely claiming its presence

NOTE IUPAC recommends default values for α and β equal to 0,05.

3.6
expanded standard measurement uncertainty

product of a combined standard measurement uncertainty and a factor larger than the number one

NOTE 1 The factor depends upon the type of probability distribution of the output quantity in a measurement model and on the selected coverage probability.

NOTE 2 The term "factor" in this definition refers to a coverage factor.

NOTE 3 Expanded measurement uncertainty is termed "overall uncertainty" in paragraph 5 of Recommendation INC-1 (1980) (see the GUM) and simply "uncertainty" in IEC documents [ISO/IEC Guide 99:2007 (VIM)].

NOTE 4 For the purpose of this document the expanded uncertainty is the combined standard uncertainty multiplied by a coverage factor $k = 2$ resulting in an interval with a level of confidence of 95 %.

3.7
measurement repeatability

measurement precision under a set of repeatability conditions of measurement

[ISO/IEC Guide 99:2007 (VIM)]

3.8
measurement reproducibility

measurement precision under reproducibility conditions of measurement

NOTE Relevant statistical terms are given in ISO 5725-1:1994 and ISO 5725-2:1994 [ISO/IEC Guide 99:2007 (VIM)].

3.9
measurement time

length of time over which the measurement instrumentation produces a single concentration value, during normal operation

NOTE 1 For "trap and desorb" instruments this will be the time period air is sampled across the gold trap prior to each thermal desorption cycle analysis; for direct measurement instruments this will be the time period in which the absorbance is averaged to produce a single value.

NOTE 2 Measurement times during the field trial campaign ranged from 30 s to 30 min.

3.10
measurement uncertainty

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

NOTE 1 Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.

NOTE 2 The parameter may be, for example, a standard deviation called standard measurement uncertainty (or a specified multiple of it), or the half-width of an interval, having a stated coverage probability [ISO/IEC Guide 99:2007 (VIM)].

3.11
method detection limit

lowest amount of an analyte that is detectable using the method, as determined by sampling and analysis of zero gas

3.12
monitoring period

time period over which monitoring is intended to take place, defined in terms of the time and date of the start and end of the period

3.13
monitoring station (for mercury)

enclosure located in the field in which an analyser has been installed to monitor TGM concentrations

3.14
monitoring time

length of time over which monitoring is intended to take place

NOTE For example: an instrument measured TGM using a measurement time of 15 min, over a sampling time of 30 days (producing 2 880 data points). The monitoring period was from 0001 h on 1 April 2008 to 0001 h on 1 May 2008.

3.15
reference conditions

ambient temperature of 293,15 K and pressure of 101,325 kPa

3.16
repeatability condition of measurement

condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

NOTE 1 A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions.

NOTE 2 In chemistry, the term "intra-serial precision condition of measurement" is sometimes used to designate this concept [ISO/IEC Guide 99:2007 (VIM)].

3.17
reproducibility condition of measurement

condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects

NOTE 1 The different measuring systems may use different measurement procedures.

NOTE 2 A specification should give the conditions changed and unchanged, to the extent practical [ISO/IEC Guide 99:2007 (VIM)].

3.18
sampling inlet

entrance to the sampling system where ambient air is taken from the atmosphere

3.19
standard uncertainty

measurement uncertainty expressed as a standard deviation

[ISO/IEC Guide 99:2007 (VIM)]

3.20
total gaseous mercury
TGM

elemental mercury vapour (Hg^0) and reactive gaseous mercury, i.e. water-soluble mercury species with sufficiently high vapour pressure to exist in the gas phase

[Directive 2004/107/EC]

NOTE This definition is taken in this standard to include all gaseous mercury species.

3.21
zero gas

gas free from mercury, interfering compounds and particles

NOTE 1 Free from mercury means containing a concentration less than the method detection limit.

NOTE 2 Zero gas is used in conjunction to calibration of automatic mercury instruments. It may consist of pure nitrogen or synthetic air from a gas cylinder. Purified air from the surrounding can also be used (see instructions in user manuals).

4 Symbols and abbreviated terms

For the purposes of this document, the following symbols and abbreviated terms apply.

4.1 Symbols

A	is a constant with numerical value - 8,134 46;
A_{Hg}	is the atomic weight of mercury, 0,20059;
α	for a given detection limit the probability of a false positive identification occurring;
B	is a constant with numerical value 3 240,87;
β	for a given detection limit the probability of a false negative identification occurring;

γ	is the mass concentration;
γ_{amb}	is the mercury concentration in a certain air volume $V\,(T, P)$;
$\gamma_{d,i}$	is the daily mass concentration value on day d from instrument i;
γ_{Hg}	is the theoretical mass concentration of mercury vapour samples that can be collected from the mercury vapour source using a syringe;
$\gamma_{\mathrm{Hg,\ sou}}$	is the mercury concentration in the source;
$\gamma_{\mathrm{Hg,\ syr}}$	is the mercury concentration in the syringe;
γ_{MDL}	is the method detection limit;
γ_{ref}	is the mass concentration of TGM in reference air at 293,15 K and 101,325 kPa;
γ_{sam}	is the mercury concentration related to a certain air temp (T_{sam}) and pressure (P_{sam});
$\bar{\gamma}$	is the mean mass concentration over all N days and across all M instruments;
$\bar{\gamma}_d$	is the mean mass concentration on day d across all M instruments;
D	is a constant with numerical value 3 216 522;
δ	is the estimated statistical uncertainty associated with the mercury vapour equation used;
$\delta_{d,i}$	is the deviation of instrument i from the mean mass concentration on day d ;
$\bar{\delta}_i$	is the mean deviation of instrument i from the mean mass concentration over all N days;
k	is the coverage factor;
η_{sam}	is the sampling efficiency;
m_{air}	is the mass of air under reference conditions;
m_{trap}	is the mass of mercury found on the gold trap;
M	is the number of parallel samplers used in a field trial;
M_{air}	is the molecular weight of air, 0,029 kg/mol;
n	is the number of measurements;
N	is the duration of the field trial in days;
P_{Hg}	is the vapour pressure of mercury;
P_{ref}	is the reference pressure, 101,325 kPa;
P_{sam}	is the actual pressure of the sampled air;
$q_{\mathrm{v,ave}}$	is the average volume flow rate of ambient air through the trap during the monitoring period;
r^2	is the correlation coefficient;

r_{flow}	is the flow calibration coefficient,
r_{syr}	is the volume calibration coefficient;
R	is the ideal gas constant, 8,314 J/K·mol;
R_{cal}	is the instrumental response produced after the injection of a volume of mercury saturated gas;
R_i	is the instrumental response generated from measurement i;
R_{sam}	is the instrumental response following analysis of the sample;
$\overline{R}$	is the average of n $(n \geq 10)$ repeat measurements of R_i ;
R_0	is the instrumental response generated upon the injection of a zero volume of mercury saturated gas;
$\overline{R}_0$	is the average of n $(n \geq 10)$ repeat measurements of $R_{0,i}$;
$R_{0,i}$	is the instrumental response generated upon introduction of zero gas from measurement i ;
σ_i	is the standard deviation of the deviation of instrument i over all N days;
σ_{R}	is the relative standard deviation of a set of n measurements;
t	is the sampling time;
T_{sam}	is the actual temperature of the sampled air;
T_{sou}	is the temperature of mercury source;
T_{syr}	is the temperature of syringe;
T_{ref}	is the reference temperature, 293,15 K;
$u_{\text{c}}(\gamma)$	is the relative combined standard uncertainty in the TGM concentration in ambient air;
$u_{\text{c},i}(\gamma)$	is the relative combined standard uncertainty from instrument i ;
$u_{i,\text{ vol}}$	is the uncertainty in the sampled volume for instrument i ;
$u_{\text{r}}(\gamma)$	is the relative random contribution to the uncertainty;
$u_{\text{r},\, i}(\gamma)$	is the random contribution to the relative combined uncertainty from instrument i ;
$u_{\text{s}}(\gamma)$	is the relative non-random contribution to the uncertainty;
$u_{\text{s},\, i}(\gamma)$	is the non-random contribution to the relative combined uncertainty from instrument i ;
U	is the expanded uncertainty;
V_{amb}	is the volume of ambient air sampled onto the trap;
$V(T,P)$	is a certain air volume;
$V_{\text{sam}}(T,P)$	is the corresponding air volume at the actual temperature T_{sam} and pressure P_{sam};

$\dot{V}_{\text{cal}}$	is the sensitivity of the analyser, determined by calibration;
$\dot{V}_{\text{cal},t=0}$	is the measured sensitivity of the instrument at time $t=0$;
$\dot{V}_{\text{cal},t=t}$	is the measured sensitivity of the instrument at time t;
$\Delta\dot{V}_{\text{cal}}$	is the drift in the sensitivity of the measuring system, over a time, t;
V_{Hg}	is the volume of mercury saturated gas from within the mercury vapour source;
V_{ref}	is the reference air volume;
x	is the mass of mercury;
y	is the measurement result;
Y	is the measurand.

4.2 Abbreviations

CVAAS	Cold Vapour Atomic Absorption Spectrometry
CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe (European Monitoring and Evaluation Programme)
FEP	Fluorinated ethylene propylene
IUPAC	International Union of Pure and Applied Chemistry
MFC	Mass flow controller
MFM	Mass flow meter
ng	Nanogram; 10^{-9} g
PTFE	Polytetrafluoroethylene
TGM	Total Gaseous Mercury
Zeeman AAS	Zeeman Atomic Absorption Spectrometry

5 Principle

The methods described in this standard are automated methods that involve either:

- adsorption of TGM from a measured air volume on a gold trap, followed by thermal desorption of total mercury from the gold trap and determination as gaseous elemental mercury by CVAAS or CVAFS;

or

- direct continuous measurement of elemental mercury by Zeeman AAS.

6 Requirements

6.1 Siting criteria

The siting requirements for TGM measurements are given in Annex A.

6.2 Method requirements

The method for the measurement of total gaseous mercury concentrations in ambient air shall be an automated method based on Atomic Absorption Spectrometry or Atomic Fluorescence Spectrometry, as specified in Annex V.III of Directive 2004/107/EC.

