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Workplace air — Determination of mercury and inorganic mercury compounds — Method by cold-vapour atomic absorption spectrometry or atomic fluorescence spectrometry

Air des lieux de travail — Détermination du mercure et des composés minéraux de mercure — Méthode par spectrométrie d'absorption atomique ou spectrométrie de fluorescence atomique de la vapeur froide

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

ISO 17733 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Introduction

The health of workers in many industries is at risk through exposure by inhalation of mercury and inorganic mercury compounds. Industrial hygienists and other public health professionals need to determine the effectiveness of measures taken to control workers' exposure, and this is generally achieved by making workplace air measurements. This International Standard presents a method for making valid exposure measurements for mercury and inorganic mercury compounds in use in industry. It will be of benefit to: agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; industrial users of mercury and inorganic mercury compounds and their workers, etc.

The procedure described in this International Standard is based upon a method published by the United Kingdom Health and Safety Executive[1], which was developed after a thorough review of sampling and analysis techniques available for determination of mercury and inorganic mercury compounds in air[2]. This procedure has been fully validated and the resulting back-up data are freely available[3],[4]. Similar methods have been published by the United States Occupational Safety and Health Administration (OSHA)[5],[6] and the United States National Institute of Occupational Safety and Health (NIOSH)[7].

It has been assumed in the drafting of this International Standard that the execution of its provisions and the interpretation of the results obtained are entrusted to appropriately qualified and experienced people.

Workplace air — Determination of mercury and inorganic mercury compounds — Method by cold-vapour atomic absorption spectrometry or atomic fluorescence spectrometry

1 Scope

This International Standard specifies a procedure for determination of the time-weighted average mass concentration of mercury vapour and inorganic mercury compounds in workplace air. Mercury vapour is collected on a solid sorbent using either a diffusive badge or a pumped sorbent tube. Particulate inorganic mercury compounds, if present, are collected on a quartz fibre filter. Samples are analysed using either cold vapour atomic absorption spectrometry (CVAAS) or cold vapour atomic fluorescence spectrometry (CVAFS) after acid dissolution of the mercury collected.

This International Standard is applicable to the assessment of personal exposure to mercury vapour and/or particulate inorganic mercury compounds in air for comparison with long-term or short-term exposure limits for mercury and inorganic mercury compounds and for static (area) sampling.

The lower limit of the working range of the procedure is the quantification limit. This is determined by the sampling and analysis methods selected by the user, but it is typically in the range 0,01 µg to 0,04 µg of mercury (see 13.1). The upper limit of the working range of the procedure is determined by the capacity of the diffusive badge, sorbent tube or filter used for sample collection, but it is at least 30 µg of mercury (see 13.2). The concentration range of mercury in air for which this International Standard is applicable is determined in part by the sampling method selected by the user, but it is also dependent on the air sample volume.

The diffusive badge method is not applicable to measurements of mercury vapour when chlorine is present in the atmosphere, e.g. in chloralkali works, but chlorine does not interfere with the pumped sorbent tube method (see 13.11.1). Gaseous organo-mercury compounds could cause a positive interference in the measurement of mercury vapour (see 13.11.2). Similarly, particulate organo-mercury compounds and gaseous organo-mercury compounds adsorbed onto airborne particles could cause a positive interference in the measurement of particulate inorganic mercury compounds (see 13.11.3).

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.

ISO 648, *Laboratory glassware — One-mark pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3585, *Borosilicate glass 3.3 — Properties*

ISO 3696:1987, *Water for laboratory use — Specifications and test methods*

ISO 7708:1995, *Air quality — Particle size fraction definitions for health-related sampling*

ISO 8655-1, *Piston-operated volumetric apparatus — Part 1: Terminology, general requirements and user recommendations*

ISO 8655-2, *Piston-operated volumetric apparatus — Part 2: Piston pipettes*

ISO 8655-5, *Piston-operated volumetric apparatus — Part 5: Dispensers*

ISO 8655-6, *Piston-operated volumetric apparatus — Part 6: Gravimetric methods for the determination of measurement error*

EN 13205:2002, *Workplace atmospheres — Assessment of performance of instruments for measurement of airborne particle concentrations*

3 Terms and definitions

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

3.1 General definitions

3.1.1
chemical agent
any chemical element or compound, on its own or admixed as it occurs in the natural state or as produced by any work activity, whether or not produced intentionally and whether or not placed on the market

NOTE This definition is taken from the “Council Directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work”.

[EN 1540[8]]

3.1.2
breathing zone
⟨general⟩ space around the worker's face from where he or she takes his or her breath

3.1.3
breathing zone
⟨technical⟩ hemisphere (generally accepted to be 0,3 m in radius) extending in front of the human face, centred on the midpoint of a line joining the ears, whose base is a plane through this line, the top of the head and the larynx

NOTE 1 This definition is not applicable when respiratory protective equipment is used.

NOTE 2 Adapted from EN 1540[8].

3.1.4
exposure
⟨by inhalation⟩ situation in which a chemical agent is present in air which is inhaled by a person

3.1.5
measuring procedure
procedure for sampling and analysing one or more chemical agents in the air, including storage and transportation of the sample

3.1.6
operating time
⟨of a sampling pump⟩ period during which a sampling pump can be operated at specified flow rate and back-pressure without recharging or replacing the battery

[EN 1232[9]]

3.1.7
time-weighted average concentration
TWA concentration
concentration of a chemical agent in the atmosphere, averaged over the reference period

NOTE A more detailed discussion of TWA concentrations has been published by the American Conference of Government Industrial Hygienists (ACGIH)[10].

3.1.8
limit value
reference figure for concentration of a chemical agent in air

NOTE An example is the Threshold Limit Value® (TLV) for a given substance in workplace air, as established by the ACGIH[10].

3.1.9
reference period
specified period of time stated for the limit value of a specific chemical agent

NOTE Examples of limit values for different reference periods are short-term and long-term exposure limits, such as those established by the ACGIH[10].

3.1.10
workplace
defined area or areas in which work activities are carried out

[EN 1540[8]]

3.2 Particle size fraction definitions

3.2.1
inhalable convention
target specification for sampling instruments when the inhalable fraction is of interest

[ISO 7708]

3.2.2
inhalable fraction
mass fraction of total airborne particles which is inhaled through the nose and mouth

NOTE The inhalable fraction depends on the speed and direction of air movement, on breathing rate and other factors.

[ISO 7708]

3.2.3
total airborne particles
all particles surrounded by air in a given volume of air

NOTE Because all measuring instruments are size-selective to some extent, it is often impossible to measure the concentration of total airborne particles.

[ISO 7708]

3.3 Sampling definitions

3.3.1
diffusive badge
dosimeter
badge-type diffusive sampler
passive badge
diffusive sampler in which the gas or vapour passes to the sorbent by permeation through a thin solid membrane or diffusion across a porous membrane

NOTE The cross-sectional area of a diffusive badge is large in relation to the internal air gap.

3.3.2
diffusive sampler
passive sampler
device which is capable of taking samples of gases or vapours from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of air through the sampler

[EN 838[11]]

3.3.3
personal sampler
device attached to a person that samples air in the breathing zone

[EN 1540[8]]

3.3.4
personal sampling
process of sampling carried out using a personal sampler

[EN 1540[8]]

3.3.5
sampler
device for collecting airborne particles

NOTE Instruments used to collect airborne particles are frequently referred to by a number of other terms, e.g. sampling heads, filter holders, filter cassettes, etc.

3.3.6
pumped sorbent tube
tube, usually made of metal or glass, containing an active sorbent or reagent-impregnated support, through which sampled atmosphere is passed at a rate controlled by an air sampling pump

[EN 1076[12]]

3.3.7
static sampler
area sampler
device, not attached to a person, that samples air in a particular location

3.3.8
static sampling
area sampling
process of air sampling carried out using a static sampler

3.4 Analytical definitions

3.4.1
blank solution
solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure used for sample preparation

3.4.2
calibration blank solution
calibration solution prepared without the addition of any working standard solution

NOTE The concentration of mercury in the calibration blank solution is taken to be zero.

3.4.3
calibration solution
solution prepared by dilution of the working standard solution, containing mercury at a concentration that is suitable for use in calibration of the analytical instrument

NOTE The technique of matrix-matching is normally used when preparing calibration solutions.

3.4.4
field blank
sorbent capsule, filter or sorbent tube that is taken through the same handling procedure as a sample, except that it is not used for sampling

NOTE For the purposes of this International Standard, the field blank is loaded into a diffusive badge, sampler or sorbent tube holder, transported to the sampling site and then returned to the laboratory for analysis.

3.4.5
laboratory blank
unused sorbent capsule, filter or sorbent tube, taken from the same batch used for sampling, that does not leave the laboratory

3.4.6
linear dynamic range
range of concentrations over which the calibration curve for mercury is linear

NOTE The linear dynamic range extends from the detection limit to the onset of calibration curvature.

3.4.7
matrix interference
matrix effect
non-spectral interference
interference of a non-spectral nature caused by a difference between the matrices of the calibration and test solutions

3.4.8
matrix-matching
technique used to minimize the effect of matrix interferences on analytical results, involving the preparation of calibration solutions in which the concentrations of acids and other major solutes are matched with those in the test solutions

3.4.9
reagent blank
combination of all reagents used in sample dissolution, in the same quantities used for preparation of laboratory blank, field blank and sample solutions

3.4.10
sample dissolution
process of obtaining a solution containing mercury from a sample, which might or might not involve complete dissolution of the sample

3.4.11
sample preparation
all operations carried out on a sample, after transportation and storage, to prepare it for analysis, including transformation of the sample into a measurable state, where necessary

3.4.12
sample solution
solution prepared from a sample by the process of sample dissolution

NOTE A sample solution might need to be subjected to further operations, e.g. dilution, in order to produce a test solution that is ready for analysis.

3.4.13
stock standard solution
solution, used for preparation of the calibration solutions, containing mercury at a certified concentration that is traceable to national standards

3.4.14
test solution
blank solution or sample solution that has been subjected to all operations, including dilution, required to bring it into a state in which it is ready for analysis

NOTE The blank test solution is the blank solution and the sample test solution is the sample solution, if these solutions are not subjected to any further operations before analysis.

3.4.15
working standard solution
solution, prepared by dilution of the stock standard solution, that contains mercury at a concentration that is better suited to preparation of calibration solutions than the concentration of mercury in the stock standard solution

3.5 Statistical terms

3.5.1
analytical recovery
ratio of the mass of analyte measured when a sample is analysed to the known mass of analyte in that sample

NOTE It is expressed as a percentage.

3.5.2
bias
consistent deviation of the measured value from the value of the air quality characteristic itself, or the accepted reference value

[ISO 6879[13]]

3.5.3
overall uncertainty
⟨of a measuring procedure or of an instrument⟩ quantity used to characterize as a whole the uncertainty of a result given by an apparatus or measuring procedure

NOTE It is expressed, as a percentage, by a combination of bias and precision, usually according to the formula:

$$\frac{\left|\bar{x} - x_{\text{ref}}\right| + 2s}{x_{\text{ref}}} \times 100$$

where

$\bar{x}$ is the mean value of results of a number (n) of repeated measurements;

x_{ref} is the true or accepted reference value of the measurement;

s is the standard deviation of the measurements.

[EN 482[14]]

3.5.4
precision
closeness of agreement between independent test results obtained under stipulated conditions

[ISO 6879[13]]

3.5.5
true value
value which characterizes a quantity perfectly defined in the conditions which exist when that quantity is considered

NOTE The true value of a quantity is a theoretical concept and, in general, cannot be known exactly.

[ISO 3534-1[15]]

3.5.6
uncertainty
〈of measurement〉 parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand

[VIM[16]]

NOTE 1 The parameter might be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components can be evaluated from the statistical distribution of the results of series of measurements and can be characterized by standard deviations. The other components, which also can be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information. The GUM[17] refers to these different cases as Type A and Type B evaluations of uncertainty, respectively.

4 Principle

Mercury vapour is collected either actively or passively. Active sampling involves drawing a known volume of air through a sorbent tube using a pump, whilst passive sampling relies upon the principle of controlled diffusion into a badge. In both the pumped and diffusive sampling methods, mercury vapour entering the sampling device is collected on a proprietary solid sorbent that is widely known as Hydrar (see 8.1.2) but is currently marketed as Anasorb C 300.

Different sampling methods are used depending on the specific application.

a) If it is known that no particulate inorganic mercury compounds are present in the test atmosphere, mercury vapour is collected using a diffusive badge or by drawing a known volume of air through a sorbent tube using a pump.

b) If it is known that no mercury vapour is present in the test atmosphere, particulate inorganic mercury compounds are collected by drawing a known volume of air through a quartz fibre filter mounted in a sampler designed to collect the inhalable fraction of airborne particles, as defined in ISO 7708, using a pump.

c) A pumped sorbent tube is also used for sampling air that contains both mercury vapour and particulate inorganic mercury compounds. The sorbent tube, which collects mercury vapour, is preceded by a quartz fibre filter to collect particulate inorganic mercury compounds, unless these do not make up a significant proportion (e.g. > 10 %) of the total inorganic mercury (mercury vapour and particulate inorganic mercury compounds) present in the test atmosphere (see 10.1.3).

After sampling, the sorbent and/or filter are treated with 2 ml of concentrated nitric acid and 2 ml of concentrated hydrochloric acid and heated in a thermostatically-controlled water bath at 50 °C for 1 h to dissolve the collected mercury. Sample solutions are mixed with tin(II) chloride solution in a continuous flow, flow injection, or discrete injection cold-vapour generation system. Mercury vapour is formed by reduction of divalent mercury ions and this is flushed by a stream of inert gas into the measurement cell of an atomic absorption spectrometer or an atomic fluorescence spectrometer equipped with a mercury hollow cathode lamp or electrodeless discharge lamp. Absorbance or fluorescence measurements are made at 253,7 nm and analytical results are obtained by the analytical curve technique (see 6.1 of ISO 6955:1982[18]).

The results may be used for the assessment of workplace exposure to mercury vapour, inorganic mercury compounds or total inorganic mercury (see EN 689[19]).

5 Interferences

The diffusive badge method is unsuitable for making measurements of mercury vapour when chlorine is present in the atmosphere, e.g. in chloralkali works. However, chlorine does not interfere with the pumped sorbent tube method (see 13.12.1). Gaseous organomercury compounds could cause a positive interference in the measurement of mercury vapour (see 13.12.2). Particulate organomercury compounds contained within airborne particles and gaseous organomercury compounds adsorbed onto airborne particles could cause a positive interference in the measurement of particulate inorganic mercury compounds (see 13.12.3). Spectral interferences are not significant when measuring mercury by CVAAS using the procedure described in this International Standard and they do not occur when measuring mercury by CVAFS (see 13.12.4).