6.3 Method detection limit

The detection limit of the gold trap analysis method (expressed in nanograms of mercury) shall not exceed 10 % of the lower limit of the working range of the mercury expected to be collected during any measurement period. This will depend on the measurement time and the sampling flow rate.

The detection limit of the Zeeman AAS method (expressed in nanograms per cubic metre) shall not exceed 10 % of the lower working range.

6.4 Field operation and quality control

After the installation at the monitoring station, the analyser shall be tested to ensure that it is working correctly.

It is essential that the expanded uncertainty of measurements in the field does not exceed the 50 % according to Directive 2004/107/EC.

Requirements and recommendations for quality assurance and quality control are given for the measurements in the field (see Clause 11).

7 Reagents

7.1 Argon, of purity greater than 99,999 %, suitable for use as a carrier gas for CVAAS and CVAFS.

7.2 Nitrogen, of purity greater than 99,999 %, suitable for use as a carrier gas for CVAAS and CVAFS.

7.3 Air, of class 3.3.3 purity or better according to ISO 8573-1:2010.

7.4 Elemental mercury, of purity 99,999 9 %, for preparation of gaseous mercury vapour standard.

WARNING — Mercury is toxic by skin absorption and inhalation of vapour. Use suitable personal protective equipment (including gloves, face shield or safety glasses, etc.) and minimize exposure by using a fume hood.

7.5 Water, resistivity greater or equal to 18 MΩ·cm at 298 K.

The ultrapure water used in this method is for cleaning purposes only.

7.6 Hydrochloric acid (HCl), concentrated, density ~ 1,18 g/ml, mass fraction 36 % to 38 %.

The concentration of mercury shall be less than 0,002 mg/l.

WARNING — Concentrated hydrochloric acid is corrosive and hydrochloric acid is an irritant. Avoid contact with the skin and eyes, or inhalation of the vapour. Use suitable personal protective equipment (including gloves, face shield or safety glasses, etc.) when working with hydrochloric acid.

Handle open vessels containing concentrated hydrochloric acid in a fume hood. The vapour pressure of hydrochloric acid is high. Therefore beware of pressure build-upin capped vessels when preparing dilute hydrochloric solutions.

7.7 Hydrochloric acid, diluted 1:49 with ultrapure water for cleaning of filter housings, glass manifolds and sampling components.

Add approximately 700 ml of water (7.5) to a 1 000 ml volumetric flask. Carefully add 20 ml of concentrated hydrochloric acid (7.6) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

8 Apparatus

8.1 Sampling equipment

8.1.1 Polytetrafluoroethylene (PTFE) filters, pore size 0,2 µm, mounted in a suitable fluorinated ethylene propylene (FEP) or PTFE housing, for installation in the sampling line to remove particles from the sampled air.

8.1.2 Sampling line, FEP or PTFE, as short as possible to avoid losses of mercury vapour.

Condensation of water vapour shall be avoided from the inlet to the analyser. Connectors between the filter housing and mercury analyser shall be of a suitable material (e.g. FEP or PTFE) to avoid losses of mercury vapour.

8.2 Analytical instrumentation

8.2.1 Mercury analyser based on amalgamation and CVAAS or CVAFS.

A mercury analyser consisting of a gold amalgamation system coupled to an atomic fluorescence or atomic absorption spectrometer.

8.2.2 Mercury analyser based on Zeeman AAS.

A mercury analyser with Zeeman background correction.

8.2.3 Mass flow controller and mass flow meter.

To measure and control the mass flowrate of air sampled through the gold trap or mercury analyser.

The flow rates of the mass flow controller (MFC) and mass flow meter (MFM) shall be traceable to (inter)nationally accepted standards.

NOTE Direct measurements of the mercury concentration with Zeeman AAS do not depend on the air flow rate, however it is highly desirable to have a steady controlled flow at a measured temperature and pressure.

The flow rates of the MFC and MFM shall be checked using a flow meter traceable to (inter)nationally accepted standards. This shall be performed during installation and commissioning and thereafter periodically. The accuracy of the MFC or MFM shall be within ± 5 %. If appropriate, record the atmospheric temperature and pressure at which the calibration of the MFC and MFM was checked.

8.3 Calibration equipment

Known amounts of mercury vapour for instrument calibration are generated using a vessel containing a small volume of elemental mercury. This allows a saturated vapour of mercury to develop within the air in the vessel, which is in equilibrium with the atmosphere via a capillary tube. The temperature of the liquid mercury inside the mercury source is monitored with a platinum resistance thermometer, and samples of the vapour are taken with the gas-tight syringe through a septum in the top of the vessel. The construction of a typical calibration apparatus is shown in Figure D.1.

NOTE 1 Calibration vessels are commercially available from several vendors. Please refer to manuals for more details.

NOTE 2 The calibration vessel should be at atmospheric pressure by use of a capillary vent. This should be capped when the vessel is not in use.

9 Sampling considerations

9.1 Inlet location

The siting requirements for TGM measurements are shown in Annex A.

The monitoring of TGM requires a container or room equipped with climate control to keep the room at a stable temperature, usually around 20 °C.

The sampling inlet shall be between 1,5 m (the breathing zone) and 4 m above the ground.

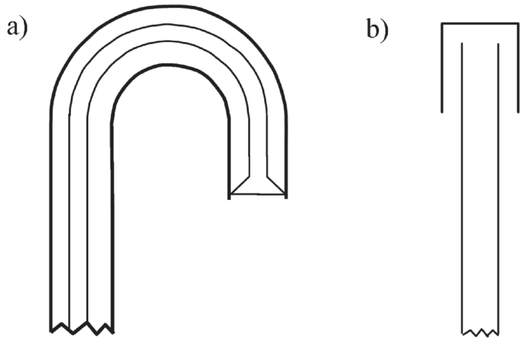
NOTE It may be necessary to position the sampling inlet higher (up to 8 m) in some circumstances.

The sampling inlet shall not be positioned in the immediate vicinity of sources in order to avoid unrepresentative sampling. Local meteorological conditions, such as prevailing wind direction and formation of stagnant air pockets, shall also be considered.

The air flow around the sampling inlet shall be unrestricted. Obstructions to the air flow from buildings, trees and other obstacles shall be avoided.

9.2 Sampling inlet and sampling line

The sampling inlet may be made from borosilicate glass, quartz, FEP or PTFE. The inlet can be made fairly simple, but it shall be well-supported and constructed so that rain or snow cannot enter into the sampling system. Suitable inlets are commercially available. Two possible inlet designs are shown in Figure 1. If the inlet only serves one instrument, the sampling line shall be connected via a dust filter directly to the instrument.

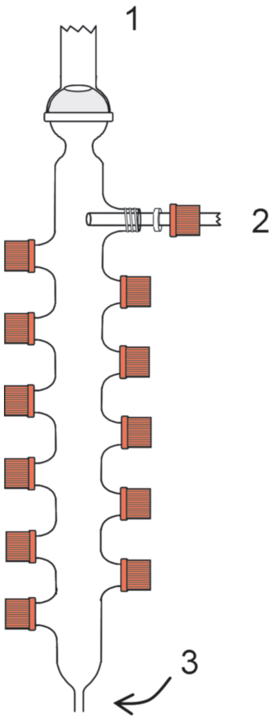


a) The air enters into a funnel made of borosilicate glass that is directly connected to the sampling line (borosilicate glass, FEP or PTFE tubing). The funnel and the sampling line can be supported by an outer tube, made from a plastic material or metal with a suitable coating.

b) Inlet and sampling line consisting of borosilicate or quartz glass. This design can require a protecting frame (not shown) which is usually made from plastic or coated metal.

Figure 1 — Sampling inlet for TGM

The principle of a manifold with a drain is shown in Figure 2.



Key

1 inlet
2 connection to instrument
3 drain

Figure 2 — Manifold made from borosilicate or quartz glass

The manifold is connected to the sampling inlet.

NOTE The residence time of the intake system depends on its dimensions and on the total flow rate. The residence time should be as short as possible. The residence time can be optimised by altering the support flow or the inner diameter of the sampling line. However, too high flow rates may create a pressure drop. Many instruments use mass flow regulators to regulate the sample flow rate and therefore are not very sensitive to the pressure. But for other instruments a pressure drop in the inlet system may be critical. Hence, the inlet and sampling line system need to be dimensioned considering the requirements at each individual instrument and sampling line.

9.3 Measurement time

The required measurement time depends on the ambient concentration. Relative uncertainty is likely to increase as measurement time decreases. The measurement time shall be long enough to collect enough mercury to satisfy the quality control and uncertainty requirements of this European Standard. However, the measurement time shall not be so long that degradation of gold traps or sample breakthrough occurs.

10 Measurement procedure

10.1 Calibration with AFS/AAS

10.1.1 Install and commission the mercury measurement system according to the manufacturer's instructions.

10.1.2 Place a small quantity of mercury carefully inside the calibration vessel. Allow the headspace to become saturated with mercury vapour. The saturated concentration is related to the temperature of the vessel.

10.1.3 Calibrate the instrument using injections of known volumes of air saturated with mercury vapour and a gas-tight syringe with an adequate volume. For verification, perform a "calibration robustness check" at least every two weeks and recalibrate, if necessary (see 11.1).

Following maintenance or any substantial changes to the instrumentation, a calibration shall be performed.

The calibration vessel shall be thermally insulated (see Annex D). It is advisable to thermostatically control the calibration vessel.

During calibration, measure the temperature of the calibration vessel using a temperature sensor calibrated to national or international standards with a valid calibration. The temperature sensor shall have a minimum resolution of ± 0,1 °C.

NOTE 1 More information on the calibration process may be found in [8].

NOTE 2 It may also be necessary to measure the temperature of the monitoring station enclosure during calibration using a temperature sensor calibrated to national or international standards with a valid calibration (see Annex D). The temperature sensor in the monitoring station enclosure should have a minimum resolution of ± 0,5 °C.

Use a gas-tight syringe traceable to national or international standards with a valid calibration. Gas-tight syringes shall be pre-conditioned with mercury vapour to minimize losses of mercury. Refer to user manuals for more details.