6 Requirement

The measurement procedure shall comply with any relevant international, european or national standard that specifies performance requirements for procedures for measuring chemical agents in workplace air (e.g. ISO 6879[13]).

7 Reagents

During the analysis, use only reagents of recognized analytical grade and only water as specified in 7.1.

7.1 Water, complying with the requirements for ISO 3696 grade 2 water (electrical conductivity less than 0,1 $mS \cdot m^{-1}$ and resistivity greater than 1 $M\Omega \cdot cm$ at 25 °C).

It is recommended that the water used be obtained from a water purification system that delivers ultrapure water having a resistivity greater than 18 $M\Omega \cdot cm$.

7.2 Nitric acid (HNO_3), concentrated, ρ ~1,42 $g \cdot ml^{-1}$, mass fraction ~70 %.

The concentration of mercury shall be less than 0,002 $mg \cdot l^{-1}$.

WARNING — Concentrated nitric acid is corrosive and oxidizing, and nitric acid fumes are irritant. Avoid contact with the skin or eyes, or inhalation of fumes. Use suitable personal protective equipment (including gloves, face shield or safety glasses, etc.) when working with nitric acid, and carry out sample dissolution with concentrated nitric acid in open vessels in a fume hood.

7.3 Nitric acid, diluted 1:9.

Add approximately 700 ml of water (7.1) to a 1 000 ml one-mark volumetric flask (8.3.1.4). Carefully add 100 ml of concentrated nitric acid (7.2) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

7.4 Hydrochloric acid (HCl)**,** concentrated, $\rho \sim 1{,}18\ g \cdot ml^{-1}$, mass fraction ~36 %.

The concentration of mercury shall be less than 0,002 $mg \cdot l^{-1}$.

WARNING —Concentrated hydrochloric acid is corrosive and hydrochloric acid vapour is irritant. Avoid contact with the skin or 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-up in stoppered flasks when preparing hydrochloric acid/water mixtures.

7.5 Nitric acid and hydrochloric acid, diluted 1:1:23.

Add approximately 700 ml of water (7.1) to a 1 000 ml one-mark volumetric flask (8.3.1.4). Carefully add 40 ml of concentrated nitric acid (7.2) and 40 ml of concentrated hydrochloric acid (7.4) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

NOTE This reagent is only required for analysis of sorbent tube samples.

7.6 Nitric acid and hydrochloric acid, diluted 2:2:21.

Add approximately 700 ml of water (7.1) to a 1 000 ml one-mark volumetric flask (8.3.1.4). Carefully add 80 ml of concentrated nitric acid (7.2) and 80 ml of concentrated hydrochloric acid (7.4) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

NOTE This reagent is only required for analysis of diffusive badge samples.

7.7 Tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$).

The concentration of mercury shall be less than 10 $\mu g \cdot kg^{-1}$.

Tin(II) chloride of a lower purity may be used if mercury contamination is removed from the tin(II) chloride solution before use by bubbling through nitrogen or clean air.

7.8 Tin(II) chloride solution, $\rho = 10\ g \cdot l^{-1}$.

Weigh 10 g of tin(II) chloride (7.7) into a 500 ml beaker (8.3.1.1), add 30 ml of hydrochloric acid (7.4), cover with a watchglass and leave for approximately 15 min until dissolved. Transfer to a 1 000 ml one-mark volumetric flask (8.3.1.4), dilute to the mark with water (7.1), stopper and mix thoroughly. Prepare this solution fresh on the day of use.

7.9 Stock mercury standard solution, $\rho = 1\ 000\ mg \cdot l^{-1}$.

Use a commercial standard solution with a certified mercury concentration traceable to national standards. Observe the manufacturer's expiration date or recommended shelf life.

WARNING — Mercury compounds are toxic by skin absorption. Take great care when working with solutions containing mercury to avoid skin contamination.

A stock mercury standard solution with a different concentration of mercury may be used, if desired. However, in such circumstances, the volumes of solution used to prepare working mercury standard solution A (7.10) and mercury standard solution B (7.11) shall be adjusted accordingly.

7.10 Working mercury standard solution A, $\rho = 10\ g \cdot l^{-1}$.

Accurately pipette 0,5 ml of stock mercury standard solution (7.9) into a 50 ml volumetric flask (8.3.1.4). Add 1 ml of concentrated nitric acid (7.2), dilute to the mark with water (7.1), stopper and mix thoroughly. Prepare this solution fresh weekly.

7.11 Working mercury standard solution B, $\rho = 1\ mg \cdot l^{-1}$.

Accurately pipette 5 ml of working mercury standard solution A (7.10) into a 50 ml volumetric flask (8.3.1.4). Add 1 ml of concentrated nitric acid (7.2), dilute to the mark with water (7.1), stopper and mix thoroughly. Prepare this solution fresh weekly.

7.12 Laboratory detergent solution.

Dilute a laboratory grade detergent, suitable for cleaning of samplers and labware, with water (7.1) according to the manufacturer's instructions.

7.13 Argon, suitable for use in cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry.

8 Apparatus

8.1 Sampling equipment for diffusive sampling

8.1.1 Diffusive badges, lightweight, reusable, designed to be used with sorbent capsules (8.1.2) for diffusive sampling of mercury vapour (see 10.3.1).

NOTE Diffusive badges suitable for sampling of mercury vapour are commercially available[22],[23]. The design of these badges is illustrated as an exploded diagram in Figure 1.

8.1.2 Sorbent capsules, suitable for sampling of mercury vapour when used in diffusive badges (8.1.1), containing 800 mg of Hydrar (Anasorb C 300), supplied in sealed plastic pouches that can be resealed after sampling to prevent contamination during transport and storage.

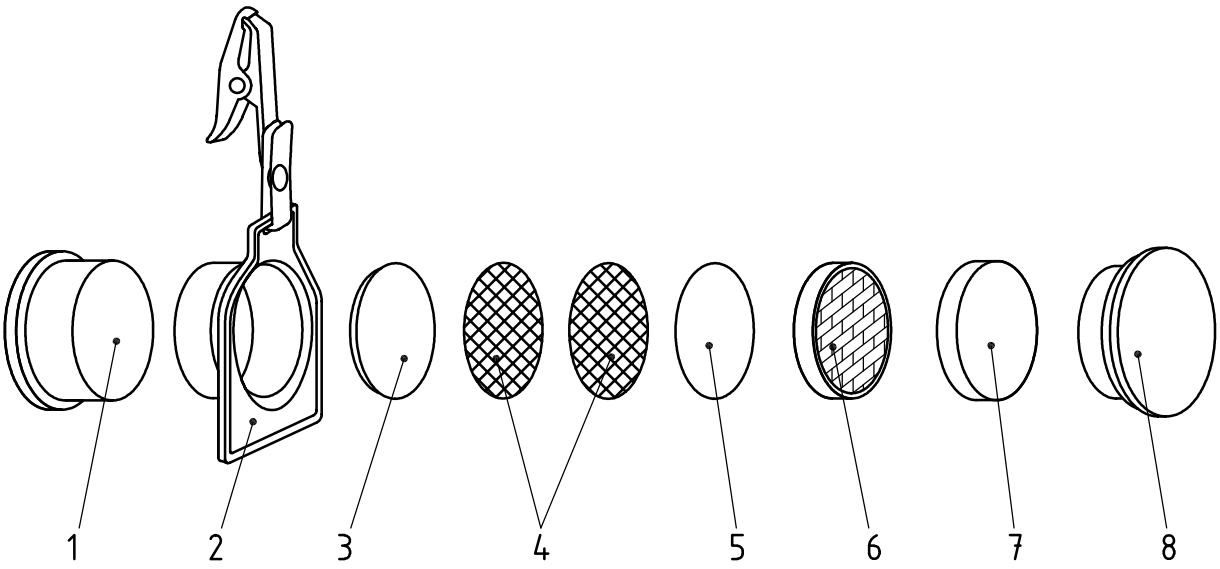
NOTE 1 Hydrar is a name previously given by SKC Inc. to the sorbent used in the diffusive badges and pumped sorbent tubes it manufactures for sampling mercury vapour. Hydrar is a granular preparation of hopcalite (a mixture of copper and manganese oxides) deposited on a ceramic substrate. It is manufactured by Carus under the trade name Carulite 300, primarily for use as an industrial catalyst. SKC uses Carulite 300 in its diffusive badges and pumped sorbent tubes, after grinding to a suitable mesh size, and it currently refers to this sorbent as Anasorb C 300[1)].

Hopcalite has been shown to have an irreversible affinity for mercury and to be a suitable sorbent for sampling mercury vapour in air[20],[21]. Hopcalite is completely dissolved by the mixture of nitric acid and hydrochloric acid used in the sample dissolution method (11.4.1), yielding a clear blue/green solution. However, an insoluble residue of ceramic substrate remains after treatment of Anasorb with acid, resulting in a milky suspension. This has to be removed before analysis by centrifugation or filtration.

NOTE 2 Mercury vapour enters the diffusive badges by positively controlled diffusion. It is then irreversibly absorbed by the Anasorb C 300 contained in the sorbent capsule. No sampling pump is required. Samplers can be cleaned and reused with new sorbent capsules.

NOTE 3 Similar diffusive badges and corresponding sorbent capsules packed with Anasorb C 300 or a similar sorbent may be used if it can be demonstrated that they give equivalent performance.

1) Anasorb C 300 is the trade name of a product supplied by SKC Inc. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.



Key

1 sealing cap
2 sampler housing
3 sampling face disc
4 mesh discs
5 “O” ring
6 sorbent capsule
7 foam disc
8 removable back cover

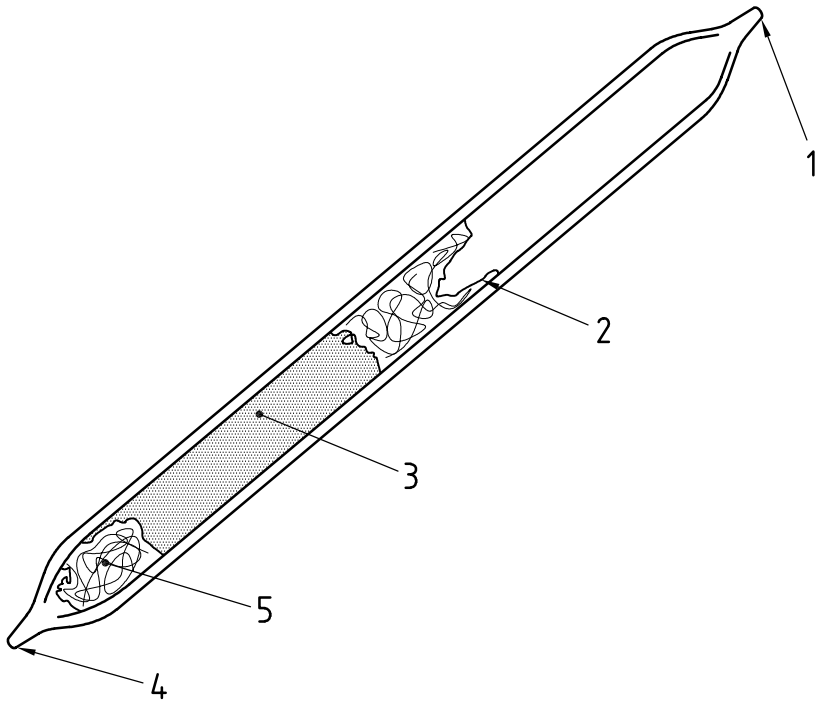
Figure 1 — Mercury diffusive badge

8.2 Sampling equipment for pumped sampling

8.2.1 Sorbent tubes, glass, containing a single section of 200 mg or 500 mg of Anasorb C 300, flame-sealed at each end, with plastic end caps, for pumped sampling of mercury vapour (see 10.4.1.1.1 and 10.4.1.1.3).

NOTE 1 Two types of sorbent tube packed with Anasorb C 300 are commercially available[24],[25]. The smaller, standard tube is 70 mm long, with an external diameter of 6 mm and an internal diameter of 4 mm, and contains 200 mg of Anasorb C 300 granules retained by small glass wool plugs. The larger tube is 110 mm long, with an external diameter of 8 mm and an internal diameter of 6 mm. It contains 500 mg of Anasorb C 300 and is intended for sampling at higher air flow rates, in order to measure low concentrations of mercury, or for shorter sampling periods ($<$ 1 h). The construction of these sorbent tubes is illustrated in Figure 2. Similar sorbent tubes packed with Anasorb C 300 or a similar sorbent may be used if it can be demonstrated that they give equivalent performance.

NOTE 2 Sorbent tubes containing Anasorb C 300 have a lower mercury content than sorbent tubes containing hopcalite. This lowers the method detection limit and reduces the minimum air sample volume that can be used. On the other hand, Anasorb C 300 has the disadvantage that it is more friable than hopcalite. This means that it is liable to be pulverized if handled roughly, and poor grades of Anasorb C 300 have a high proportion of “fines”. These can cause problems by clogging the glass wool plugs of the sorbent tubes, reducing the achievable air sampling rates.



Key

1 flame-sealed end through which the sampled air is drawn after tip is broken
2 metal wire spring-clip holding glass wool plug in place
3 Anasorb C 300 sorbent
4 flame-sealed end to which suction is applied after tip is broken
5 glass wool plug

Figure 2 — Mercury sorbent tube

8.2.2 Sorbent tube holders, suitable for use with the sorbent tubes (8.2.1), designed so that the internal surfaces have minimal contact with sampled air in order to reduce the risk of loss of mercury vapour by surface adsorption, and so that when assembled, the tube and holder do not allow any leakage of sampled air.

8.2.3 Sorbent tube and prefilter assemblies, consisting of a quartz-fibre filter (8.2.6) mounted in a plastic sampling cassette (8.2.4) or an inhalable sampler (8.2.5) connected to the inlet of the sorbent tube (8.2.1) with a minimum length of inert plastic tubing, e.g. polytetrafluoroethylene (PTFE) or modified polyvinyl chloride tubing, for sampling of mercury vapour in the presence of high concentrations of airborne particles (see 10.4.1.1.1) or sampling of mercury vapour and particulate inorganic mercury compounds (see 10.4.1.1.3).