This procedure is outlined below for systems with amalgamation:

a) Calculate the concentration of mercury in the syringe using the following formula:

$$\gamma_{\mathrm{Hg}} = \delta \frac{\mathrm{D}}{\mathrm{T}_{\mathrm{syr}}} \times 10^{-(\mathrm{A}+\frac{\mathrm{B}}{\mathrm{T}_{\mathrm{sou}}})} \qquad T_{\mathrm{syr}} \geq T_{\mathrm{sou}} \qquad (1)$$

where

γ_{Hg}	is the theoretical mass concentration of mercury vapour samples that can be collected from the mercury vapour source using a syringe in nanograms per millilitre;
T_{syr}	is the temperature of the syringe in kelvins;
T_{sou}	is the temperature of the mercury source in kelvins;
A	is a constant with numerical value - 8,134 46;
B	is a constant equal to 3 240,87;
D	is a constant equal to 3 216 523;

δ is a factor associated with the mercury vapour equation used which is taken to be equal to 1,0.

Withdraw a known volume of the saturated mercury vapour using a gas-tight syringe of adequate volume, inject into the instrument and initiate the measurement sequence.

b) Calculate the mass of mercury injected into the instrument from the injection volume and the concentration of mercury vapour using Equation (1).

c) Repeat the above procedure using different injection volumes to cover a suitable range of masses of mercury and generate a calibration line. Further guidance is given in Annex E.

NOTE 3 Equation (1) is only valid when T_{syr} is greater or equal to T_{sou}. Thermostatting the mercury vapour source at temperatures lower than room temperature will decrease the mercury vapour concentration and allow collection of smaller amounts of mercury. Equation (1) is based on the equilibrium vapour pressure of mercury [2]. More information on Equation (1) is found in Annex D.

NOTE 4 The choice of an equation for calculating the vapour pressure of mercury is still a point of discussion. Equation (1) stems from a validation programme and is equal to that suggested in Ebdon *et al*. [3]. However, other equations to describe the vapour pressure of mercury are also available [4].

10.1.4 Calculate the concentration of mercury in nanograms per cubic metre using the calibration function (see Clause 12).

10.2 Calibration with Zeeman AAS

10.2.1 Install and commission the mercury measurement system according to the manufacturer's instructions.

Zeeman AAS is calibrated using cells containing mercury saturated vapour at known temperature. For verification, perform a "calibration robustness check" at least every three months, or more often if required by the guidelines of the laboratory practice. The calibration robustness check can be done the same way as the CVAAS/CVAAF calibration robustness check (see 11.1).

10.2.2 Make a measurement of the mercury mass concentration in zero gas to ensure that an acceptably low blank is found. This is particularly important after performing a calibration to ensure that the system has not become contaminated (see 11.2).

10.2.3 Activate the automated measurement sequence.

10.2.4 Calculate the concentration of mercury in nanograms per cubic metre using the calibration function (see Clause 12).

11 Quality control

11.1 Calibration robustness check

To verify the calibration, a known mass of mercury shall be measured every two weeks according to Clause 10. If the sensitivity (response per nanogram of mercury) of the instrument has changed by more than 10 % it is necessary to recalibrate.

NOTE For CVAAS and CVAFS it is important to consider the artificial nature of the calibration procedure and how this might affect the accuracy of measurements. Ideally an equal or greater mass of mercury should be injected during calibration as is collected during sampling. The majority of sample results reported should fall towards the centre of the calibration range where the uncertainty associated with predicted concentrations is at its minimum. The uncertainty associated with extrapolated results or results generated from the lowest portion of the calibration line will have a much higher uncertainty. This is particularly true when the calibration intercept is significantly different to the instrumental zero readings or if the measurement technique exhibits non-linearity.

11.2 Zero gas check

A zero gas check shall be performed at least every two weeks. This test shall involve the introduction of a known volume of zero gas through the sampling manifold and into the instrument and then performing an analysis. This check shall be performed using the same sampling and measurement conditions as the sample measurements.

The zero gas reading shall be a maximum of 10 % of the lower working range.

Appropriate steps shall be made to reduce the zero gas readings if this criterion is not met.

11.3 Degradation of gold traps

The accuracy of measurements will be affected when gold trap degradation occurs. Gold traps shall be replaced or cleaned according to the manufacturers' guidelines. Measurements using gold traps which have shown some degradation will be accepted, provided that inclusion of the data does not increase the expanded uncertainty of the measurements above the 50 % data quality objective, as specified in Directive 2004/107/EC.

NOTE 1 The uptake efficiency of new gold traps is close to 100 %, but may change with time probably due to poisoning from certain atmospheric constituents. Low uptake efficiency leads to underestimation of the actual TGM concentration. Unfortunately this phenomenon is not always revealed in terms of low response from mercury gas standards. The reason seems to be that the uptake efficiency depends on concentration. During standard injections (i.e. adding small samples of saturated mercury vapour) the gold traps are for a short moment exposed to very high mercury concentrations.

NOTE 2 Each instrumental provider uses their own gold traps and their individual characteristics may vary. No general rules regarding maintenance and replacement of gold traps are therefore given. But the performance of each instrument should carefully be observed following the recommendations given in the user manual.

11.4 Proficiency testing scheme

If laboratories carry out measurement of TGM on a regular basis, it is recommended that they participate in a relevant proficiency testing scheme at regular intervals.

11.5 Accreditation

Laboratories using this European Standard shall demonstrate that they are working in accordance with the requirements of European quality systems. One of the ways of demonstrating compliance with these requirements is through formal accreditation by an accreditation body falling under the Multi-Lateral Agreement of the European Co-operation for Accreditation.

11.6 Measurement uncertainty

Measurement uncertainties shall be calculated for each time averaged value to be reported. These shall be calculated according to Clause 13.

12 Calculation of results

12.1 General

Following sampling, the mean of the data will be taken over any given time period. Unless the purpose of sampling is to examine acute high concentration events over short timescales, it is recommended that data be averaged over time periods not shorter than 24 h.

The expanded measurement uncertainty shall be less than or equal to 50 %, the minimum data capture shall be 90 %, and the minimum time coverage shall be 14 %, as specified in the data quality objectives of Directive 2004/107/EC.

12.2 Calculation of TGM concentrations to reference conditions

From the ideal gas law, the mass of air under reference conditions, in kilograms per cubic metre, m_{air}, can be calculated according to:

$$\mathrm{m_{air}} = \frac{\mathrm{P_{ref}}}{\mathrm{R\ T_{ref}}} \mathrm{M_{air}} \tag{2}$$

where

m_{air}	is the mass of air under reference conditions in kilograms per cubic metre;
P_{ref}	is the reference pressure, 101 300 Pa;
R	is the ideal gas constant, 8,314 J/K·mol;
T_{ref}	is the reference temperature, 293,15 K;
M_{air}	is the molecular weight of air, 0,029 kg/mol.

Many instruments used for air monitoring are equipped with MFCs to regulate sampling flow rates and to determine sample volumes. In other words air volumes are defined according to Equation (2). The use of MFCs is recommended because it is independent of ambient pressure and temperature. Actual air volumes can easily be converted to reference air volumes as shown below. Equation (2) shows that the mass of air per cubic metre is proportional to $P_{\text{ref}}/T_{\text{ref}}$, hence:

$$\frac{\mathrm{P_{ref}}}{\mathrm{T_{ref}}} \mathrm{V_{ref}} = \frac{\mathrm{P_{sam}}}{\mathrm{T_{sam}}} \mathrm{V_{sam}(T, P)} \tag{3}$$

And therefore it follows that

$$V_{\text{ref}} = \frac{P_{\text{sam}}\ T_{\text{ref}}}{T_{\text{sam}}\ P_{\text{ref}}} V_{\text{sam}}(T, P) \tag{4}$$

where

P_{sam}	is the actual pressure of the sampled air in kilopascals;
T_{sam}	is the actual temperature of the sampled air in kelvins;
V_{ref}	is the reference air volume in cubic metres;
$V_{\text{sam}}(T, P)$	is the corresponding air volume at the actual temperature T_{sam} and pressure P_{sam} in cubic metres.

With Equation (4) volumes obtained at T_{sam} and P_{sam} can be converted to a reference volume (V_{ref}). Likewise, since $\gamma_{\text{sam}} = \frac{m_{\text{trap}}}{V_{\text{sam}}}$, the mass concentration (γ_{sam}) determined from the measurement of the mass of mercury collected, m_{trap}, in a certain air volume, $V_{\text{sam}}(T, P)$, can be converted to the concentration under reference conditions (γ_{ref}) using Equation (5).

$$\gamma_{ref} = \frac{\gamma_{sam}\ V_{sam}(T,P)}{V_{ref}} = \frac{T_{sam}\ P_{ref}}{P_{sam}\ T_{ref}}\gamma_{sam} \tag{5}$$

where

γ_{sam} is the mercury concentration related to a certain air temp (T_{sam}) and pressure (P_{sam}) in nanograms per cubic metre;

γ_{ref} is the mass concentration of TGM in reference air at 293,15 K and 101,325 kPa.

12.3 Method detection limit

The method detection limit, γ_{MDL}, expressed in nanograms per cubic metre, is defined as:

$$\gamma_{MDL} = \frac{3}{\dot{V}_{cal}V_{amb}}\sqrt{\frac{\sum_{i=1}^{n}\left(\overline{R}_0 - R_{0,i}\right)^2}{n-1}} \tag{6}$$

where

$\dot{V}_{cal}$ is the sensitivity of the analyser, determined by calibration in 1/ng;

V_{amb} is the volume of ambient air sampled onto the trap in cubic metres;

$R_{0,i}$ is the instrumental response generated upon introduction of gas with a mercury mass concentration of zero from measurement i;

$\overline{R}_0$ is the average of n ($n \geq 10$) repeat measurements of $R_{0,i}$.

The method detection limit shall not exceed 0,2 ng/m^3.

12.4 Repeatability

The repeatability is the closeness of agreement of successive measurements of the same measurand carried out under the same conditions of measurements. Quantitatively this can be expressed as the relative standard deviation of a set of repeat measurements thus:

$$\sigma_R = \frac{1}{\overline{R}}\sqrt{\frac{\sum_{i=1}^{n}\left(\overline{R} - R_i\right)^2}{n-1}} \tag{7}$$

where

σ_R is the relative standard deviation of a set of n measurements;

R_i is the instrumental response generated from measurement i;

$\overline{R}$ is the average of n ($n \geq 10$) repeat measurements of R_i.

To express this quantity in percentage terms, the value of $100\sigma_R$ needs to be computed. The allowable limits for this quantity are given in Clause 13.

12.5 Drift in instrument sensitivity

The drift in the sensitivity of the instrument, $\Delta\dot{V}_{\mathrm{cal}}$, over a time, t, is given by:

$$\Delta\dot{V}_{\mathrm{cal}} = \frac{\dot{V}_{\mathrm{cal},t=0} - \dot{V}_{\mathrm{cal},t=t}}{\dot{V}_{\mathrm{cal},t=o}} \qquad (8)$$

where

$\dot{V}_{\mathrm{cal},t=t}$ is the measured sensitivity of the instrument at time t;

$\dot{V}_{\mathrm{cal},t=0}$ is the measured sensitivity of the instrument at time t =0.

To express this quantity in percentage terms, the value of $100\Delta\dot{V}_{\mathrm{cal}}$ needs to be computed. The allowable limit for drift between calibration robustness checks is 10 %.

13 Estimation of the measurement uncertainty method and performance criteria

13.1 Introduction

The expanded measurement uncertainty of the concentration of TGM in ambient air has to fulfil the data quality objective of 50 %, as specified in Directive 2004/107/EC.

The uncertainty (expressed at a 95 % confidence level) of the methods used for the assessment of ambient air concentrations shall be evaluated in accordance with the principles of EN ISO 20988, ENV 13005, ISO 5725-2, and the guidance provided in CR 14377. The percentages for uncertainty are given for individual measurements, which are averaged over typical sampling times, for a 95 % confidence interval. Fixed and indicative measurements shall be evenly distributed over the year in order to avoid skewing of results.

The uncertainty of the method has been calculated from the results of a series of field trials to:

a) demonstrate that this standard method meets the uncertainty requirements; and

b) provide sufficient information on performance criteria which have to be met to ensure that individual users can also meet the uncertainty requirements.

See Annex C for details of the results of the field trials.

This European Standard uses appropriate parts of EN ISO 20988, CR 14377, ENV 13005 and ISO 5725-2 to produce a framework for assessing uncertainties against target values for individual laboratories (see 13.2). This approach to uncertainty estimation not only provides the user of this standard with a method of calculating his/her own uncertainty; more importantly it provides guidance as to the major uncertainty contributions to this method and identifies:

c) the maximum allowable level for each of these contributions for the method to be considered under control;

d) the maximum level for each contribution if the target overall uncertainty is to be met.

13.2 Assessment against target measurement uncertainty for individual laboratories

The set of measurement equations that fully describe the measurement of the TGM mass concentration in ambient air, γ, is described below.

For instruments that sample a known volume of air onto gold traps, followed by desorption and measurement, use Equation (1) and the following equations:

$$\dot{V}_{\text{cal}} = \frac{\left(R_{\text{cal}} - R_0\right)}{\gamma_{\text{Hg}} V_{\text{Hg}} r_{\text{syr}}} \tag{9}$$

$$m_{\text{tube}} = \frac{R_{\text{sam}}}{\dot{V}_{\text{cal}}\,\eta_{\text{sam}}} \tag{10}$$

$$V_{\text{amb}} = q_{v,\text{ave}}\, t\, r_{\text{flow}} \tag{11}$$

$$\gamma_{ref} = \frac{m_{\text{trap}}}{V_{\text{amb}}} \tag{12}$$

where

$\dot{V}_{\text{cal}}$	is the sensitivity of the analyser determined by calibration in 1/ng;
R_{cal}	is the instrumental response produced after the injection of a volume of mercury saturated gas (unitless/arbitrary units);
γ_{Hg}	is the theoretical mass concentration of mercury vapour samples that can be collected from the mercury vapour source using a syringe;
V_{Hg}	is the volume of mercury saturated gas from within the mercury vapour source in millilitres;
r_{syr}	is the volume calibration coefficient in millilitres per millilitre;

NOTE 1 This quantity describes the relationship between the graduations on the syringe and the actual volume, traceable to national standards, represented by these graduations.

R_0	is the instrumental response generated upon the injection of a zero volume of mercury saturated gas (unitless/arbitrary units);
R_{sam}	is the instrumental response following analysis of the sample;
m_{trap}	is the mass of mercury found on the gold trap in nanograms;
V_{amb}	is the volume of ambient air sampled onto the trap in cubci metres;
$q_{\text{v,ave}}$	is the average volume flow rate of ambient air through the trap during the monitoring period in cubic metres per second;
t	is the sampling time in seconds;
r_{flow}	is the flow calibration coefficient in millilitres per millilitre;

NOTE 2 This is the ratio of the flow rate measured using the on-site flowmeter to the actual flow traceable to national standards.

η_{sam} is the sampling efficiency in nanograms per nanogram;

NOTE 3 This is the ratio of the mass of mercury captured by the gold trap to the actual mass of mercury in the sampled air.

γ_{ref} is the mass concentration of TGM in reference air at 293,15 K and 101,325 kPa, usually expressed in nanograms per cubic metre.

For instruments which measure the mass concentration of mercury directly by optical methods, use Equations (1), (5) and the following equations:

$$\dot{V}_{\text{cal}} = \frac{\left(R_{\text{cal}} - R_0\right)}{\gamma_{\text{Hg}}} \qquad (13)$$

$$\gamma_{\text{amb}} = \frac{R_{\text{sam}}}{\dot{V}_{\text{cal}} \, .\eta_{\text{sam}}} \qquad (14)$$

where the definitions which differ from those listed above are

$\dot{V}_{\text{cal}}$ is the sensitivity of the analyser determined by calibration;

R_{cal} is the instrumental response produced after the introduction of a mass concentration γ_{Hg} of mercury saturated gas;

R_0 is the instrumental response generated upon introduction of gas with a mercury mass concentration of zero;

R_{sam} is the instrumental response following analysis of the sample;

γ_{amb} is the mercury concentration in a certain air volume $V\,(T, P)$.

NOTE 4 The uncertainty in the average temperature and average pressure during the monitoring period should be estimated from the accuracy of meteorological data collected during the monitoring period.

The uncertainty estimate of $\dot{\text{V}}_{\text{cal}}$ shall include a component to account for drift in the sensitivity of the analyser between calibrations. For low masses of collected mercury this component is likely to be small in comparison to the repeatability of the instrument.

Generally, the sensitivity of the instrument shall not drift by more than 10 % between calibrations. If the drift exceeds 10 %, acceptance of the data shall not increase the expanded uncertainty of measurements above the data quality objective of Directive 2004/107/EC.

The relative target expanded uncertainty for this measurement, as required by Directive 2004/107/EC is 50 %.

The uncertainty may be calculated according to the application of ENV 13005 on Equations (9) to (14). Assessment against the target expanded uncertainty by an individual laboratory may also be made according to Annex F.

13.3 Use of uncertainties in reporting of results

When reporting the result of a measurement, and when the measure of uncertainty is the expanded uncertainty:

a) give a full description of how the measurand, Y, is defined;

b) state the result of the measurement as $Y = y \pm U$, where y is the measurement result and U is the expanded uncertainty, and give the units of y and U;

c) give the value of the coverage factor k used to obtain U and the approximate level of confidence this factor confers on the interval $y \pm U$.

14 Performance characteristics determined in field tests

The performance characteristics calculated for this method are based upon the data gathered in the field tests carried out to validate this method and assess its uncertainty.

The field trials were undertaken at four locations, over a one-year period. Eight (or, at one location, seven) instruments, made by four different manufactures, were present at each field trial location. The characteristics of the four sites were chosen in order to obtain as much information as possible on the performance of the method under different ambient and meteorological conditions. Details of the performance characteristics and their calculation are given in Annex C.

15 Interferences

15.1 General

Both CVAAS and CVAFS require special techniques to provide selectivity for mercury determination as some gases, volatile atmospheric compounds, and particles may cause interference due to non-selective light absorbance and scattering.

In the case of CVAFS, mercury is collected and pre-concentrated on selective traps (amalgamation, double amalgamation on gold traps), and pure argon is used as carrier gas to exclude quenching of fluorescence by atmospheric molecular gases.

In the case of CVAAS, the selectivity is provided either with the selective traps or by spectroscopic means (Zeeman background correction). Ambient air is used as carrier gas.

The automated methods described in this standard are relatively free of interferences.

15.2 Mercury analyser based on amalgamation and CVAAS or CVAFS

Volatile compounds that absorb at the same wavelength of mercury (253,7 nm) such as ozone or volatile organics may cause positive interference with CVAAS. In contrast, CVAFS is less prone to this type of positive interference because there are no significant levels of volatile atmospheric compounds that will fluoresce at the wavelength of excitation and detection (253,7 nm). However, signal suppression by molecular quenching of excited elemental mercury is possible with CVAFS if unwanted molecular gaseous compounds are present in the fluorescence atom cell. For both detection systems, these interferences are minimized by using a gold amalgamation system and can be eliminated by heating the gold amalgamation unit during the monitoring period at approximately 50 °C to 80 °C so that deleterious compounds pass through resulting in highly selective capture of gaseous mercury on the gold amalgamation system.

Free halogens such as chlorine or bromine may reduce the collection efficiency of mercury on gold. Concentrations found in ambient air are not expected to cause interference.

Gold trap collection efficiency may be reduced by poisoning of the gold surface. Poisoning of the gold trap surface is minimized by having a large surface area, maintaining a 50 °C to 80 °C sample temperature, collecting small air volumes and heating for analysis as frequently as possible to "clean" the gold surface.

15.3 Mercury analyser based on Zeeman AAS

In this approach only elemental mercury vapour is determined; total gaseous mercury is not determined. However, the expected concentration of oxidized gaseous mercury and organo-mercury in ambient air is sufficiently low at most sites so that comparable data can be obtained with Zeeman AAS as with the gold amalgamation CVAAS or CVAFS methods. However Zeeman AAS may report lower results at selected locations very near point sources of gaseous oxidized mercury or organo-mercury compounds (e.g. chlor-alkali plants, coal-fired power plants, waste incinerators, municipal landfill, etc.) and sites influenced by marine boundary layer air. This is not an interference of the Zeeman AAS, but rather a difference in methodology. In special cases, Zeeman CVAAS can be combined with a gold trap or speciation technique.