NOTE Sorbent tube and prefilter assemblies are only necessary if the concentration of airborne particles could be sufficiently high that there is a risk of blockage of the glass wool plugs that retain the Anasorb C 300 sorbent in the tubes (see 10.4.1.1.1), or if it is believed that particulate inorganic mercury compounds could make up a significant proportion (e.g. $>$ 10 %) of the sum of mercury vapour and particulate inorganic mercury compounds present in the test atmosphere (see 10.4.1.1.3).

8.2.4 Sampling cassettes, plastic, disposable, for mounting quartz-fibre filters (8.2.6) to form part of sorbent tube and prefilter assemblies (8.2.3) for sampling of mercury vapour in the presence of high concentrations of airborne particles (see 10.4.1.1.1).

8.2.5 Samplers, designed to collect the inhalable fraction of airborne particles (as defined in ISO 7708), complying with EN 13205, for mounting quartz-fibre filters (8.2.6) for sampling of particulate inorganic mercury compounds in the absence of mercury vapour (see 10.4.1.1.2), or for mounting quartz-fibre filters (8.2.6) to form part of sorbent tube and prefilter assemblies (8.2.3) for sampling of mercury vapour and particulate inorganic mercury compounds (see 10.4.1.1.3).

If possible, the samplers should be manufactured from conducting material, since samplers comprised of non-conducting material have electrostatic properties that can influence representative sampling.

The operating instructions supplied by the sampler manufacturer should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample.

NOTE 1 In general, personal samplers for collection of the inhalable fraction of airborne particles do not exhibit the same size-selective characteristics if used for static (area) sampling.

NOTE 2 Some inhalable samplers are designed to collect the fraction of airborne particles on a filter, so that any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles that pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge that can be removed from the sampler to enable this material to be easily recovered.)

8.2.6 Filters, quartz fibre, of a diameter suitable for use in the sampling cassettes (8.2.4) or inhalable samplers (8.2.5), with a collection efficiency of not less than 99,5 % for particles with a 0,3 µm diffusion diameter (see 2.2 of ISO 7708:1995).

NOTE Quartz-fibre filters have been shown[4] to have low mercury blanks and not to absorb mercury vapour from the sampled air or mercury from sample solutions. They are therefore suitable for use as prefilters and for collecting samples of particulate inorganic mercury compounds. Mixed cellulose ester filters have been used successfully as prefilters, but it is necessary to use a different procedure[6] for their analysis if they are used for collecting samples of particulate inorganic mercury compounds. It has been reported[26] that there can be significant loss of mercury vapour if mixed cellulose ester filters are used as prefilters. However these results were not reproduced in subsequent work[27].

8.2.7 Sampling pumps, with an adjustable flow rate, capable of maintaining the selected flow rate (see 10.4.1.1) to within ± 5 % of the nominal value throughout the sampling period (see 10.4.1.2).

NOTE 1 A flow-stabilized pump may be required to maintain the flow rate within the specified limits.

For personal sampling, the pumps shall be capable of being worn by the worker without impeding normal work activity. Sampling pump flowmeters shall be calibrated using either a primary or secondary standard. If a secondary standard is used, it shall be calibrated using a primary standard.

The pump should have, as a minimum, the following features:

— an automatic control that keeps the volumetric flow rate constant in the case of a changing back pressure;

— either a malfunction indicator which, following completion of sampling, indicates that the air flow has been reduced or interrupted during sampling; or an automatic cut-out, which stops the pump if the flow rate is reduced or interrupted; and

— a facility for the adjustment of flow rate, such that it can only be actuated with the aid of a tool (e.g. a screwdriver) or requires special knowledge for operation (e.g. via software), so as to preclude inadvertent readjustment of the flow rate during use.

An integral timer is a highly desirable additional feature.

NOTE 2 EN 1232[9] requires that the performance of the pumps be such that

— the pulsation of the flow rate does not exceed 10 %,

— a flow rate set within the nominal range does not deviate by more than ± 5 % from the initial value under increasing back-pressure,

— within the range of ambient temperatures from 5 °C to 40 °C, the flow rate measured under operating conditions does not deviate by more than ± 5 % from the flow rate at 20 °C,

— the operating time is at least 2 h and preferably 8 h, and

— the flow rate does not deviate by more than ± 5 % from the initial value during the operating time.

If the sampling pump is used outside the range of conditions specified in EN 1232[9], appropriate action should be taken to ensure that the performance requirements are met. For instance, at sub-zero temperatures it might be necessary to keep the pump warm by placing it under the worker's clothes.

8.2.8 Flowmeter, portable, with an accuracy that is sufficient to enable the volumetric flow rate (see 10.4.1.1) to be measured to within ± 5 %.

The calibration of the flowmeter shall be checked against a primary standard, i.e. a flowmeter whose accuracy is traceable to national standards. If appropriate (see 10.2.2), the atmospheric temperature and pressure at which the calibration of the flowmeter is checked shall be recorded.

It is advisable to use a flowmeter that is capable of measuring the volumetric flow rate to within ± 2 % or better.

8.2.9 Ancillary equipment

8.2.9.1 Flexible tubing, of a diameter and length suitable for making a leak-proof connection between the sampling pumps and the sorbent tubes and/or the samplers.

8.2.9.2 Belts or harnesses, to which the sampling pumps can conveniently be fixed for personal sampling (except where the sampling pumps are small enough to fit inside worker's pockets)**.**

8.2.9.3 Forceps, flat-tipped, for loading and unloading of filters and sorbent capsules into and out of samplers.

8.2.9.4 Filter transport cassettes, or similar, if required to transport samples for laboratory analysis.

8.2.9.5 Barometer, suitable for measurement of atmospheric pressure, if required (see 10.2).

8.2.9.6 Thermometer, minimum temperature range of 0 °C to 50 °C, with graduated divisions of 1 °C or less, for measurement of atmospheric temperature, if required (see 10.2).

For applications at temperatures below freezing, the range of the thermometer shall extend to the appropriate desired range.

8.3 Laboratory apparatus

Ordinary laboratory apparatus and the following.

8.3.1 Glassware, made of borosilicate glass 3.3 and complying with the requirements of ISO 3585.

It is preferable to reserve a set of glassware for analysis of mercury by this method in order to ensure that problems do not arise from incomplete removal of mercury contamination by cleaning.

8.3.1.1 Beaker, 500 ml capacity.

8.3.1.2 One-mark pipettes, complying with the requirements of ISO 648.

8.3.1.3 Measuring cylinders, of capacities between 10 ml and 1 000 ml.

8.3.1.4 One-mark volumetric flasks, of capacities between 50 ml and 1 000 ml, complying with the requirements of ISO 1042.

8.3.2 Centrifuge tubes, disposable, with screw caps or push-fit closures, suitable for performing the sample dissolutions described in 11.3.1 and 11.4.1.

The tubes shall have graduations at 25 ml capacity if sorbent capsule samples are to be analysed, and at 50 ml if sorbent tube samples are to be analysed. The graduations shall be accurate to ± 5 %. The tubes shall be free of mercury contamination. The plastic shall be demonstrated to resist the acid digestion process and not to affect the recovery of mercury from spiked sorbent tubes.

NOTE If sample solutions are to be filtered, the tubes used need not be centrifuge tubes.

8.3.3 Piston-operated volumetric instruments, complying with the requirements of ISO 8655-1 and tested in accordance with ISO 8655-6:

a) pipettors, complying with the requirements of ISO 8655-2, as an alternative to one-mark pipettes, for the preparation of standard solutions, calibration solutions and dilution of samples; and

b) dispensors, complying with the requirements of ISO 8655-5, for dispensing acids.

8.3.4 Glass-cutting equipment, for opening sorbent tubes.

8.3.4.1 Special tool, commercially available, for breaking the sealed ends of the sorbent tubes and retaining the broken glass shards produced.

Alternatively, a glass-cutting knife may be used.

8.3.4.2 Glass-cutting wheel, designed for scoring glass tubing, for breaking open sorbent tubes.

Alternatively, a glass-cutting knife may be used.

Rubber grips designed for safely breaking glass tubing are also advisable.

8.3.5 Water bath, thermostatically controlled, capable of maintaining a temperature of approximately 50 °C (see 11.3.1.3 and 11.4.1.5).

8.3.6 Centrifuge, equipped with rotor buckets suitable for use with the centrifuge tubes (8.3.2).

8.3.7 Analytical balance, capable of weighing to an accuracy of ± 0,1 mg.

8.3.8 Disposable gloves, impermeable, for prevention of contamination and to protect the hands from contact with toxic and corrosive substances.

PVC gloves are suitable.

8.3.9 Tweezers, pointed, and/or a needle or short length of wire, or other suitable tools, for removing glass wool plugs from sorbent tubes and screens from sorbent capsules.

8.3.10 Filter funnels, polypropylene, of a size suitable for use in transferring washings from the internal surfaces of an inhalable sampler (8.2.5) into a centrifuge tube (8.3.2), if required (see third paragraph in 11.4.1.4).

8.4 Analytical instrumentation

8.4.1 Spectrometer, either 8.4.1.1 or 8.4.1.2.

8.4.1.1 Atomic absorption spectrometer, equipped with a mercury hollow cathode lamp or electrodeless discharge lamp.

8.4.1.2 Atomic fluorescence spectrometer, designed for mercury analysis.

NOTE Atomic fluorescence spectrometers used for mercury analysis are usually part of dedicated systems designed solely for mercury analysis, or dual-purpose systems designed for analysis of mercury and hydride-forming elements such as arsenic, antimony, selenium, etc.

8.4.2 Mercury cold-vapour generation system, either 8.4.2.1 or 8.4.2.2.

8.4.2.1 Flow injection analysis system (see Figure 3), set up for mercury cold-vapour generation and operated according to the manufacturer's instructions, incorporating

a) reservoirs for tin(II) chloride solution and acid blank,

b) multi-channel peristaltic pumps, fitted with appropriate acid-resistant pump tubing,

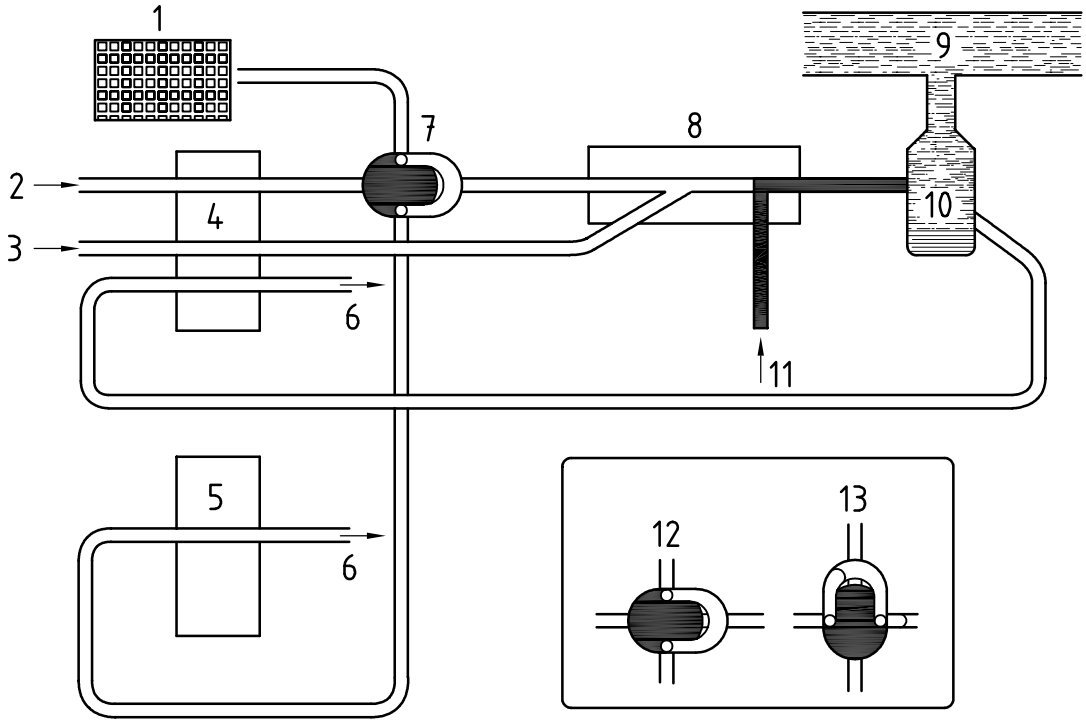
c) an autosampler for presentation of the test solution,

d) an inert injection valve, either solenoid or pneumatically actuated, to inject a reproducible volume of test solution into the acid blank stream,

e) chemically inert mixing piece(s) to facilitate mixing of acid blank or test solution, tin(II) chloride solution and inert purge gas streams,

f) a reaction coil (optional) and

g) a gas/liquid separator with an inlet for the reaction liquid stream and outlets for waste liquid and the purge gas plus gaseous products. A schematic diagram of a typical system is given in Figure 3.