16 Reporting of results

A report on the measurement of TGM in ambient air shall contain at least the following information:

- reference to this European Standard;
- type of instrument used;
- description of each sampling location;
- flow rate and monitoring period;
- the measurement result expressed in nanograms per cubic metre of air;

NOTE 1 If the measured concentration of TGM in ambient air is less than the method detection limit the result should be reported as "less than the method detection limit".

NOTE 2 If the measured concentration of TGM in ambient air is less than the quantification limit an indication should be given that the result, if it is reported, is "less than the quantification limit".

- an expanded uncertainty and how it was estimated;
- any unusual features noted during the determination;
- method detection limit;
- any deviations from this European Standard.

Annex A
(informative)

Sampling sites

A.1 Background sites

Usually, background stations are selected in order to be representative of a large area. The EU legislative criteria laid down in paragraph 9 of Article 4 of Directive 2004/107/EC requires one station per 100 000 km² for indicative measurement and each Member State is required to establish at least one monitoring station. Also, monitoring has to be coordinated with the EMEP programme.

Each background station has to be located so that it is not influenced by any urban location or industrial sites to avoid direct influence of their mercury gaseous emissions. Furthermore, it has to be a minimum of 50 km from large point sources such as coal combustion plants, chlor-alkali industry or other large mercury emission sources.

A.2 Urban sites

For urban background locations the measurement site has to be representative of several square kilometres and avoid measuring very small micro-environments in their immediate vicinity.

A.3 Industrial sites

A.3.1 General

At industrial sites, a sampling station has to be representative of the air quality in at least the surrounding 250 m × 250 m. Where contributions from industrial sources are to be assessed, at least one sampling station has to be positioned downwind of the source in the nearest residential area.

A.3.2 Recommendations for operation at industrial sites

It is recommended that the instrument should be able to measure a suitable wide range of total gaseous mercury concentrations. If the instrument uses gold traps, make sure the gold trap can adsorb high amounts of mercury without any breakthrough during the monitoring period;

It shall be determined whether the high amounts of mercury adsorbed during the monitoring period are being fully released from the gold trap after each analysis cycle.

Annex B
(informative)

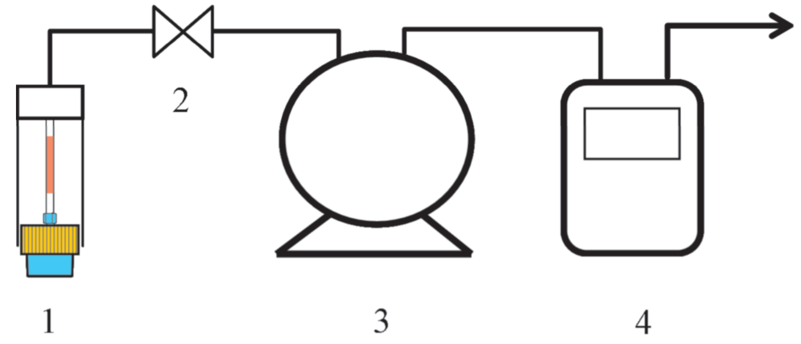
Manual method TGM

B.1 Introduction

Manual sampling of TGM in air is made using gold traps with gas meters or mass flow controllers for air volume measurements. This method is well described in the EMEP manual [7] and will only briefly be explained here.

B.2 Sampling

Gold traps comprised of 12 cm to 15 cm quartz glass tubes (with 4 mm/6 mm inner/outer diameter) filled with gold adsorbent. The gold adsorbent can be small pieces (1 mm to 2 mm) of 1 mm solid gold wire mixed with a crushed-quartz glass bearer or, alternatively, sand, glass beads or quartz glass coated with a thin layer of gold. The latter trap type usually generates lower blank values. The gold trap is equipped with an inlet filter to avoid interference from particles.



Key
1 Au-trap with inlet filter
2 precision needle valve or alternatively mass flow controller
3 pump
4 air volume meter

Figure B.1 — Set-up for manual measurements of TGM

The measurement set-up shown in Figure B.1 uses a needle valve and air volumes are determined by a volume meter (i.e. a diaphragm/bellows gas meter). The different parts can be connected with PTFE or PE tubing. Since the volume meter is placed on the outlet side of the pump air volumes at ambient pressure and temperature are obtained.

NOTE Placing the volume meter on the inlet side of the pump will give erroneous results since the pressure is lower on this side. The entire system including the pump should be air tight to ensure that exactly the same amount of air as is pulled through the gold trap also is measured by the volume meter. The volume meter should be placed in a thermostatted room with an as constant temperature as possible.

The measurement system can be made simpler by using a mass flow controller to set the flow rate. In this case the total sample volume is obtained as a function of time and the air volume meter is not needed. The optimal air sample flow rate is around 300 ml/min.

B.3 Analysis

Mercury samples collected on gold traps in the field are analysed by thermal desorption and mercury detection. Normally the dual amalgamation technique is used. Hence, the mercury desorbed from the field trap is first transferred to a second Au trap, denoted the analytical Au trap, using Hg-free carrier gas with a flow rate of 30 ml/min to 100 ml/min. The mercury sample is finally desorbed from the analytical trap and detected. The use of a second trap increases the accuracy and reproducibility. The sampling and transfer lines are made of PTFE tubing. Glass to glass connections (i.e. between the sampling trap and the analytical trap) are made with silicone or Viton®[1] tubing.

B.4 Quality control – Quality assurance

The necessary quality control steps involve maintenance of the sampling system at the measurement site and testing the analytical system as well as the mercury collection efficiency of the Au traps.

The most critical point regarding sampling is the air volume measurement. Mass flow controllers or volume meters shall be calibrated on a regular basis to ensure correct performance. The entire sampling system shall also be leak tested.

The analytical system needs to be calibrated in conjunction to each analysis. This is performed by injecting volumes of saturated mercury vapour (see Clause 10). Sample air volumes shall be corrected to reference volumes (see Clause 12).

Degraded gold traps shall be discarded (see Table F.2). Each trap is blanked by heating and purging with Hg-free argon gas prior to sampling. In-between sampling the Au traps are stored with stoppers and double bagged in air tight PE plastic bags.

A detection limit of 0,02 ng/m^3 can be obtained from 24 h monitoring periods at a sample flow rate of 300 ml/min. The precision is normally ± 0,1 ng/m^3 or better.

---

1) Viton® is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

Annex C
(informative)

Summary of field validation tests

C.1 Introduction

The performance characteristics listed in this annex are based upon the data gathered in field tests carried out to validate this standard method. Sampling was undertaken at four locations, over a one-year period. Eight (or, at one location, seven) instruments, made by four different manufacturers, were present at each field trial location. The characteristics of the four sites were chosen in order to obtain as much information as possible on the performance of the method under different ambient and meteorological conditions.

C.2 TGM field trial locations

C.2.1 Site 1

Site: Rural coastal/background site under the influence of local open and natural sources.

Monitoring period: November 2006 – January 2007.

C.2.2 Site 2

Site: Industrial site near a chlor-alkali plant.

Monitoring period: February 2007 – May 2007.

C.2.3 Site 3

Site: Background site (coastal).

Monitoring period: June 2007 – August 2007.

C.2.4 Site 4

Site: Industrial site near a chlor-alkali plant.

Monitoring period: September 2007 – December 2007.

C.2.5 Number of instruments and length of studies

The number of instruments at each field trial location, and the length of each study were as follows:

- Site 1: 8 instruments, 64 days;
- Site 2: 7 instruments, 79 days;
- Site 3: 8 instruments, 57 days;
- Site 4: 8 instruments, 63 days.

For the purposes of data analysis the data produced by each instruments was averaged over the period of one day to produce a usable and consistent data set. The monitoring period of the instruments used in the field trials was considerably shorter (ranging from 30 s to 30 min).

The data capture at each field trial location as a percentage of usable days was as follows:

- Site 1: 96 %;
- Site 2: 84 %;
- Site 3: 93 %;
- Site 4: 88 %.

A small percentage of data was subsequently rejected as outlying (those points more than double, or less than half the daily average). In the vast majority of cases the outlying data was explained by an instrumental fault. This accounted for the following percentage of all data at the field trial locations:

- Site 1: 3 %;
- Site 2: 3 %;
- Site 3: 0 %;
- Site 4: 1 %.

Results were expressed as mass concentration values in nanograms per cubic metre corrected to 293,15 K and 101,325 kPa.

C.3 Uncertainty estimation from the field trial process

The theory underpinning the field trial process is that the mean value yielded by several different types of instruments at an individual location when measuring different concentration levels represent the best estimate of the "true value" of the TGM concentration in ambient air. In general the spread of these results is a good estimate of the uncertainty in the mean value. Both the random and non-random contributions to the uncertainty are considered by the general form:

$$u_{\mathrm{c}}(\gamma)=\sqrt{u_{\mathrm{r}}^{2}(\gamma)+u_{\mathrm{s}}^{2}(\gamma)} \tag{C.1}$$

where

$u_{\mathrm{c}}(\gamma)$ is the relative combined uncertainty in the TGM concentration in ambient air;

$u_{\mathrm{r}}(\gamma)$ is the relative random contribution to the uncertainty;

$u_{\mathrm{s}}(\gamma)$ is the relative non-random contribution to the uncertainty.

Each field trial consists of M parallel samplers operating over N days. The data produced by each sampler was averaged to produce a daily mass concentration value $\gamma_{\mathrm{d,i}}$ on day d from instrument i. Therefore we can define the terms:

$$\bar{\gamma}=\frac{1}{N}\sum_{d=1}^{N}\bar{\gamma}_{d} \tag{C.2}$$

$$\bar{\gamma}_d = \frac{1}{M}\sum_{i=1}^{M}\gamma_{d,i} \tag{C.3}$$

$$\delta_{d,i} = \gamma_{d,i} - \bar{\gamma}_d \tag{C.4}$$

$$\bar{\delta}_i = \frac{1}{N}\sum_{d=1}^{N}\delta_{d,i} \tag{C.5}$$

$$\sigma_i = \sqrt{\frac{\sum_{d=1}^{N}(\delta_{d,i} - \bar{\delta}_i)^2}{N-1}} \tag{C.6}$$

where

$\bar{\gamma}$ is the mean mass concentration over all N days and across all M instruments;

$\bar{\gamma}_d$ is the mean mass concentration on day d across all M instruments;

$\gamma_{d,i}$ is the daily mass concentration value on day d from instrument i;

$\delta_{d,i}$ is the deviation of instrument i from the mean mass concentration on day d;

$\bar{\delta}_i$ is the mean deviation of instrument i from the mean mass concentration over all N days;

σ_i is the standard deviation of the deviation of instrument i over all N days.