Key

1 autosampler
2 acid blank
3 $SnCl_2$
4 pump 1
5 pump 2
6 waste
7 flow injection valve with sample loop (see inset diagram for valve positions)
8 mixing piece
9 AAS measurement cell
10 gas/liquid separator
11 argon
12 FIA valve in fill position
13 FIA valve in injection position

Figure 3 — Schematic diagram of a typical flow injection CVAAS system

8.4.2.2 Continuous flow (see Figure 4) **or discrete injection mercury cold-vapour generation system** (see Figure 5), set up and operated according to the manufacturer's instructions, incorporating

a) reservoirs for tin(II) chloride solution and acid blank,

b) an autosampler for presentation of the test solution (optional),

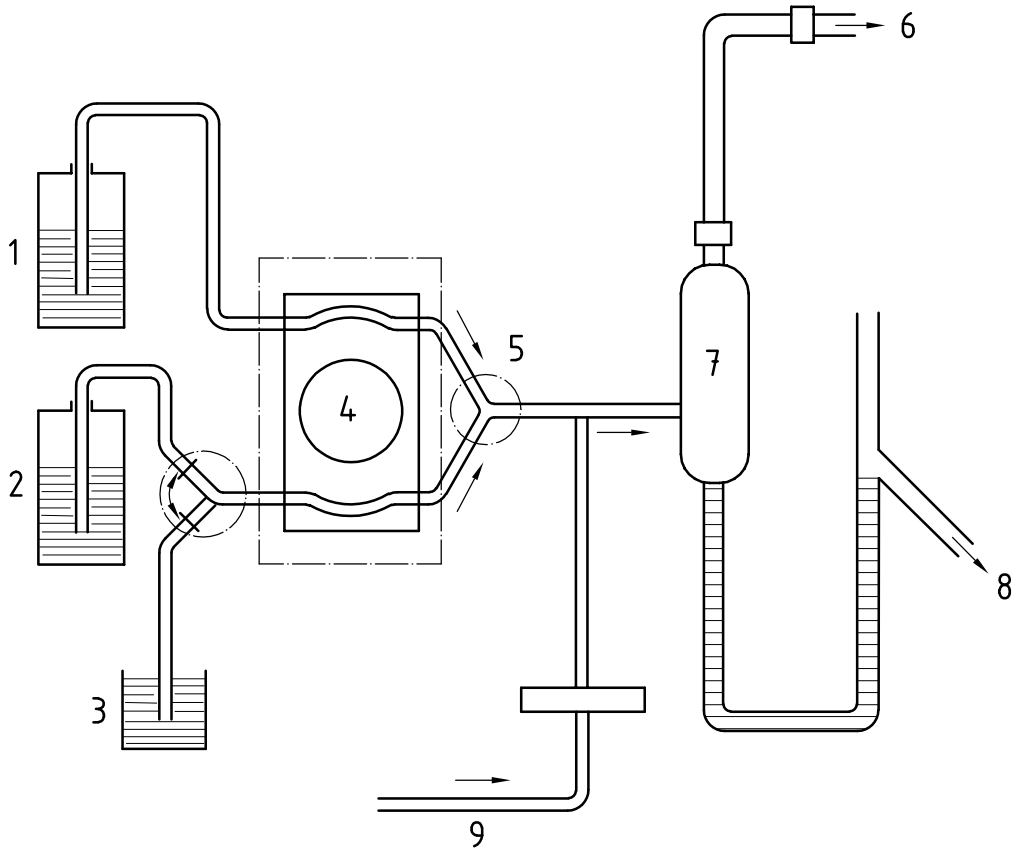
c) an inert switching valve(s), solenoid or pneumatically actuated, to facilitate switching between sample and acid blank streams (optional),

d) peristaltic pumps or a multi-channel peristaltic pump, fitted with appropriate acid-resistant pump tubing,

e) chemically inert mixing piece(s) to facilitate mixing of acid blank or test solution, tin(II) chloride solution and inert gas streams,

f) a reaction coil (optional) and

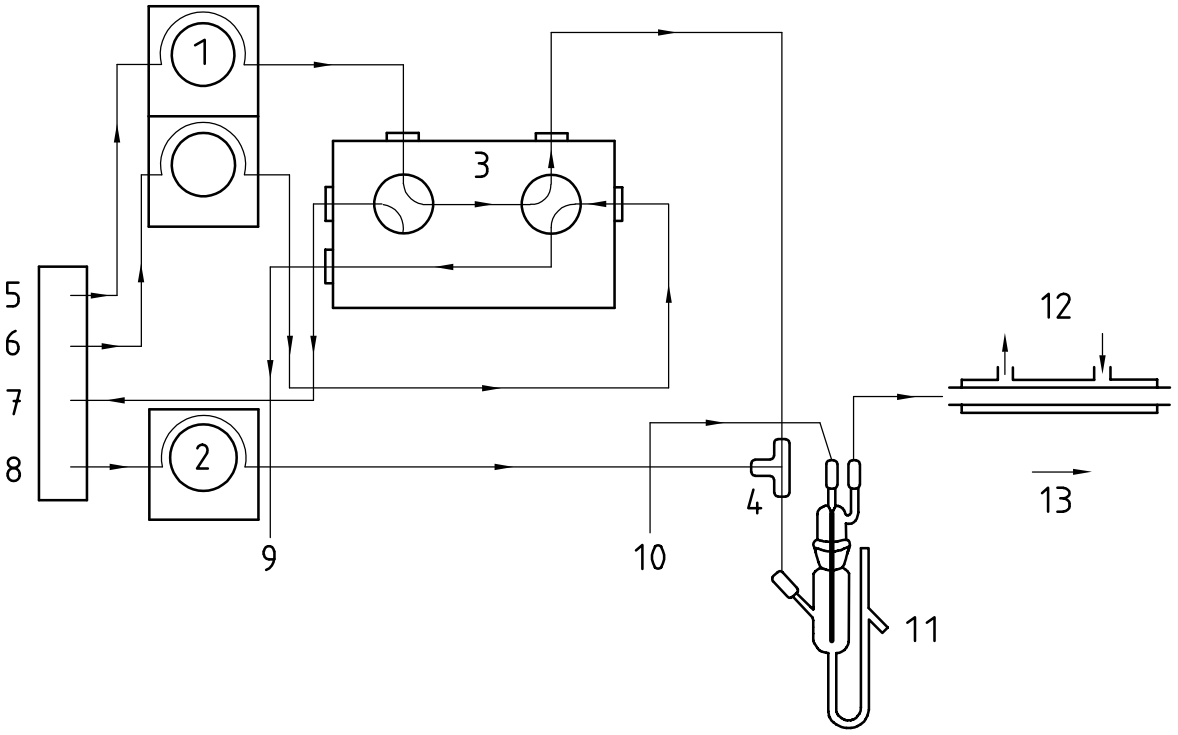
g) a gas/liquid separator with appropriate inlets for the reaction liquid stream and inert purge gas, and outlets for waste liquid and the purge gas plus gaseous products.



Key

1 $SnCl_2$
2 acid blank
3 sample
4 pump
5 mixing piece
6 to heated AAS measurement cell
7 gas/liquid separator
8 waste
9 argon

Figure 4 — Schematic diagram of a typical continuous flow CVAAS system



Key

1 pump 1
2 pump 2
3 sample injection valves (operated simultaneously) — shown in blank flow position
4 mixing piece
5 acid blank
6 sample solution
7 recycled blank solution
8 $SnCl_2$
9 waste
10 argon
11 gas/liquid separator
12 drier gas in/out
13 to AFS measurement cell

Figure 5 — Schematic diagram of a typical discrete injection CVAFS system

Flow injection and discrete injection systems require a smaller volume of test solution than continuous flow systems. They are consequently preferable in this application since the volume of test solution is limited and because mercury readings from continuous flow CVAAS and CVAFS systems can be slow to stabilize.

NOTE 1 In both flow injection and discrete injection systems, a volume of sample is introduced into the acid blank stream resulting in a peak atomic spectrometer output (see Figures 6 and 7). In flow injection systems, the sample volume introduced is determined by the volume of the sample loop. In discrete injection systems, the sample volume introduced is controlled by the length of time for which the sample valve is switched.

NOTE 2 Continuous flow mercury cold-vapour generation systems all work on the same principle, but the plumbing of the various systems is different. In particular, the configuration of some continuous flow hydride-generation systems is such that there is no switching valve(s) and both acid and test solutions are continuously pumped to an additional mixing piece situated upstream of the mixing piece into which the tin(II) chloride solution is introduced. In either case, the effect is a step change in the atomic spectrometer output (see Figure 8).

NOTE 3 Mercury cold-vapour generation systems commonly do double duty as hydride-generation systems for the determination of such elements as arsenic and antimony. For this other purpose, the reductant used is usually sodium tetrahydroborate rather than tin(II) chloride. Even small residues of sodium borohydride are detrimental to the performance of mercury cold-vapour systems using tin(II) chloride. Similarly, traces of iodide from potassium iodide used as a

pre-reductant to reduce arsenate to arsenite will complex with mercury to form HgI_4^{2-}, which does not react with acidic tin(II) chloride. It is therefore a sensible precaution to use different gas liquid separators and reductant tubing for the two reductants.

WARNING — Mercury vapour is generated when solutions containing mercury are reacted with tin(II) chloride. This vapour is very toxic, but is normally produced only in very small quantities. However, in order to eliminate the possibility of exposure to mercury vapour, it is essential that the liquid waste container used be equipped with efficient local exhaust ventilation to prevent any gases emanating from the liquid waste from entering the general laboratory environment.

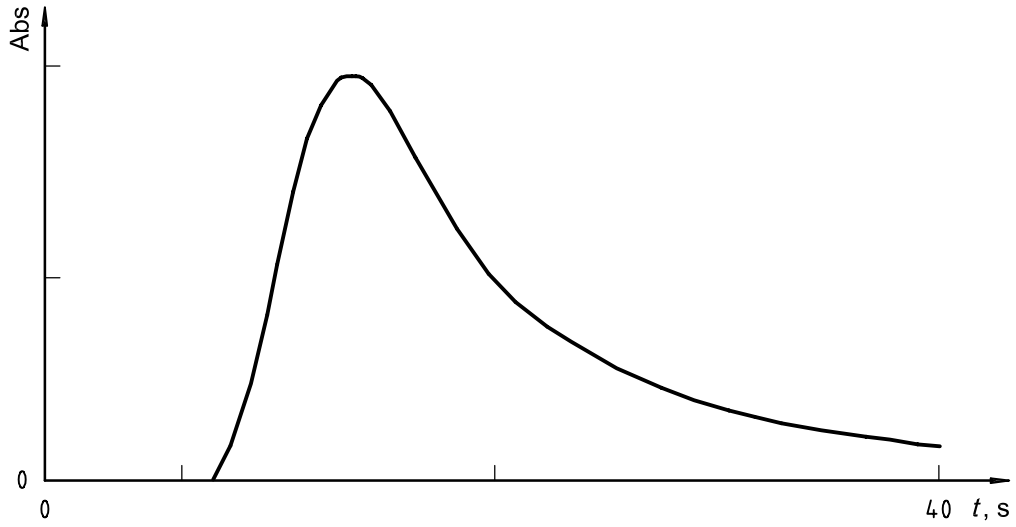


Figure 6 — Typical output of a flow injection CVAAS system (see Figure 3)

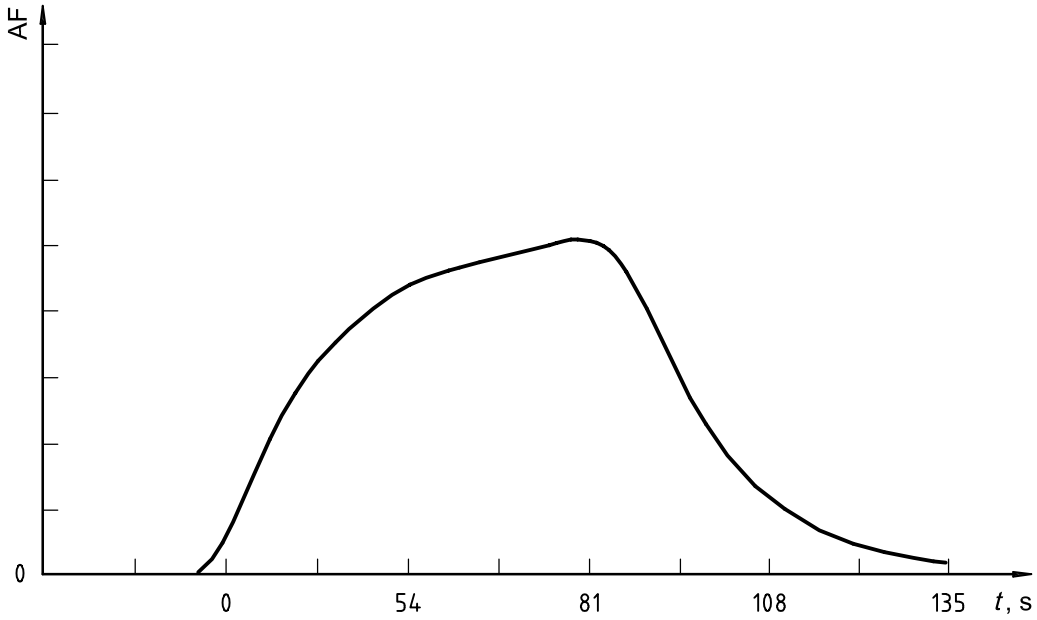
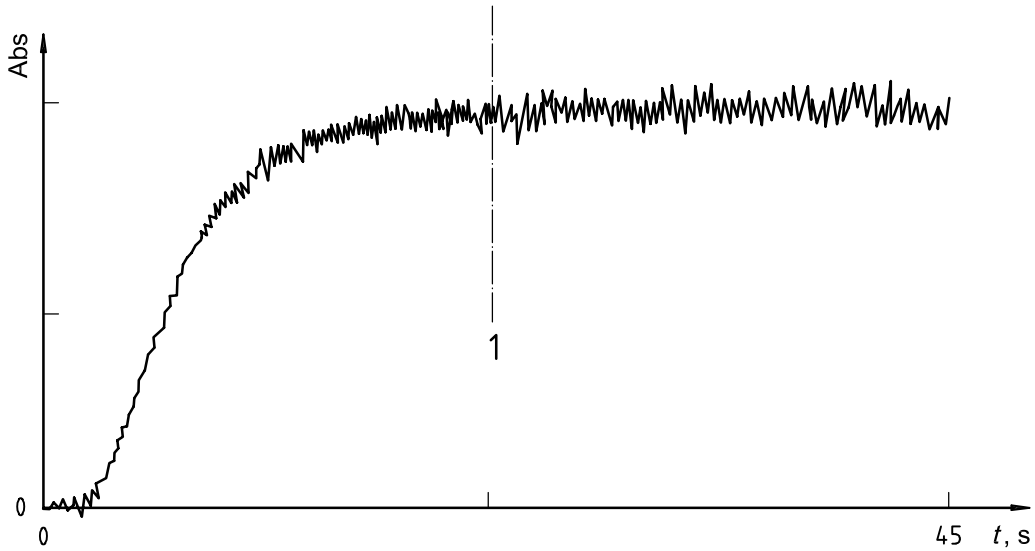


Figure 7 — Typical output of a discrete injection CVAFS system (see Figure 5)



Key

1 start of integration

Figure 8 — Typical output of a continuous flow CVAAS system (see Figure 4)

8.4.3 Spectrometer measurement cell, of silica or quartz, heated electrically to 100 °C to prevent condensation of water vapour on the windows, mounted in the optical path of the atomic absorption spectrometer or the atomic fluorescence spectrometer.

NOTE 1 Measurement cells are usually an integral part of atomic fluorescence spectrometry systems.

NOTE 2 Spray from gas/liquid separators can be carried into the measurement cell by the argon stream in some cold-vapour generation systems. In the case of an atomic absorption system, this is detrimental to the stability of response of the system and damaging to quartz cells. This potential problem can be avoided by inserting a membrane filter made of PTFE into the tubing from the gas/liquid separator to the measurement cell. Alternatively, a tube containing drying granules can be used to remove water droplets in the argon stream. In the case of an atomic fluorescence system, it is essential that water vapour be removed from the gas entering the measurement cell, otherwise the atomic fluorescence of mercury would be quenched. A drying tube, consisting either of drying granules or of a water-permeable membrane[1] in contact with a stream of dry inert gas, is typically used to dry the gas entering the measurement cell.

9 Occupational exposure assessment

9.1 General

This International Standard pertains to the taking of personal and static samples. Refer to relevant international, european or national standards (e.g. EN 689[19], ASTM E 1370-96[37], etc.) for guidance on how to develop an appropriate assessment strategy and for general guidance on measurement strategy.

9.2 Personal sampling

Exposure of workers to mercury shall normally be determined by personal sampling, since the concentration of mercury and inorganic mercury compounds in the breathing zone can be different from the background level in the workplace.

9.3 Static (area) sampling

Static (area) sampling may be carried out, if appropriate, to assess the exposure of workers in a situation where personal sampling is not possible; to characterize the background level of mercury and inorganic mercury compounds in the workplace; to give an indication of the efficiency of ventilation or other engineering controls; or to provide information on the location and intensity of an emission source.

9.4 Selection of measurement conditions and measurement pattern

9.4.1 General

9.4.1.1 Sampling shall be carried out in such a way as to cause the least possible interference with the worker and the normal performance of the job and to provide samples that are representative of normal working conditions and compatible with the analytical method.

9.4.1.2 The pattern of sampling shall take into consideration practical issues, such as the nature of the measurement task and the frequency and duration of particular work activities.

9.4.2 Screening measurements of variation of concentration in time and/or space

Screening measurements of variation of concentration in time/and or space may be performed to provide information on the likely pattern of concentration of chemical agents. They can be used to identify locations and periods of elevated exposure and to set the duration and frequency of sampling for measurements for comparison with limit values. Emission sources can be located and the effectiveness of ventilation or other technical measures can be estimated (see 4.3 of EN 482:1994[14]).

9.4.3 Screening measurements of time-weighted average concentration and worst case measurements

9.4.3.1 Screening measurements of time-weighted average concentration may be performed to obtain relatively crude information on the exposure level in order to decide whether an exposure problem exists at all and, if so, to appraise its possible seriousness. They may also be used to determine if the exposure is well below or well above the limit value (see 4.2 of EN 482:1994[14]).

9.4.3.2 Screening measurements of time-weighted average concentration are typically carried out in the initial stages of a survey to assess the effectiveness of control measures. Sampling may be carried out during representative work episodes to obtain clear information about the level and pattern of exposure, or worst case measurements may be made.

NOTE Screening measurements of time-weighted average concentration made to clearly identify work episodes during which highest exposure occurs are typically referred to as “worst-case measurements” (see 5.2.3.2 of EN 689:1995[19]).

9.4.4 Measurements near an emission source

Measurements may be performed near an emission source to provide information on the location and intensity of the source. In association with other information they can allow the elimination of a suspected source as a significant contributor to exposure (see 4.4 of EN 482:1994[14]).

9.4.5 Measurements for comparison with limit values and periodic measurements

9.4.5.1 Measurements for comparison with limit values

9.4.5.1.1 Measurements for comparison with limit values are performed to provide accurate and reliable information on, or allow the prediction of, the time-weighted average concentration of a specific chemical agent in the air, which could be inhaled (see 4.5 of EN 482:1994[14]).

9.4.5.1.2 For making measurements for comparison with a short-term exposure limit, the sampling time shall be as close as possible to the reference period, which is typically 15 min, but can be anything between 5 min and 30 min.

9.4.5.1.3 For making measurements for comparison with a long-term exposure limit, samples shall be collected for the entire working period, if possible, or during a number of representative work episodes (see 10.3.1.2 and 10.4.1.2.2 for the minimum sampling time).

NOTE The best estimate of long-term exposure is obtained by taking samples over the entire working period, although this might not always be practicable.

9.4.5.2 Periodic measurements

Periodic measurements are performed to determine whether exposure conditions have changed since measurements for comparison with limit values were made, or whether control measures remain effective (see 4.6 of EN 482:1994[14]).

10 Sampling

10.1 Selection of sampling method

10.1.1 Measurement of mercury vapour

If results are required for comparison with a limit value for mercury vapour or for total inorganic mercury (mercury vapour and inorganic mercury compounds) and it is known that no particulate inorganic mercury compounds are used in the workplace and that none are produced in the processes carried out, use either the diffusive badge method specified in 10.3 or the pumped sorbent tube method specified in 10.4.1.1.1 to collect samples of mercury vapour. See Annex A for guidance on the advantages and disadvantages of the diffusive and pumped sampling methods.

10.1.2 Measurement of particulate inorganic mercury compounds

If results are required for comparison with a limit value for inorganic mercury compounds or with a limit value for total inorganic mercury (mercury and inorganic mercury compounds) and it is known that no elemental mercury is used in the workplace and that no mercury vapour is produced in the processes carried out, use the filter sampling method specified in 10.4.1.1.2 to collect samples of particulate inorganic mercury compounds.

10.1.3 Measurement of mercury vapour and particulate inorganic mercury compounds

If both mercury vapour and particulate inorganic mercury compounds are believed to be present in significant proportions in the test atmosphere, collect samples of mercury vapour and particulate inorganic mercury compounds with a pumped sorbent tube and prefilter using the method specified in 10.4.1.1.3. Then analyse the sorbent tube and filter separately or together, depending upon whether the results are required for comparison with separate limit values for mercury and inorganic mercury compounds or for comparison with a limit value for total inorganic mercury (mercury and inorganic mercury compounds).

NOTE The prefilter may be omitted if it is believed that particulate inorganic mercury compounds do not make up a significant proportion (e.g. are < 10 %) of the sum of mercury vapour and particulate inorganic mercury compounds present in the test atmosphere (see Note in 10.4.1.1.3).

10.2 Consideration of temperature and pressure effects

10.2.1 Effect of temperature and pressure on the uptake rate of diffusive badges

The sample uptake rate of diffusive badges is temperature- and pressure-dependent, but the effect is relatively small. Nevertheless, temperature and pressure corrections of the sample uptake rate can improve accuracy at extremes of temperature and pressure. Consider whether the difference between the temperature and pressure at which the nominal sample uptake rate given by the manufacturer of the diffusive badge applies and the atmospheric temperature and pressure during sampling is likely to be great enough to justify applying a correction, e.g. if the error could be greater than ± 5 %. See B.1. If a correction is to be made, measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see 10.3.4.1 and 10.3.4.2). Then calculate a temperature- and pressure-corrected sample uptake rate following the procedure given in B.1.

10.2.2 Effect of temperature and pressure on volumetric flow rate in the pumped sampling method

See the manufacturer's instructions to determine if the volumetric flow rate indicated on the flowmeter (8.2.8) is dependent upon temperature and pressure. Consider whether the difference between the atmospheric temperature and pressure at the time of calibration of the flowmeter and during sampling is likely to be great enough to justify applying a correction to take this into account, e.g. if the error could be greater than $\pm$ 5 %. See B.2. If a correction is necessary, measure and record the atmospheric temperature and pressure at which the calibration of the flowmeter is checked (see 8.2.8), and measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see 10.4.4.1 and 10.4.4.3). Then calculate a temperature- and pressure-corrected volumetric flow rate following the procedure given in B.2.

10.2.3 Expression of results

Consider whether it is necessary to recalculate mercury in air concentrations to reference conditions (such as in high altitude situations). If so, measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see 10.3.4.1 and 10.3.4.2 or 10.4.4.1 and 10.4.4.3), and follow the procedure given in B.3 to apply the necessary correction to the mercury-in-air concentrations calculated in 12.2.1.

NOTE The concentration of mercury in air is generally stated for actual environmental conditions (temperature, pressure) at the workplace during the sampling period.

10.3 Diffusive sampling

10.3.1 Selection and use of diffusive badges

10.3.1.1 Sampling of mercury vapour

Use diffusive badges (8.1.1) to collect samples for measurement of personal exposure to mercury vapour or the background concentration of mercury vapour in air.

10.3.1.2 Sampling period

Select a sampling period that is appropriate for the measurement task (see 9.4), but ensure that it is long enough to enable mercury to be determined with acceptable overall uncertainty at levels of industrial hygiene significance. It is recommended that sampling be carried out over the entire working period, but in any case the sampling time shall not be less than 6 h (see 13.6.1).

10.3.1.3 Sample handling

To minimize the risk of damage or contamination, only handle sorbent capsules (8.1.2) using flat-tipped forceps (8.2.9.3) in a clean area where the concentration of mercury vapour is as low as possible.

10.3.2 Preparation for sampling

10.3.2.1 Cleaning of diffusive badges

10.3.2.1.1 Disassemble each diffusive badge (8.1.1) and place all parts except the attachment clip, two polyethylene mesh discs, retaining internal metal O-ring and foam disc in a suitable container. Soak in 1:9 nitric acid (7.3) for at least 1 h.

10.3.2.1.2 Soak the two polyethylene mesh discs separately in 1:9 nitric acid (7.3) for at least 1 h, ensuring that any traces of Anasorb C 300 dust are removed, since these will otherwise trap mercury vapour when the badge is reused, thus preventing it from entering the capsule.

10.3.2.1.3 Rinse all parts of the diffusive badge at least three times in water (7.1). Dry as quickly as possible, then reassemble the badge for storage without a new sorbent capsule or foam disc (see Figure 1). Store in a clean area where the sampler will not become contaminated with mercury until ready to use again.

10.3.2.2 Loading of diffusive badges with sorbent capsules

10.3.2.2.1 Remove the required number of sorbent capsules (8.1.2) from the plastic pouches in which they were supplied, by carefully cutting one edge off each pouch. Discard any particles of Anasorb that have become dislodged from the sorbent capsule during transit. Load each sorbent capsule into a clean diffusive badge (10.3.2.1.3) with the mesh side facing towards the sampling face (see Figure 1). Place a clean foam disc in the back cover of each sampler and then fit the back cover to the sampler housing (see Figure 1). Label each sampler so that it can be uniquely identified, and seal with its protective cover to prevent contamination. Retain the pouches in which the sorbent capsules were supplied for storage of the samples after sampling. Always use samplers within a few days of loading with sorbent capsules, as the sealing caps do not provide a hermetic seal.

10.3.2.2.2 Retain in unopened pouches at least four unused sorbent capsules from the same batch used for sample collection. Use these for preparation of calibration solutions (see 11.3.2) so that calibration solutions and sample solutions are matrix-matched.

10.3.2.3 Field blanks

10.3.2.3.1 Retain as field blanks at least one unused diffusive badge (10.3.2.2.1) from each batch of ten prepared, subject to a minimum of two. Treat these in the same manner as those used for sampling with respect to storage and transport to and from the sampling position, but do not expose them by removing the protective caps.

If sorbent capsules from different batches are used, it is necessary to retain unused sorbent capsules from each batch for use as field blanks and to note the batch number of the sorbent capsule used for each sample.

NOTE It has been found that the mercury content of sorbent capsules differs very little from one box of sorbent capsules to the next, provided that they have the same batch number.

10.3.3 Sampling position

10.3.3.1 Personal sampling

Remove the diffusive badge from its plastic pouch and position it in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, e.g. fasten it to the worker's shirt collar or lapel with the attached clip. Position it in such a way that it is unlikely to get knocked or be contaminated with liquid mercury.

10.3.3.2 Static (area) sampling

10.3.3.2.1 If static sampling is carried out to characterize the background concentration of mercury in air, select a sampling position that is sufficiently remote from the work processes, such that results will not be directly affected by mercury from emission sources. Remove the diffusive badge from its plastic pouch and fix it to a stand or convenient fixture in a suitable position to monitor the background concentration of mercury in air at breathing height.

10.3.3.2.2 If the air is very still (air speed $< 7{,}5\ \text{m}\cdot\text{min}^{-1}$), use the pumped sorbent tube method (10.4) or take note of the fact that low results will be obtained (see 13.7.3). In windy conditions (air speed $> 230\ \text{m}\cdot\text{min}^{-1}$), provide shielding from the wind.

10.3.4 Sample collection

10.3.4.1 Remove the protective cap from the diffusive badge and record the time at the start of the sampling period. If appropriate (see 10.2.1 and 10.2.3), measure the atmospheric temperature and pressure

at the start of the sampling period, using the thermometer (8.2.9.6) and barometer (8.2.9.5) respectively, and record the measured values.

10.3.4.2 At the end of the sampling period (see 10.3.1.2), replace the protective cap, record the time and calculate the duration of the sampling period. If appropriate (see 10.2.1 and 10.2.3), measure the atmospheric temperature and pressure at the end of the sampling period using the thermometer (8.2.9.6) and barometer (8.2.9.5) and record the measured values.

10.3.4.3 Carefully record the sample identity and all relevant sampling data (see Clause 14).

10.3.5 Transportation of samples

10.3.5.1 Remove the sorbent capsule from the badge taking care not to contaminate it (see 10.3.1.3) and place it in the plastic pouch in which it was received. Seal the pouch with the label provided by the manufacturer for this purpose. Write the sample number and other details pertinent to the sample on the label.

10.3.5.2 Transport the sealed plastic pouches containing the sorbent capsules (10.3.5.1) to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

10.3.5.3 Follow sampling chain of custody procedures to ensure sample traceability. Ensure that the documentation which accompanies the samples is suitable for a “chain of custody” to be established (see, for example, ASTM D 4840–88[28]).

10.3.5.4 Follow the same procedure for the field blanks (10.3.2.3).

10.3.5.5 Analyse the samples within four weeks of sampling.

10.4 Pumped sampling

10.4.1 Preliminary considerations

10.4.1.1 Selection and use of sorbent tubes, prefilters and inhalable samplers

10.4.1.1.1 Sampling of mercury vapour

Use sorbent tubes (8.2.1) to collect samples for measurement of personal exposure to mercury vapour or the background concentration of mercury vapour in air. Precede the sorbent tubes with prefilters (see 8.2.3) if the concentration of airborne particles could be sufficiently high that there is a risk of blockage of the glass wool plugs that retain the Anasorb sorbent in the tubes. Use a flow rate within the range recommended by the manufacturer of the sorbent tube, normally 200 $ml \cdot min^{-1}$ for a 200 mg tube or 2 $l \cdot min^{-1}$ for a 500 mg tube.