It follows that the random contribution to the relative combined uncertainty from instrument i, $u_{r,i}^2(\gamma)$, is given by:

$$u_{r,i}(\gamma) = \frac{\sigma_i}{\gamma\sqrt{N}} \tag{C.7}$$

and that the non-random contribution to the relative combined uncertainty from instrument i, is given by:

$$u_{s,i}(\gamma) = \sqrt{\left(\frac{\bar{\delta}_i}{\gamma}\right)^2 + u_{i,\text{vol}}^2} \tag{C.8}$$

where

$u_{i,\text{vol}}$ is the uncertainty in the sampled volume for instrument i.

The relative combined uncertainty from instrument i, is given by:

$$u_{c,i}(\gamma) = \sqrt{u_{r,i}^2(\gamma) + u_{s,i}^2(\gamma)} \tag{C.9}$$

and $u_c(\gamma)$, the relative combined uncertainty, is then given by:

$$u_{\mathrm{c}}(\gamma)=\frac{1}{\mathrm{M}}\sum_{i=1}^{\mathrm{M}}u_{\mathrm{c},i}(\gamma) \tag{C.10}$$

The relative combined uncertainties at each field trial site, were plotted against average mass concentration γ at each site to provide a means of estimating uncertainty at a range of concentrations by extrapolation.

The relative expanded uncertainty U is then calculated by using a coverage factor k, corresponding to a level of confidence of approximately 95 %, thus:

$$U=k\times u_{\mathrm{c}}(\gamma) \tag{C.11}$$

For the field validation tests $\mathrm{k}=2$ (based on > 30 degrees of freedom).

The relative expanded uncertainties at each field trial site, were plotted against average mass concentration γ at each site as a means of estimating uncertainty at a range of concentrations by extrapolation.

C.4 Results

Using the rationale described in C.3, the random and non-random components of the uncertainty contributions from the field trials were calculated. For the TGM measurements each instrument was assumed to be independent – even if two or more were present on the field trial that were manufactured by the same company. These results are presented in Table C.1.

Table C.1 — The average random and non-random deviations observed at each field trial location

Sampling location	Average deviation	
	Random	Non-random
Site 1	2,3 %	26,9 %
Site 2	2,3 %	13,1 %
Site 3	1,6 %	7,5 %
Site 4	3,4 %	8,3 %

For completeness the average deviation between and within the different instrument types are also displayed in Tables C.2. and C.3

Table C.2 — The average random and non-random deviations between the various instrument types tested at each field trial location

Manufacturer	Average deviation <u>between</u> instrument types	
	Random	Non-random
Manufacturer 1	2,2 %	10,0 %
Manufacturer 2	1,6 %	13,9 %
Manufacturer 3	2,3 %	18,4 %
Manufacturer 4	2,2 %	10,1 %

Table C.2 shows how well instruments made by different manufacturers compare with each other.

Table C.3 — The average random and non-random deviations within the various instrument types tested at each field trial location

Manufacturer	**Average deviation within instrument types**	
	Random	**Non-random**
Manufacturer 1	2,3 %	6,7 %
Manufacturer 2	1,2 %	8,7 %
Manufacturer 3	2,2 %	6,1 %
Manufacturer 4	1,2 %	4,4 %

Table C.3 shows how well instruments made by the same manufacturer compare with each other.

For the four field trials, the procedure described in C.3, yielded expanded uncertainties at the 95 % confidence interval (assuming a coverage factor of *k*=2) of:

- Site 1: 54,3 % at an average TGM concentration of 1,9 ng/m^3;
- Site 2: 27,3 % at an average TGM concentration of 3,6 ng/m^3;
- Site 3: 16,6 % at an average TGM concentration of 1,5 ng/m^3;
- Site 4: 18,8 % at an average TGM concentration of 32 ng/m^3.

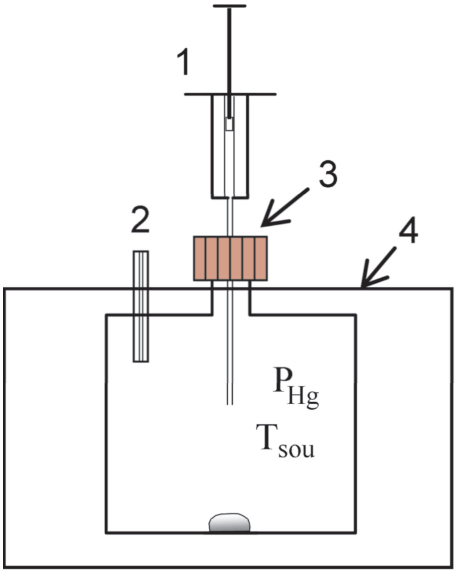
In order to meet the data quality objectives of the Fourth Daughter Directive a maximum expanded uncertainty of 50 % for the measurement method is permitted. In order to determine the lowest concentration at which this required uncertainty is met, the relationship between the individual uncertainties and the measured concentration from each daily monitoring period over the four field trials was extrapolated to estimate how the expanded measurement uncertainty is expected to vary with TGM concentration.

This process predicted that the expanded measurement uncertainty will reach 50 % at a concentration of approximately 1 ng/m^3. Therefore, this concentration level has been proposed as the lower range of the standard method. This value represents the best estimate of the lower range of the method given the data available, but should only be treated as an estimate because of the relatively poor fit of the data extrapolations.

Annex D
(informative)

Characteristics of the mercury vapour source

The mercury concentration in the source is determined by the mercury vapour pressure (P_{Hg}) over the liquid mercury phase. Since P_{Hg} is strongly dependent on temperature, it is necessary to know exactly the temperature in the calibration vessel. The temperature of the liquid mercury shall be measured by a resolution which is not more than 0,1 °C. A thermometer that is certified traceable to a national or international standard shall be used. Another requirement concerns the total pressure inside the container. If the surrounding pressure, due to change in the weather, suddenly becomes lower than in the source, some of the mercury may get lost when handling samples collected by a syringe. The pressure in the source shall be maintained equal to the ambient by help of a narrow capillary tube. The principles of using the saturated mercury source for calibration are described below.



Key

1	gas tight syringe
2	narrow capillary
3	septum
4	thermostatted container
P_{Hg}	mercury vapour pressure
T_{sou}	temperature of the source

Figure D.1 — A mercury source housed in a thermostatted water bath

Figure D.1 shows how a sample of gaseous mercury is collected from a saturated mercury vapour source. A syringe is inserted via a septum on top of a thermostatted flask containing liquid elemental mercury in equilibrium with its vapour. The syringe is conditioned by slowly moving the plunger up and down one or two times. A certain volume is then collected and used as a standard amount of mercury. The mercury concentration in the source $\gamma_{\mathrm{Hg,\,sou}}$ can be calculated by help of the Ideal Gas Law according to

Equation (D.1):

$$\gamma_{\mathrm{Hg,\,sou}} = \frac{P_{\mathrm{Hg}}}{\mathrm{R} \times T_{\mathrm{sou}}} A_{\mathrm{Hg}} \qquad \text{(D.1)}$$

where

$\gamma_{\mathrm{Hg,\,sou}}$ is the mercury concentration in the source, in nanograms per millilitre;

P_{Hg} is the vapour pressure of mercury, at T_{Sou}, in pascals;

R is the ideal gas constant (8,314 J/K·mol);

T_{sou} is the temperature of the source, in kelvins;

A_{Hg} is the atomic weight of mercury (0,200 59 kg/mol).

It should be noted that the mercury concentration in the syringe is only strictly equal to $\gamma_{\mathrm{Hg,\,sou}}$ when $T_{\mathrm{syr}} = T_{\mathrm{sou}}$. Hence, if the temperature of the syringe happens to be lower than T_{sou}, some of the gaseous mercury may condense on the surfaces inside the syringe. On the other hand, if the mercury source temperature is lower than the ambient the concentration in the syringe will be lower than in the source. Below is an accurate and precise correction for the temperature difference made.

When the plunger is pulled upwards air saturated with mercury vapour is flushed into the syringe because moving the plunger creates a pressure difference between the syringe and the source. Very soon after the plunger is left at rest the pressure difference becomes zero. Hence, the total pressure in the syringe is equal to the pressure in the source. This is also true regarding the partial pressure of mercury (P_{Hg}) in the two compartments. On the other hand, the temperature of the syringe gas may be different to that of the source. The gas temperature in the syringe is forced to attain the same temperature as the syringe. This is a quick process due to the great difference in heat capacity between the small gas volume in the syringe and the syringe material. A temperature difference between the source and the syringe means that the mercury concentration in the two compartments is not equal. Specifically, if the temperature of the syringe is higher than the source temperature, the concentration of mercury in the syringe will be lower than that of the source. Using the conclusion that P_{Hg} is equal in both compartments, Equation (D.2) can be derived.

$$\gamma_{\mathrm{Hg,\,syr}} = \frac{P_{\mathrm{Hg}}}{\mathrm{R} \times T_{\mathrm{syr}}} A_{\mathrm{Hg}} \qquad (T_{\mathrm{syr}} \geq T_{\mathrm{sou}}) \tag{D.2}$$

where

$\gamma_{\mathrm{Hg,\,syr}}$ is the mercury concentration in the syringe, in milligrams per millilitre;

T_{syr} is the temperature of the syringe, in kelvins.