10.4.1.1.2 Sampling of particulate inorganic mercury compounds

Use quartz-fibre filters (8.2.6) mounted in inhalable samplers (8.2.5) to collect samples for measurement of personal exposure to particulate inorganic mercury compounds or to measure the background concentration of particulate inorganic mercury compounds in air. Use the samplers at their design flow rate and in accordance with the manufacturer's instructions, so that they collect the inhalable fraction of airborne particles.

10.4.1.1.3 Sampling of mercury vapour and particulate inorganic mercury compounds

Use sorbent tubes (8.2.1) to collect samples of mercury vapour and particulate inorganic mercury compounds for measurement of personal exposure to mercury vapour and particulate inorganic mercury compounds or the background concentration of mercury vapour and particulate inorganic mercury compounds in air. Precede the sorbent tubes with prefilters (see 8.2.3) if it is believed that particulate inorganic mercury compounds could make up a significant proportion (e.g. > 10 %) of the sum of mercury vapour and particulate inorganic mercury compounds present in the test atmosphere (see Note), using an inhalable sampler (8.2.5) rather than a plastic

sampling cassette (8.2.4) in the sorbent tube and prefilter assembly. Use a flow rate within the range recommended by the manufacturer of the sorbent tube, normally 200 ml·min^{-1} for a 200 mg tube or 2 l·min^{-1} for a 500 mg tube.

Exposure limits for particulate inorganic mercury compounds generally apply to the inhalable fraction of airborne particles, as defined in ISO 7708. Under such circumstances, in order to meet national requirements, an inhalable sampler should be used in the sorbent tube and prefilter assembly. If an inhalable sampler is not available that has a design flow rate compatible with the manufacturer's recommended range of flow rates for the sorbent tube, it will be necessary to collect separate samples for determination of mercury vapour and particulate inorganic mercury compounds using the methods referred to in 10.4.1.1.1 and 10.4.1.1.2.

NOTE If prefilters are not used with sorbent tubes, particulate inorganic mercury compounds will be trapped on the glass wool plugs that retain the sorbent in the tubes and on the sorbent itself. Although it is fair to assume that the efficiency with which particulate inorganic mercury compounds are trapped by sorbent tubes is reasonably high, this has not been confirmed experimentally. Furthermore, the sampling characteristics of sorbent tubes for airborne particles are unknown. Exposure limits for inorganic mercury compounds and for total inorganic mercury (mercury and inorganic mercury compounds) generally apply to the inhalable fraction of airborne particles, as defined in ISO 7708. Under such circumstances, in order to meet national requirements, sorbent tubes should act as inhalable samplers, which they are not designed to do. In consideration of these two sources of potential sampling bias, it is acceptable to analyse the sorbent and glass wool plugs in order to estimate total mercury-in-air concentrations, but only if it is known that the majority of the mercury sampled is in the vapour state. In this case the overall bias of the sampling method will be acceptably small.

10.4.1.2 Sampling period

10.4.1.2.1 Select a sampling period that is appropriate for the measurement task (see 9.4), but ensure that it is long enough to enable mercury to be determined with acceptable overall uncertainty at levels of industrial hygiene significance. For example, estimate the minimum sampling time required to ensure that the amount of mercury collected is above the lower limit of the working range of the analytical method when it is present in the test atmosphere at a concentration of 0,1 times its limit value, using the following equation:

$$t_{\text{min}} = \frac{m_{\text{low}}}{q_V \times 0{,}1 \times L}$$

where

t_{min} is the minimum sampling time, in minutes;

m_{low} is the lower limit (mass) of the analytical range, in micrograms;

q_V is design flow rate of the sampler, in litres per minute;

L is the limit value (mass concentration), in milligrams per cubic metre.

10.4.1.2.2 The sampling time shall not be less than 1 h for a 200 mg sorbent tube used at a flow rate of 200 ml·min^{-1} (see 13.6.2). If this minimum sampling time is too short for the method to be useful for the intended measurement task, use a 500 mg sorbent tube at a flow rate of 2 l·min^{-1} (see Note 1 in 8.2.1). Sampling times may be as short as 15 min for an inhalable sampler (see 13.2).

10.4.1.2.3 When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading with particulate matter the glass wool plugs that retain the Anasorb sorbent in the tubes; or use a prefilter.

10.4.1.3 Sample handling

To minimize the risk of damage or contamination, only handle quartz-fibre filters (8.2.6) and sorbent tubes (8.2.1) in a clean area, where the concentration of mercury in air is as low as possible, and only handle quartz-fibre filters using flat-tipped forceps (8.2.9.3).

10.4.2 Preparation for sampling

10.4.2.1 Cleaning of inhalable samplers

If required (see 10.4.1.1), clean the inhalable samplers (8.2.5) before use. Disassemble the samplers, soak in laboratory detergent solution (7.12), rinse thoroughly with water (7.1), wipe with absorbent tissue and allow to dry before reassembly.

Alternatively, use a laboratory washing machine.

10.4.2.2 Loading of samplers with filters

If required (see 10.4.1.1), load plastic filter cassettes (8.2.4) or clean inhalable samplers (10.4.2.1) with filters (8.2.6). Label each sampler or filter cassette so that it can be uniquely identified, and seal with its protective plug or cover to prevent contamination.

Alternatively, commercially available pre-loaded plastic filter cassettes may be used.

10.4.2.3 Preparation of sorbent tubes or sorbent tube and prefilter assemblies

10.4.2.3.1 Break the flame-sealed ends off the required number of sorbent tubes (8.2.1) using a special glass cutting tool (8.3.4.1) or a glass cutting wheel (8.3.4.2). Label each sorbent tube so that it can be uniquely identified and, if desired, mount it in a sorbent tube holder (8.2.2).

10.4.2.3.2 If required (see 10.4.1.1.3), construct a sorbent tube and prefilter assembly (see 8.2.3) by connecting a loaded sampler (10.4.2.2) to each sorbent tube or sorbent tube holder (10.4.2.3.1) with a minimum length of inert plastic tubing, e.g. modified polyvinyl chloride or PTFE tubing, ensuring that no leaks can occur (see 8.2.3).

Alternatively, use a sorbent tube holder to which the sampler can be directly attached.

10.4.2.3.3 Seal the exposed end(s) of sorbent tubes with the plastic end caps supplied by the manufacturer.

10.4.2.3.4 Retain six sorbent tubes from the same batch used for sampling for use in the preparation of calibration solutions (11.4.2.1).

10.4.2.4 Setting the volumetric flow rate

Perform the following in a clean area, where the concentration of mercury in air is low.

Remove the protective cover, plug and/or cap(s) from each loaded sampler (10.4.2.2), sorbent tube (10.4.2.3.1) or sorbent tube and prefilter assembly (10.4.2.3.2) and connect it to a sampling pump (8.2.7) using flexible tubing (8.2.9.1), ensuring that no leaks can occur. Switch on the sampling pump, attach the flowmeter (8.2.8) to the sampler, sorbent tube or sorbent tube and prefilter assembly so that it measures the flow through the inlet orifice(s) and set the required volumetric flow rate (see 10.4.1.1). Switch off the sampling pump and seal the sampler, sorbent tube or sorbent tube and prefilter assembly with its protective cover, plug and/or cap(s) to prevent contamination during transport to the sampling position.

If necessary, allow the sampling pump operating conditions to stabilize before setting the volumetric flow rate (refer to the manufacturer's instructions).

10.4.2.5 Field blanks

Retain as field blanks, at least one unused loaded sampler (10.4.2.2), sorbent tube (10.4.2.3.1) or sorbent tube and prefilter assembly (10.4.2.3.2) from each batch of ten prepared, subject to a minimum of two. Treat these in the same manner as those used for sampling with respect to storage and transport to and from the sampling position, but draw no air through them.

10.4.3 Sampling position

10.4.3.1 Personal sampling

Position the sampler, sorbent tube or sorbent tube and prefilter assembly (10.4.2.4) in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, e.g. fastened to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, e.g. to a belt (8.2.9.2) around the waist, or place it in a convenient pocket.

10.4.3.2 Static (area) sampling

10.4.3.2.1 If static sampling is carried out to assess the exposure of a worker in a situation where personal sampling is not possible (e.g. due to the need to sample at a volumetric flow rate higher than the design flow rate of available personal samplers), position the sampler, sorbent tube or sorbent tube and prefilter assembly (10.4.2.4) in the immediate vicinity of the worker and at breathing height. If in doubt, take the sampling position to be the point where the risk of exposure is considered to be greatest.

10.4.3.2.2 If static sampling is carried out to characterize the background level of mercury in the workplace, select a sampling position that is sufficiently remote from the work processes so that results will not be directly affected by mercury from emission sources.

10.4.4 Collection of samples

10.4.4.1 When ready to begin sampling, remove the protective cover, plug and/or cap(s) from the sampler, sorbent tube or sorbent tube and prefilter assembly and switch on the sampling pump. If the sampling pump is fitted with an integral timer, check that this is reset to zero prior to turning it on. Record the time and volumetric flow rate at the start of the sampling period. If appropriate (see 10.2.2 and 10.2.3), measure the atmospheric temperature and pressure at the start of the sampling period using the thermometer (8.2.9.6) and barometer (8.2.9.5) and record the measured values.

Integral timers built into sampling pumps can be imprecise and should only be used to provide evidence that the sampler has been operating properly throughout the sampling period (see 10.4.4.3).

NOTE If the temperature or pressure at the sampling position is different from that where the volumetric flow rate was set (see 10.4.2.4), the volumetric flow rate could change and it might need to be re-adjusted before sampling.

10.4.4.2 Monitor the performance of the pumps frequently, a minimum of once every 2 h. Measure the flow rate using the flowmeter (8.2.8) and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within $\pm$ 5 % of the nominal value throughout the sampling period.

10.4.4.3 At the end of the sampling period (see 10.4.1.2), record the time. Check the malfunction indicator and/or the reading on the integral timer, if fitted, and consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout the sampling period. Measure the volumetric flow rate at the end of the sampling period using the flowmeter (8.2.8) and record the measured value. If appropriate (see 10.2.2 and 10.2.3), measure the atmospheric temperature and pressure at the end of the sampling period using the thermometer (8.2.9.6) and barometer (8.2.9.5), and record the measured values.

10.4.4.4 Carefully record the sample identity and all relevant sampling data (see Clause 14).

10.4.5 Transportation of samples

10.4.5.1 If sorbent tube and prefilter assemblies were used for sampling, disassemble them and seal the sorbent tubes with plastic end caps. Discard the prefilters if they were used simply to prevent blockage of the glass wool plugs (see 10.4.1.1.1). If the prefilters were used to collect particulate inorganic mercury compounds (see 10.4.1.1.3), unload them from the samplers as described in 10.4.5.2 through 10.4.5.4.

10.4.5.2 For inhalable samplers which collect airborne particles on the filter (see Note 2 in 8.2.5), remove the filter from each sampler, place in a labelled filter transport cassette (8.2.9.4) and close with a lid. Take particular care to prevent the collected sample from becoming dislodged from heavily loaded filters. Alternatively, transport samples to the laboratory in the samplers in which they were collected.

10.4.5.3 For samplers which have an internal filter cassette (see Note 2 in 8.2.5), remove the filter cassette from each sampler and fasten with its lid or transport clip.

10.4.5.4 For disposable sampling cassettes, transport samples to the laboratory in the samplers in which they were collected.

10.4.5.5 Transport the sorbent tube samples (10.4.5.1) and, if appropriate, the filter samples (10.4.5.2 through 10.4.5.4) to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

10.4.5.6 Follow sampling chain of custody procedures to ensure sample traceability. Ensure that the documentation which accompanies the samples is suitable for a “chain of custody” to be established (see, for example, ASTM D 4840–88[28]).

10.4.5.7 Follow the same procedure for the field blanks (10.4.2.5).

10.4.5.8 Analyse the samples within four weeks of sampling.

11 Analysis

11.1 General

WARNING — Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with acid, and carry out sample dissolution in a fume hood. See the WARNINGS in 7.2 and 7.4.

The procedure described is designed so that the complete sample dissolution process can be carried out in the same disposable, plastic centrifuge tube. The tube can then be loaded directly into the rack of an autosampler for analysis. This minimizes manipulations and reduces the chance of contamination of the sample.

For samples collected using a sorbent tube and prefilter assembly, the procedure described may be used to jointly analyse the contents of a sorbent tube and its associated prefilter in order to obtain a combined result for mercury vapour and particulate inorganic mercury compounds. The result can then be compared with an occupational exposure limit for total inorganic mercury (mercury vapour and inorganic mercury compounds). Alternatively, the procedure may be used to separately analyse the samples to determine the mercury vapour collected by the sorbent tubes and the particulate inorganic mercury compounds collected on the quartz-fibre filters.

11.2 Cleaning of glassware and plasticsware

11.2.1 Before use, clean all glassware (8.3.1) to remove any residual grease or chemicals by first soaking in laboratory detergent solution and then rinsing thoroughly with water (7.1). Alternatively, use a laboratory glass washing machine.

11.2.2 After initial cleaning (11.2.1), clean all glassware by soaking in 1:9 nitric acid (7.3) for a minimum of 24 h and then rinsing thoroughly with water (7.1).

11.2.3 Glassware that has been previously subjected to the cleaning procedure described in 11.2.1 and 11.2.2, and which has been reserved for the analysis of mercury by this method, can be cleaned adequately by rinsing with 1:9 nitric acid (7.3) and then with water (7.1).

11.3 Preparation of blank, sample and calibration solutions for analysis of diffusive badges

11.3.1 Preparation of blank and sample solutions

11.3.1.1 Open the plastic pouches containing the sorbent capsules (10.3.5.1). Carefully remove the screen from the top of each sorbent capsule, using pointed tweezers or a needle (8.3.9). Take care not to lose any sorbent. Carefully pour the sorbent from each capsule into separate, labelled, disposable 50 ml plastic centrifuge tubes (8.3.2). Transfer any particles of Anasorb that have become dislodged from the sorbent capsule during transit into the tube. Discard the screen and empty capsule.

11.3.1.2 Add 2,0 ml of concentrated nitric acid (7.2) followed by 2,0 ml concentrated hydrochloric acid (7.4) to each centrifuge tube.

It is important that nitric acid is added before hydrochloric acid to ensure that mercury is oxidized to the divalent state. Otherwise mercury left in an elemental state may be lost due to volatilization[20].

11.3.1.3 Tightly seal the centrifuge tubes with their screw caps or push-fit closures and roll the tubes to wash any Anasorb from the walls. Place the tubes in a test tube rack in a thermostatically controlled water bath (8.3.5) at 50 °C for 1 h, periodically agitating and rolling the tubes to ensure that all hopcalite is dissolved from the ceramic support material of the Anasorb granules.