Note that P_{Hg} in Equation (D.2) corresponds to the saturation mercury vapour pressure at the temperature of the source. Secondly, Equation (D.2) is only valid for situations where T_{syr} is equal to or higher than the temperature of the mercury source. Inspection of Equation (3) shows that it becomes equal to Equation (D.1) if $T_{\mathrm{syr}} = T_{\mathrm{sou}}$ but $\gamma_{\mathrm{Hg,\,syr}}$ will be significantly lower if the temperature difference is large. At a temperature difference (ΔT) of 1 K the difference is less than 0,5 %, but increases with ΔT, making $\gamma_{\mathrm{Hg,\,syr}}$ about 7 % lower than $\gamma_{\mathrm{Hg,\,sou}}$ if ΔT is 20 K. The advantage with using Equation (D.2) is that it allows keeping the source temperature much lower than room temperature, which is useful when relatively small gaseous mercury standards are required.

If substituting P_{Hg} in Equation (D.2) with Equation D.3 [2]:

$$P_{\mathrm{Hg}} = 133{,}32 \times 10^{-(A + \frac{B}{T_{\mathrm{sou}}})} \tag{D.3}$$

Equation (D.2) becomes

$$\gamma_{\mathrm{Hg}} = \delta \frac{\mathrm{D}}{T_{\mathrm{syr}}} \times 10^{-(\mathrm{A} + \frac{\mathrm{B}}{T_{\mathrm{sou}}})} \qquad (T_{\mathrm{syr}} \geq T_{\mathrm{sou}}) \tag{D.4}$$

where

γ_{Hg} is the theoretical mass concentration in ng/ml of mercury vapour samples that can be collected from the mercury calibration source using a syringe;

A, B, and D are constants with numerical values - 8,134 46, 3 240,87 and 3 216 522, respectively;

δ is the estimated statistical uncertainty associated with the mercury vapour equation used.

Annex E
(informative)

Calibration

E.1 Multiple-point calibration

The recommended calibration methodology is a three-point calibration plus an additional point at zero mercury (four points in total). Ideally these points should be spread out evenly throughout the calibration range. The calibration range should encompass the expected range of daily average values to be measured. Ideally, the uncertainty of the calibration relationship should be at a minimum at the expected average value during the monitoring period. It is recognised that performing multiple point calibration may not always be possible, because of the very low levels recorded at certain sites, and the difficulty of injecting the very small quantities of mercury required to calibrate the instruments. In such cases, making multiple injections at a single calibration point is an acceptable alternative calibration procedure.

Calibration, for measurement and to established instrument linearity, shall be repeated until the correlation coefficient, $r^2 \geq 0{,}995$. A single point calibration will achieve $r^2 = 1$ by definition, however this calibration methodology shall only be used once it has been shown that a multiple point calibration with the same instrument yields $r^2 \geq 0{,}995$.

Calibration robustness checks shall be repeated every two weeks to ensure that the instrument sensitivity does not drift by an amount greater than the repeatability of analysis.

Following maintenance or any changes to the instrumentation, a multiple point calibration shall be performed.

E.2 Multiple injections at a single calibration point

If the instrumentation has been shown via recent previous experimentation to provide extremely linear responses to mercury concentration then a single point calibration involving multiple injections plus an additional point at zero mercury, also involving multiple injections, is allowable. If the instrument is extremely linear it should not matter the concentration at which that calibration is performed, providing it is within the linear range. However, to give the lowest uncertainty if the expected average mass of mercury measured is x ng then the preferred calibration value would be a mass of x ng.

Annex F
(informative)

Assessment against target uncertainty by an individual laboratory

An individual laboratory is able to produce an assessment of the uncertainty of any individual measurement by performing a full ISO GUM [5] treatment on the measurement equations given in 13.2.

Equation (F.1) has been established for the amalgamation/cold-vapour atomic absorption spectrometry method, by substituting Equations (5), (9), (10), (11) and (D.4) into Equation (12) so that this equation includes the majorities of sources contributing to uncertainty of measurement. Equation (D.4) has been simplified by assuming that T_{syr} equal to T_{sou} (named T): the temperature of the syringe is equal to the temperature in the mercury source.

Equation (F.3) has been established for the direct optical measurement method by substituting Equations (13) and (14) into Equation (5).

The relative combined uncertainties are estimated using Equations (F.2) and (F.4) obtained by derivation of Equations (F.1) and (F.3) according to the GUM method [5].

$$\gamma_{\text{ref}} = \left(\frac{101\,300}{P_{\text{sam}}}\frac{T_{\text{sam}}}{293{,}15}\right)\left(\frac{R_{\text{sam}}}{\eta_{\text{e}}}\right)\left(\delta\frac{D}{T}\times 10^{-(A+\frac{B}{T})}\frac{V_{\text{Hg}}r_{\text{syr}}}{R_{\text{cal}}-R_0}\right)\left(\frac{\eta_{\text{sam}}}{q_{v,ave}\,t\,r_{\text{flow}}}\right) \tag{F.1}$$

$$\begin{aligned}\frac{u_c^2(\gamma)}{\gamma^2} &= \frac{u^2(P_{\text{sam}})}{P_{\text{sam}}^2}+\frac{u^2(T_{\text{sam}})}{T_{\text{sam}}^2}+\frac{u^2(R_{\text{sam}})}{R_{\text{sam}}^2}+\frac{u^2(\eta_{\text{e}})}{\eta_e^2}+\frac{u^2(\delta)}{\delta^2}+\frac{(B\ln(10)-T)^2}{T^2}\frac{(u(T))^2}{T^2}+\frac{u^2(V_{\text{Hg}})}{V_{\text{Hg}}^2}\\ &+\frac{u^2(r_{\text{syr}})}{r_{\text{syr}}^2}+\frac{u^2(R_{\text{cal}})+u^2(R_0)}{(R_{\text{cal}}-R_0)^2}+\frac{u^2(\eta_{\text{sam}})}{\eta_{\text{sam}}^2}+\frac{u^2(q_{v,ave})}{q_{v,ave}^2}+\frac{u^2(t)}{t^2}+\frac{u^2(r_{\text{flow}})}{r_{\text{flow}}^2}\end{aligned} \tag{F.2}$$

$$\gamma_{ref} = \left(\frac{101\,300}{P_{\text{sam}}}\frac{T_{\text{sam}}}{293{,}15}\right)\left(\frac{R_{\text{sam}}}{\eta_{\text{sam}}}\right)\left(\frac{\delta\times D\times 10^{-(A+\frac{B}{T})}}{T(R_{\text{cal}}-R_0)}\right) \tag{F.3}$$

$$\begin{aligned}\frac{u_c^2(\gamma)}{\gamma^2} &= \frac{u^2(P_{\text{sam}})}{P_{\text{sam}}^2}+\frac{u^2(T_{\text{sam}})}{T_{\text{sam}}^2}+\frac{u^2(R_{\text{sam}})}{R_{\text{sam}}^2}+\frac{u^2(\eta_{\text{sam}})}{\eta_{\text{sam}}^2}+\frac{u^2(\delta)}{\delta^2}+\frac{(B\ln(10)-T)^2}{T^2}\frac{(u(T))^2}{T^2}\\ &+\frac{u^2(R_{\text{cal}})+u^2(R_0)}{(R_{\text{cal}}-R_0)^2}\end{aligned} \tag{F.4}$$

An example of a full uncertainty budget of TGM measured using the amalgamation/cold-vapour atomic absorption spectrometry method is given in Table F.1. The actual values for this budget are taken from [6]. Each quantity is listed on the left-hand side of the table with its value, standard uncertainty and relative standard uncertainty to be used in Equation (F.2). The relative combined uncertainty of TGM ($u_{\text{c}}(\gamma_{\text{ref}})/\gamma_{\text{ref}}$) calculated using Equation (F.2) is given on the last line of the table in the right column.

The relative expanded uncertainty, U_r, of the measurement result is calculated using Equation (F.5).

$$U_r = k\times\frac{u_c(\gamma_{\text{ref}})}{\gamma_{\text{ref}}} \tag{F.5}$$

where

k is the coverage factor assumed to be equal to 2. In the example given in Table F.1, the relative expanded uncertainty for TGM is 15 %.

Table F.1 — Uncertainty budget for the measurement of mercury vapour mass concentration in ambient air

Symbol	**Quantity / units**	**Value**	**Standard uncertainty**	**Relative standard uncertainty** %
P_{sam}	Average actual pressure of the air sampled, in pascals	101 300	1443	1,4
T_{sam}	Average actual temperature of the air sampled, in kelvins	293,15	2,9	1,0
R_{sam}	Instrumental response following analysis of the sample	950	24	2,5
η_{e}	Desorption efficiency, in grams per gram	1,00	0,005 8	0,6
δ	Relative bias between Equation (D.4) and reality	1,00	0,043	4,3
T^{b}	Temperature in kelvins	293,0	0,10	0,8
V_{Hg}	Volume of mercury saturated gas from within the mercury vapour source, in millilitres	0,10	0,000 50	0,5
R_{syr}	Syringe calibration coefficient, in cubic metres per cubic metre	0,98	0,010	1,0
$R_{\text{cal}}{}^{a}$	Instrumental response produced after the injection of a volume of mercury saturated gas (arbitrary units)	10 000	25	2,5
$R_{0}{}^{a}$	Instrumental response generated upon the injection of a zero volume of mercury saturated gas (arbitrary units)	1,00	1,0	0,1
η_{sam}	Sampling efficiency, in grams per gram	1,00	0,005 8	0,6
$q_{\text{v,ave}}$	Average flow rate over the sampling period, in millilitres per minute	100	4,0	4,0
T	Sampling time, in minutes	30	0,10	0,3
r_{flow}	Flow calibration coefficient in cubic metres per cubic metre	1,00	0,017	1,7
$\gamma_{\text{re,f}}$	Mass concentration of TGM in reference air at 293,15,15 K and 101,325 kPa, usually expressed in nanograms per cubic metre	403,75	-	7,5

[a] The relative standard uncertainty of R_{cal} and R_0 are divided by ($R_{\text{cal}} - R_0$) instead of R_{cal} and R_0 according to Equation (F.2).

[b] The relative standard uncertainty of T is multiplied by (B (ln(10) –T)/T according to Equation (F.2).

Some guidance is given for estimating the standard uncertainties of the main contributing parameters:

— $u(P_{\text{sam}})$: The average pressure during monitoring is affected by the accuracy and calibration uncertainty of the barometer used to measure it. A reasonable estimate of the maximum error of the pressure during monitoring can be 2 500 Pa. If a rectangular distribution of the error is assumed, $u(P_{\text{sam}})$, the standard uncertainty in P_{sam} is 2 500/1,732 = 1 443 Pa.