Sample dissolution may also be carried out by allowing the tubes to stand at room temperature for a prolonged period, e.g. overnight. Another alternative is to use ultrasonic extraction, but this could result in shattering of the ceramic substrate which in turn could make it more difficult to separate from the sample solution by centrifugation or filtration (see 11.3.1.6).

11.3.1.4 Remove the tubes from the heated water bath and place them to cool in a bath of cold water. When the solutions have cooled to room temperature, carefully unscrew the caps from the tubes or remove the push-fit closures to release any pressure built up due to the formation of oxides of nitrogen.

11.3.1.5 Make up to the 25 ml graduation of the centrifuge tube with water (7.1), reseal the tubes and shake to mix.

NOTE Dissolution of the sample yields a dark brown liquid. When diluted to volume with water, this forms a milky blue-green suspension above a white ceramic residue from the Anasorb sorbent.

11.3.1.6 Centrifuge the sample solutions to remove the ceramic support material from suspension. Alternatively, filter the suspension, having confirmed in tests that the filter used will not contaminate the solution with mercury or remove any mercury from solution.

NOTE The use of a centrifuge is preferable to filtration since it enables the sample to be prepared and presented to the instrument without transfer from the centrifuge tube, speeding analysis and making contamination less likely.

11.3.1.7 Prior to analysis, uncap the centrifuge tubes and let stand in a fume hood for at least 1 h to allow dissolved oxides of nitrogen to degas from the solutions.

Thorough dispersion of oxides of nitrogen from solution is particularly important when CVAFS is used, since they will otherwise quench mercury cold-vapour fluorescence. Degassing can be accelerated by passing a stream of an inert gas, such as nitrogen, through the solution prior to centrifugation.

11.3.2 Preparation of calibration solutions

Prepare a set of calibration solutions, including a calibration blank solution, for use in the analysis of diffusive badges. Take four sorbent capsules from the same batch used to collect the samples (see 10.3.2.2.1) and prepare solutions from them following the procedure in 11.3.1.1 through 11.3.1.4. Make up almost to the 25 ml graduation of the centrifuge tubes with water (7.1) and then accurately pipette 125 µl, 250 µl and 500 µl of working mercury standard solution B (7.11) into three of the tubes. Finally, make up to volume, centrifuge and degas as described in 11.3.1.5 through 11.3.1.7. The prepared calibration solutions have mercury concentrations of 0 $\mu g \cdot l^{-1}$, 5 $\mu g \cdot l^{-1}$, 10 $\mu g \cdot l^{-1}$ and 20 $\mu g \cdot l^{-1}$. Label them accordingly.

NOTE 1 The reason for matrix-matching the calibration solutions in this manner is that the slope of the calibration is influenced by acid concentration, and the acid concentration of the sample solutions is unknown due to consumption of acid during dissolution of the sorbent. Correspondingly, it has been demonstrated[4] that failure to properly matrix-match calibration and test solutions can produce high results. On the other hand, some hydride-generation systems are believed to be less sensitive to acid concentration than the system used in the validation of this method. In such circumstances, simply matching the acid content of the calibration and test solutions might be adequate to produce results of sufficient accuracy (i.e. by preparing calibration solutions in 2:2:21 nitric acid/hydrochloric acid). Alternatively, for hydride-generation systems that are sensitive to acid concentration, it might be possible to obtain satisfactory results by preparing calibration solutions in an intermediate acid concentration (e.g. 1:1:23 nitric acid/hydrochloric acid). In both cases, this would reduce the cost of analysis by eliminating the need to use sorbent capsules in the matrix-matching process. However, if the procedure described in 11.3.2 is modified in any way, it should be demonstrated that the results obtained exhibit an acceptable bias, e.g. < 5 %.

NOTE 2 An alternative means of reducing the cost of analysis could be to prepare 50 ml of blank solution from two sorbent capsules and carry out a standard-additions calibration by spiking aliquots of this solution with appropriate volumes of mercury standard solution.

11.4 Preparation of blank, sample and calibration solutions for analysis of pumped samples

11.4.1 Preparation of blank and sample solutions

11.4.1.1 Remove the plastic end-caps from the sorbent tubes. Score each tube with the glass cutting wheel (8.3.4.2), approximately halfway across the middle section, where it is packed with glass wool. Then break off the front section of the tube above the glass wool (see CAUTION). Draw out the glass wool plug from each tube using pointed tweezers (8.3.9), discarding the retaining spring, if present, and place the glass wool plug in a labelled, 50 ml disposable centrifuge tube (8.3.2). Pour the released sorbent granules into the centrifuge tube. Then poke a wire (8.3.9) into the open end of the remaining section of tube in order to push out the remaining glass wool plug into the centrifuge tube.

CAUTION — Grip the tube with either special rubber tube grips (see 8.3.4.2) or a cloth to reduce the chance of being cut by broken glass whilst breaking open the tube.

11.4.1.2 If a quartz-fibre filter was used to collect particulate inorganic mercury compounds and it is to be analysed together with the contents of the sorbent tube to produce a combined result for mercury vapour and particulate inorganic mercury compounds, open the samplers, sampler filter cassettes or transport filter cassettes (see 10.4.5.2 through 10.4.5.4), remove the quartz-fibre filter using flat-tipped forceps (8.2.9.3) and place it in the same centrifuge tube as the sorbent and glass wool plug (11.4.1.1). Alternatively, if a separate analysis for particulate inorganic mercury compounds is required, place the filter in a separate 50 ml disposable centrifuge tube (8.3.2).

11.4.1.3 If a quartz-fibre filter was used in an inhalable sampler to determine particulate inorganic mercury compounds only, open the samplers, sampler filter cassettes or transport filter cassettes (see 10.4.5.2 through 10.4.5.4), remove the quartz-fibre filter using flat-tipped forceps (8.2.9.3) and place in a separate labelled 50 ml disposable centrifuge tube (8.3.2).

11.4.1.4 Add 2,0 ml of concentrated nitric acid (7.2) followed by 2,0 ml concentrated hydrochloric acid (7.4) to each centrifuge tube.

It is important that nitric acid be added before hydrochloric acid to ensure that mercury is oxidized to the divalent state. Otherwise mercury left in an elemental state could be lost due to volatilization[20].

If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample (see Note 2 in 8.2.5), use the nitric acid to carefully wash any particulate material adhering to the internal surfaces into the centrifuge tube, utilising a polypropylene filter funnel (8.3.10) to avoid spillage.

11.4.1.5 Tightly seal the centrifuge tubes with their screw caps or push-fit closures, and roll the tubes to wash any Anasorb from the walls. Place the tubes in a test-tube rack in a thermostatically controlled water bath (8.3.5) at 50 °C for 1 h, periodically agitating and rolling the tubes to ensure that all hopcalite is dissolved from the ceramic support material of the Anasorb granules.

Sample dissolution may also be carried out by allowing the tubes to stand at room temperature for a prolonged period, e.g. overnight.

Another alternative is to use ultrasonic extraction, but this could result in shattering of the ceramic substrate, which in turn could make it more difficult to separate from the sample solution by centrifugation or filtration (see 11.4.1.8).

11.4.1.6 Remove the tubes from the heated water bath and place them to cool in a bath of cold water. When the solutions are cool, carefully unscrew the caps from the tubes or remove the push-fit closures to release any pressure built up due to the formation of oxides of nitrogen.

11.4.1.7 Make up to the 50 ml graduation of the centrifuge tube with water (7.1), reseal the tubes and shake to mix.

NOTE Dissolution of the sample yields a dark brown liquid. When diluted to volume with water, this forms a milky blue-green suspension above a white ceramic residue from the Anasorb sorbent. The sample tubes will also contain glass wool from the sorbent tube plugs and the quartz-fibre prefilter (if used).

11.4.1.8 Centrifuge the sample solutions to remove the ceramic support material from suspension and to drive the glass wool and quartz-fibre filter to the bottom of the tubes. Alternatively, filter the suspension, having confirmed in tests that the filter used will not contaminate the solution with mercury or remove any mercury from solution.

The use of a centrifuge is preferable to filtration, since it enables the sample to be prepared and presented to the instrument without transfer from the centrifuge tube, thus speeding analysis and making contamination less likely.

11.4.1.9 Prior to analysis, uncap the centrifuge tubes and stand in a fume hood for at least 1 h to allow dissolved oxides of nitrogen to degas from the solutions.

Thorough dispersion of oxides of nitrogen from solution is particularly important when CVAFS is used, since they will otherwise quench mercury cold-vapour fluorescence. Degassing can be accelerated by passing a stream of an inert gas, such as nitrogen, through the solution prior to centrifugation.

11.4.2 Preparation of calibration solutions

11.4.2.1 Preparation of calibration solutions for the analysis of sorbent tube samples

Prepare a set of calibration solutions, including a calibration-blank solution, for use in the analysis of sorbent tubes (see 11.4.1.1) or sorbent tubes and filters (see 11.4.1.2). Take six sorbent tubes from the same batch used to collect the samples (see 10.4.2.3.4) and prepare solutions from them following the instructions given in 11.4.1.1 and 11.4.1.4 through 11.4.1.6. Make up almost to the 50 ml graduation of the centrifuge tubes with water (7.1) and then accurately pipette 100 µl, 200 µl, 300 µl, 400 µl and 500 µl of working mercury standard solution A (7.10) into five of the tubes. Finally make up to volume, centrifuge and degas as described in 11.4.1.7 through 11.4.1.9. The prepared calibration solutions have mercury concentrations of 0 $\mu g \cdot l^{-1}$, 20 $\mu g \cdot l^{-1}$, 40 $\mu g \cdot l^{-1}$, 60 $\mu g \cdot l^{-1}$, 80 $\mu g \cdot l^{-1}$ and 100 $\mu g \cdot l^{-1}$. Label the tubes accordingly.

An alternative means of reducing the cost of analysis could be to prepare 50 ml of blank solution from a single sorbent tube and carry out a standard-additions calibration by spiking aliquots of this solution with appropriate volumes of mercury standard solution.

NOTE 1 The reason for matrix-matching the calibration solutions in this manner is because the slope of the calibration is influenced by acid concentration and the acid concentration of the sample solutions is unknown due to consumption of acid during dissolution of the sorbent. Correspondingly, it has been demonstrated[4] that failure to properly matrix-match calibration and test solutions can produce high results. On the other hand, some hydride-generation systems are believed to be less sensitive to acid concentration than the system used in the validation of this method. In such circumstances, simply matching the acid content of the calibration and test solutions might be adequate to produce results of sufficient accuracy (i.e. by preparing calibration solutions in 1:1:23 nitric acid/hydrochloric acid). This would reduce the cost of analysis by eliminating the need to use sorbent tubes in the matrix-matching process. However, if the procedure described in 11.4.2 is modified in any way, it should be demonstrated that the results obtained exhibit an acceptable bias, e.g. < 5 %.

NOTE 2 The concentration range of the set of calibration solutions is given only as a guide. It is generally appropriate for sampling times of 4 to 8 h at a flow rate of 200 ml·min^{-1}. Lower concentrations might be more appropriate for shorter sampling periods.

11.4.2.2 Preparation of calibration solutions for the analysis of filter samples

Prepare a set of calibration solutions, including a calibration blank solution, for use in the analysis of filter samples only (see 11.4.1.3). Add 2,0 ml of concentrated nitric acid (7.2) and 2,0 ml of concentrated hydrochloric acid (7.4) to six 50 ml disposable centrifuge tubes (8.3.2). Make up almost to the 50 ml graduation with water (7.1) and then accurately pipette 100 µl, 200 µl, 300 µl, 400 µl and 500 µl of working mercury standard solution A (7.10) into five of the tubes. Finally, make to volume with water, tightly seal the tubes with their screw caps or push-fit closures and shake to mix. The prepared calibration solutions have mercury concentrations of 0 µg·l^{-1}, 20 µg·l^{-1}, 40 µg·l^{-1}, 60 µg·l^{-1}, 80 µg·l^{-1} and 100 µg·l^{-1}. Label the tubes accordingly.

The concentration range of the set of calibration solutions is given only as a guide. Sample dilution will be necessary to make measurements within this concentration range if the concentration of mercury in the air is relatively high (e.g. up to 0,05 mg·m^{-3}) and the air sample volume is relatively large (e.g. when sampling for $>$ 1 h at a flow rate of 2 l·min^{-1}). Accordingly, it might be desirable to vary the range of the set of calibration solutions. However, when making any changes ensure that the response of the spectrometer over the alternative range of concentrations is such that it complies with the limitations on curvature specified in 11.5.5.3. The upper limit of the working range is dependent upon the performance characteristics of the cold-vapour generation system used (8.4.2.1 or 8.4.2.2) and other instrumental factors that affect sensitivity and the linearity of the calibration.

11.5 Instrumental analysis

11.5.1 Setting up the instrument

11.5.1.1 Setting up the mercury cold-vapour system

11.5.1.1.1 Prepare the mercury cold-vapour generation system (8.4.2.1 or 8.4.2.2) for operation, following the manufacturer's instructions. Fill the reservoir for reductant with tin(II) chloride solution (7.8). If analysing sorbent tube samples, fill the acid blank reservoir with 1:1:23 nitric acid/hydrochloric acid (7.5). If analysing diffusive badge samples, fill the acid blank reservoir with 2:2:21 nitric acid/hydrochloric acid (7.6).

11.5.1.1.2 Set the purge-gas flow rate to the value recommended for the application by the manufacturer of the mercury cold-vapour generation system.

11.5.1.1.3 Mercury cold-vapour generation systems are sensitive to change in temperature. Reagents and test solutions should therefore be allowed to equilibrate to room temperature before commencing analysis.

11.5.1.1.4 The length of tubing connecting the measurement cell to the outlet of the gas/liquid separator of the mercury cold-vapour generation system should be kept to a minimum.

NOTE Optimum concentrations of reagents, liquid flow rates, purge-gas flow rate, etc. could vary somewhat according to the exact configuration of the mercury cold-vapour generation system.

11.5.1.2 Setting up the spectrometer

Set up the spectrometer (8.4.1.1 or 8.4.1.2) to make atomic absorbance measurements or atomic fluorescence measurements at the 253,7 nm mercury line, following the manufacturer's recommendations for specific instrument operating parameters.

11.5.2 Introduction of solutions into the mercury cold-vapour generation system

11.5.2.1 Introduce the calibration solutions and the blank and sample test solutions into the mercury cold-vapour generation system by placing the sample uptake tubing into the solution concerned. This may be carried out manually or by using an autosampler.