— $u(T_{\text{sam}})$: The average temperature during monitoring is affected by the accuracy and calibration uncertainty of the thermometer used to measure it and by the inhomogeneity of the temperature between the thermometer and the spectrometer. A reasonable estimate of the maximum error of the temperature can be 5 K. If a rectangular distribution of the error is assumed, $u(T_{\mathrm{sam}})$, the standard uncertainty in T_{sam} is 5/1,732 = 2,9 K.

— $u(R_{\mathrm{sam}})$: The standard uncertainty of the instrumental response is estimated determining the standard deviation of repeat measurements and by adding in quadrature the deviation from linearity of the spectrometer. If the measurement is made a long time after calibration a contribution of the drift of the spectrometer over time should also be included.

— $u(\eta_{\mathrm{e}})$: The efficiency of desorption is affected by mercury that becomes irreversibly adsorbed within the tube and loses resulting from adsorption to the walls of the pipework, or any minor leaks, during the desorption process. It has been shown [6] that the total loss of mercury may be as high as 1 % of the total. If a rectangular distribution of the efficiency of desorption is assumed, $u(\eta_{\mathrm{e}})$, the standard uncertainty in η_{e} is 0,01/1,732 = 0,005 8.

— $u(\delta)$: The possible discrepancy between the empirical equation describing the mercury vapour concentration within the mercury source, and reality has been estimated in [6]. This results in a value of unity and maximum deviation from reality of 0,75. If a rectangular distribution of the deviation to reality is assumed, $u(\delta)$, the standard uncertainty in δ is 0,075/1,732 = 0,043.

— $u(T)$: Temperature in the mercury source is affected by the accuracy and calibration uncertainty of the thermometer used to measure it and by the inhomogeneity of the temperature within the mercury source vessel itself. A reasonable estimate of $u(T)$, the standard uncertainty in T can be 0,1 °C at the temperatures of interest.

— $u(V_{\mathrm{Hg}})$: The uncertainty in the volume of mercury saturated air injected during calibration, depends on the ability to acquire volumes of mercury-saturated vapour precisely to the gradations on the syringe during the calibration procedure. A conservative estimate of this relative standard uncertainty is 0,5 %.

— $u(r_{\mathrm{syr}})$: The uncertainty of the volume calibration coefficient for the syringe depends on the uncertainty in weighing the syringe and on the ability of the analyst to acquire volumes of water precisely to gradations on the syringe. A good estimate of this relative standard uncertainty is 1 %.

— $u(R_{\mathrm{cal}})$ and $u(R_0)$: These standard uncertainties are estimated by determining the standard deviation of repeat measurements of standard calibration injections of mercury and zero gas.

— $u(\eta_{\mathrm{sam}})$: The uncertainty in the fraction of the total mercury containing species that is actually sampled and retained depends on such things as losses within the sampling train (such as adsorption to the particulate filter or pipework walls) and any mercury that passes through the gold trap without being trapped. The maximum deviation of the sampling efficiency from the ideal figure of 100 % is estimated to be less than 1 % [6]. If a rectangular distribution of the sampling efficiency is assumed, $u(\eta_{\mathrm{sam}})$, the standard uncertainty in η_{sam} is 0,01/1,732 = 0,005 8.

— $u(q_{\mathrm{v,ave}})$: The uncertainty on the stability of the flow rate that may vary during a sampling period, depending on a number of factors including: drift in the performance of the pump, increased fouling of the pre-filter, or movement of sorbent material with the gold trap causing changes in flow restriction. An appropriate estimate of the relative standard uncertainty can be between 2 % and 5 % depending on the equipment being employed (3 % is used in the example).

— $u(r_{\mathrm{flow}})$: The relative standard uncertainty of the flow rate can approximately be 3 %.

Aside from the application of a full ISO GUM approach, an individual laboratory can ensure that the uncertainty meets the relative target expanded uncertainty of 50 % by using the data listed in Table F.2.

Table F.2 lists the major contributing factors to the uncertainty of the TGM measurement, notes on their estimation, and limits for the maximum allowable uncertainty of each component:

a) for the measurement to meet the target measurement uncertainty; and

b) for the operation of the instrument and method to be considered under control. It is still important that robust assessments are made of the individual uncertainty components in order to compare against these requirements. See [6] for details of how this can be done.

Table F.2 — Major contributing factors to the uncertainty of the TGM measurement

Quantity	Unit	Trap and desorb		Direct optical measurement		Notes
		Allowable relative standard uncertainty in order to achieve relative target uncertainty	**Allowable relative standard uncertainty for method to be acceptable**	**Allowable relative standard uncertainty in order to achieve relative target uncertainty**	**Allowable relative standard uncertainty for method to be acceptable**	
Temperature of mercury vapour source	K	0,25 %	0,50 %	-	-	Includes the calibration of the thermometer and the stability of the temperature within the mercury source.
Instrument response from analysis of a standard at top of the calibration range	unitless / arbitrary units	5 %	10 %	5 %	10 %	Estimated by repeatability studies at relevant concentrations.
Instrument response at zero concentration	unitless / arbitrary units	50 %	100 %	50 %	100 %	Estimated by repeatability studies at zero concentrations.
Volume of mercury saturated air injected during calibration	ml	2 %	5 %	-	-	Estimated by assessing the ability to repeatably acquire the same volume with the calibration syringe.
Syringe calibration coefficient	ml/ml	2 %	5 %	-	-	Estimated by weighing volume of water drawn up into syringe.
Instrument response from analysis of unknown sample	unitless / arbitrary units	10 %	20 %	10 %	20 %	Estimated by repeatability studies at relevant concentrations. Includes drift between calibration.

Table F.2 *(continued)*

Quantity	Unit	Trap and desorb		Direct optical measurement		Notes
		Allowable relative standard uncertainty in order to achieve relative target uncertainty	**Allowable relative standard uncertainty for method to be acceptable**	**Allowable relative standard uncertainty in order to achieve relative target uncertainty**	**Allowable relative standard uncertainty for method to be acceptable**	
Desorption efficiency	ng/ng	3 %	5 %	-	-	Estimated from recovery studies on dosed traps.
Average flow rate over the monitoring period	ml/min	5 %	10 %	-	-	Drift in flow during monitoring period.
Sampling time	min	1 %	2 %	-	-	Should be negligible for all but the shortest time periods.
Flow calibration coefficient	unitless	5 %	10 %	-	-	Estimated from the calibration of sampling pump system.
Sampling efficiency	ng/ng	2 %	5 %	2 %	5 %	Estimated from studies to assess the loses to tubing and other components when doing traps.
Average pressure during monitoring period	Pa	2 % (if required)	4 % (if required)	2 %	4 %	Estimated from the meteorological data gathered during the monitoring period.
Average termperature during monitoring period	K	2 % (if required)	4 % (if required)	2 %	4 %	Estimated from the meteorological data gathered during the monitoring period.
See 10.1.3, Note 4, regarding uncertainty in the vapour pressure equation.						

Annex G
(informative)

Relationship between this European Standard and the Essential Requirements of EU Directives

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association and supports Essential Requirements of the Council Directive on Ambient Air Quality Assessment and Management [9] and the Council Directive 2004/107/EC [1].

WARNING — Other requirements and other EU Directives may be applicable to the product(s) falling within the scope of this standard.

Bibliography

[1] Council Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air; Official Journal L 23, 26/1/2005 P. 0003 – 0016

[2] Knudsen, M., 1909. Ann. D. Phys. 28, p. 179-193

[3] Ebdon L.; Corns W. T.; Stockwell P. B.; Stockwell P. M.; *Application of a computer-controlled adsorber/desorber system to monitor mercury in air or gas samples: Part 1. Calibration and system description;* Journal of Automatic Chemistry (1989), Vol. 11, No 6, p. 247-253

[4] Huber, M.L.; Laesecke, A.; Friend, D.G: *Correlation for the Vapor Pressure of Mercury*. Ind. Eng. Chem. Res. 45 (2006), p. 7351-7361

[5] ISO Guide to the Expression of Uncertainty in Measurement (GUM)

[6] Brown, R.J.C.; Brown, A.S.; Yardley, R.E.; Corns, W.T.; Stockwell, P.B.; *A practical uncertainty budget for ambient mercury vapour measurement*, Atmospheric Environment (2008), Volume 42, Issue 10, p. 2504-2517

[7] Berg, T.; Dye, C.; Hanssen J.E.; Krognes, T.; Munthe, J.; Reissell, A.; Schaug, J.; Schmidbauer, N.; Semb, A.; Tørseth, K.; Uggerud, H.T.; Aas, A..; Aasarød, K.; Lisbeth Berntsen, L.: *EMEP manual for sampling and chemical analysis (2002)*, /http://www.nilu.no/projects/ccc/manual/index.htmlS

[8] Brown, R.J.C.; Brown, A.S.; *Accurate calibration of mercury vapour measurements*, Analyst (2008), 133, p. 1611-1618

[9] Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management

[10] EN 14884, *Air quality — Stationary source emissions — Determination of total mercury: automated measuring systems*

[11] EN ISO 14956, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956:2002)*

[12] ISO/IEC Guide 99:2007, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

BSI - British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover. Tel: +44 (0)20 8996 9000. Fax: +44 (0)20 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001. Fax: +44 (0)20 8996 7001 Email: orders@bsigroup.com You may also buy directly using a debit/credit card from the BSI Shop on the Website http://www.bsigroup.com/shop

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact Information Centre. Tel: +44 (0)20 8996 7111 Fax: +44 (0)20 8996 7048 Email: info@bsigroup.com

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration. Tel: +44 (0)20 8996 7002 Fax: +44 (0)20 8996 7001 Email: membership@bsigroup.com

Information regarding online access to British Standards via British Standards Online can be found at http://www.bsigroup.com/BSOL

Further information about BSI is available on the BSI website at http://www.bsigroup.com.

Copyright

BSI Group
Headquarters 389
Chiswick High Road,
London, W4 4AL, UK
Tel +44 (0)20 8996 9001
Fax +44 (0)20 8996 7001
www.bsigroup.com/
standards