11.5.2.2 Begin with the mercury cold-vapour system in the configuration in which acid blank is pumped to the mixing piece.

11.5.2.3 In the case of a continuous-flow system, change the configuration so that the test solution is pumped to the mixing piece until a maximum atomic spectrometer signal is obtained (see Figure 8).

11.5.2.4 In the case of a flow-injection system, operate the sample injection valve so that a precise volume of the test solution is injected into the acid blank stream, resulting in a peak in the atomic spectrometer signal (see Figure 6).

11.5.2.5 In the case of a discrete injection system, change the configuration to pump test solution for a precise period of time, so that a precise volume is delivered to the mixing piece, resulting in a peak in the atomic absorption or atomic fluorescence signal (see Figure 7).

11.5.2.6 Blockages are likely to occur if ceramic residue, glass fibre or quartz fibre driven to the bottom of the centrifuge tubes is drawn into the uptake tubing. Care should be taken that this undissolved material is not disturbed during analysis. When using an autosampler, it is important that the tip of the sample probe be positioned well away from the bottom of the tube during solution uptake.

11.5.3 Conditioning the mercury cold-vapour generation system

11.5.3.1 Condition the mercury cold-vapour system before use in order to ensure that a stable signal is obtained before proceeding to carry out a calibration.

11.5.3.2 Place the reductant, acid blank and sample uptake tubing in a container of water (7.1) and allow the pump(s) to operate for at least 5 min for the flow rates to stabilize. Fill a 10 ml measuring cylinder (8.3.1.3) to a convenient mark with water and determine each flow rate in turn by placing the appropriate uptake tubing in the measuring cylinder of water and observing the volume of water pumped out in 1 min. Verify that the flow rates are within the nominal specification recommended by the manufacturer of the mercury cold-vapour generation system, and adjust the pressure exerted on the peristaltic pump tubing by the pump head and/or install new pump tubing if necessary. Replace the uptake tubing for reductant and acid blank in the appropriate reservoirs.

Follow either a) or b).

a) For **continuous flow** and **discrete injection** mercury cold-vapour generation systems, alternately pump acid blank (7.5 or 7.6) and the high calibration solution (11.3.2 or 11.4.2) to the mixing piece and make repeat absorbance or fluorescence measurements with a suitably short integration period. Continue this sequence until a repeatable analytical response is obtained, and record the parameters necessary for operation of the continuous cold-vapour system used.

   In the case of continuous-flow systems, record the stabilization delay time, which is the time taken for the analytical response to reach a stable value when a solution is presented to the system, and the baseline delay time, which is the time taken for the signal response to return to the baseline when the acid blank is pumped again.

   In the case of discrete injection systems, select a suitable injection period during which test solution is pumped to the mixing piece in order to obtain an output signal peak of the required height. Note the peak delay time, which is the time taken for the peak maximum to be obtained, and the baseline delay time, which is the time taken for the signal response to return to the baseline when the acid blank is pumped again.

b) For **flow injection analysis** mercury cold-vapour generation systems, fill the sample loop by pumping the high calibration solution (11.3.2 or 11.4.2) through it and then inject into the acid blank (7.5 or 7.6) stream. Note the peak delay time and the baseline delay time.

11.5.3.3 Optimize integration or peak-height measurement parameters and then make repeat injections until a repeatable analytical response is obtained. If a repeatable analytical response cannot be obtained, this is likely to be due to contamination of the system. In this case, suspend further operations and clean the gas/liquid separator and the silica or quartz absorption cell.

11.5.3.4 If the cold-vapour/atomic spectrometer system is interfaced to a microprocessor or personal computer for automatic control, set the necessary delay times and other parameters to the appropriate value(s).

11.5.4 Check for contamination of the reagents and/or system

11.5.4.1 Place the reductant, acid blank and sample uptake tubing into a container of water (7.1) and, after allowing sufficient time for flushing out the system, adjust the spectrometer zero.

11.5.4.2 Replace the uptake tubing for reductant and acid blank in the appropriate reservoirs. Pump acid blank (7.5 or 7.6) and reductant (7.8) to the mixing piece and measure the atomic absorbance or atomic fluorescence signal after allowing sufficient time for the water to be displaced.

11.5.4.3 If the atomic absorbance or atomic fluorescence background signal is significantly higher than expected, based on previous experience, consider whether contamination of the reagents or contamination of the system is the more likely cause of the elevated response. If it is considered that contamination of the reagents is the more likely explanation, prepare new reductant (7.8) and acid blank (7.5 or 7.6). If it is considered that contamination of the system is the more likely explanation, clean the gas/liquid separator of the mercury cold-vapour generation system (8.4.2). Then repeat the check described in 11.5.4.1 and 11.5.4.2.

NOTE If the atomic absorbance or atomic fluorescence background signal is elevated, the analytical performance of the system will be degraded and, in particular, the instrumental detection limit will be poorer.

11.5.5 Calibration

11.5.5.1 Adjust the spectrometer zero whilst pumping acid blank (7.5 or 7.6) and reductant (7.8) to the mixing piece of the cold-vapour generation system.

Then follow either a) or b).

a) For **continuous flow** and **discrete injection** cold-vapour generation systems, pump each calibration solution (11.3.2 or 11.4.2) in turn through the sample uptake tubing to the mixing piece and take the maximum atomic absorbance or atomic fluorescence reading after the determined stabilisation delay time or peak delay time [see 11.5.3.2 a)]. Pump acid blank (7.5 or 7.6) to the mixing piece in between each calibration solution and wait for the determined baseline delay time [see 11.5.3.2 a)] before proceeding to measure the next calibration solution.

b) For **flow injection** cold-vapour generation systems, inject each calibration solution (11.3.2 or 11.4.2) in turn into the acid blank stream, measure the peak height or peak area of the atomic absorbance or atomic fluorescence signal and wait for the determined baseline delay time [see 11.5.3.2 b)] before proceeding to measure the next calibration solution.

11.5.5.2 For instruments controlled by a microprocessor or personal computer, use a suitable algorithm to generate the calibration function. For instruments without this capability, prepare a calibration graph by plotting the absorbance or fluorescence of the calibration solutions versus the concentration of mercury, in $\mu g \cdot l^{-1}$.

11.5.5.3 In general it is best to work in the linear range of an atomic absorption calibration, where absorbance is proportional to the concentration of mercury in solution. A certain amount of curvature can be tolerated but ideally the slope of the top 20 % of the calibration curve should be not less than 70 % of the

slope of the bottom 20 %, calculated in the same manner. Discretion should be exercised in assessing whether recalibration over a lower concentration range is necessary. Mercury cold-vapour atomic fluorescence calibration curves are, by contrast, typically close to linear over several orders of magnitude of concentration.

11.5.6 Determination

11.5.6.1 Follow the procedure given in either a) or b) below.

a) For **continuous flow** or **discrete injection** cold-vapour generation systems, adjust the spectrometer zero whilst pumping the acid blank (7.5 or 7.6) to the mixing piece. Pump the blank and sample test solutions (11.3.1 or 11.4.1) in turn through the sample uptake tubing to the mixing piece, and take the maximum atomic absorbance or atomic fluorescence reading after the determined stabilization delay time or peak delay time [see 11.5.3.2 a)]. Pump acid blank to the mixing piece in between each test solution and wait for the determined baseline delay time [see 11.5.3.2 a)] before proceeding to measure the next test solution.

b) For **flow injection** cold-vapour generation systems, pump sample and blank and sample test solutions (11.3.1 or 11.4.1) sequentially through the sample valve, inject into the acid blank stream (7.5 or 7.6) and measure the peak height or peak area of the atomic absorbance or atomic fluorescence signal. Pump acid blank to the mixing piece in between each test solution, and wait for the determined baseline delay time (see 11.5.3.4) before proceeding to measure the next test solution.

11.5.6.2 If baseline drift is observed whilst pumping acid blank, then readjust the spectrometer zero.

11.5.6.3 For instruments controlled by a microprocessor or personal computer, use the calibration function (see 11.5.5.2) to calculate the concentration of mercury in the blank and sample test solutions and obtain a direct read out of the results in concentration units. For instruments without this capability, determine the concentration of mercury in the blank and sample test solutions from the peak height or peak area measurements using the calibration graph (see 11.5.5.2).

11.5.6.4 Analyse a mid-range calibration solution after each five to ten test solutions. If the absorbance reading indicates that the sensitivity has changed by more than $\pm$ 5 %, take one of the following corrective measures. Either use the available software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility) or suspend analysis and recalibrate the spectrometer as described in 11.5.5.1 through 11.5.5.3. In either case, reanalyse the test solutions that were analysed during the period in which the sensitivity change occurred.

11.5.6.5 Analyse reagent blank and laboratory blank solutions, as specified in 11.7.1.1, and quality control solutions, as specified in 11.7.1.2, and use the results to monitor the performance of the method as specified in 11.7.2.1 and 11.7.2.2.

11.5.6.6 If the concentrations of mercury found are above the upper limit of the calibration range, dilute the sample solution by a suitable factor with calibration blank solution (11.3.2, 11.4.2.1 or 11.4.2.2) and repeat the analysis. Record the dilution factor.

11.5.6.7 Calculate the mean mercury concentration of the blank test solutions.

11.6 Estimation of detection and quantification limits

11.6.1 Estimation of the instrumental detection limit

11.6.1.1 Estimate the instrumental detection limit under the working analytical conditions following the procedure described in 11.6.1.2 and 11.6.1.3 and repeat this exercise whenever the experimental conditions are changed.

NOTE The instrumental detection limit is of use in identifying changes in instrument performance, but it is not a method detection limit[29]. An instrumental detection limit is likely to be lower than the method detection limit because it

only takes into account the variability between individual instrumental readings; determinations made on one solution do not take into consideration contributions to variability from the matrix or sample.

11.6.1.2 Prepare a test solution with a mercury concentration near the anticipated instrumental detection limit, e.g. 0,001 $mg \cdot l^{-1}$ of mercury, by diluting working mercury standard solution B (7.11) by an appropriate factor with 1:1:23 nitric acid and hydrochloric acid (7.5).

11.6.1.3 Make at least ten atomic absorbance or atomic fluorescence measurements on the test solution (11.6.1.2) and calculate the instrumental detection limit as three times the sample standard deviation of the mean concentration value.

NOTE An alternative procedure for estimating the instrumental detection limit involves the analysis of calibration blank solution fortified with the mercury at concentrations spanning the predicted instrumental detection limit[29].

11.6.2 Estimation of the method detection limit and the quantification limit

11.6.2.1 Estimate the method detection limit and the quantification limit under the working analytical conditions, following the procedure described in 11.6.2.2 and 11.6.2.3, and repeat this exercise whenever the experimental conditions are changed significantly.

11.6.2.2 Prepare at least ten laboratory blank test solutions from unused sorbent capsules (8.1.2), sorbent tubes (8.2.1) or filters, as appropriate, following the sample dissolution procedure used to prepare sample test solutions in 11.3 or 11.4.

11.6.2.3 Make atomic absorbance or atomic fluorescence measurements on the test solutions (11.6.2.2) and calculate the method detection limit and the quantification limit as three times and ten times the sample standard deviation of the mean concentration, respectively.

11.7 Quality control

11.7.1 Reagent blanks and laboratory blanks

11.7.1.1 Carry reagent blanks (see 3.4.9) and laboratory blanks (see 3.4.5) throughout the entire sample preparation and analytical process. Prepare and analyse reagent blank and laboratory blank test solutions according to a frequency of at least 1 per 20 samples, or a minimum of one per batch.

11.7.1.2 If results for reagent blanks and/or laboratory blanks are significantly higher than expected, based on previous experience, investigate whether contamination is occurring from laboratory activities and/or the batch of filters used for sampling and take appropriate corrective action to ensure that this does not re-occur.

11.7.2 Quality control solutions

11.7.2.1 Carry spiked samples and spiked duplicate samples throughout the entire sample preparation and analytical process to estimate the method accuracy on the sample batch, expressed as a percent recovery relative to the true spiked value. Spiked samples and spiked duplicate samples consist of sorbent capsules or sorbent tubes to which known amounts of mercury have been added. (This can be accomplished by spiking with known volumes of mercury standard solution at amounts within the dynamic range of the instrument. The mercury standard solution used shall be prepared from a stock standard solution from a source different than that used for preparing the calibration solutions.) Prepare and analyse these quality control solutions according to a frequency of at least 1 per 20 samples, or a minimum of one per batch.

11.7.2.2 Monitor the performance of the method by plotting control charts of the relative percent recoveries and of the relative percent differences between the spiked samples and the spiked duplicate samples. If QC results indicate that the method is out of control, investigate the reasons for this, take appropriate corrective action and reanalyse the samples if necessary. See ASTM E 882-97[30] for general guidance on the use of quality control charts.

11.7.3 Certified reference materials (CRMs)

If available, certified reference materials (CRMs) for mercury shall be analysed prior to routine use of the method to establish that the percent recovery relative to the certified value is satisfactory.

11.7.4 External quality assessment

If laboratories carry out mercury in air analysis on a regular basis, it is recommended that they participate in a relevant external quality assessment scheme or proficiency testing scheme, if such a scheme exists and they have access to it.

11.8 Measurement uncertainty

It is strongly recommended that laboratories estimate and report the uncertainty of their measurements in accordance with the ISO GUM[17]. The first step is to construct a cause and effect diagram[31] to identify the individual sources of random and systematic error in the method. These are then estimated and/or determined experimentally and combined in an uncertainty budget. Finally, the combined uncertainty is multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of 2 is recommended, which gives a level of confidence of approximately 95 % in the calculated value.

NOTE 1 References [32] and [33] describe the application of cause-and-effect analysis to analytical methods.

NOTE 2 Terms that contribute to the random variability of the method are generally accounted for in the measurement precision, which can be determined from quality control data. Error associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the drift permitted before the instrument is recalibrated (see 11.5.6.4) by $\sqrt{3}$.

NOTE 3 Systematic errors include, for example, those associated with method recovery, sample recovery, preparation of working standard solutions, dilution of test solutions, etc.

12 Expression of results

12.1 Calculation of the volume of air samples

12.1.1 Diffusive sampling

Calculate the volume of the air sampled, in litres, by multiplying the sample uptake rate given by the manufacturer of the diffusive badge, in millilitres per minutes, by the duration of the sampling period, in minutes, and dividing by 1 000. If appropriate (see 10.2.1), calculate the mean atmospheric temperature and pressure by averaging the measurements taken at the start and end of the sampling period and apply a temperature and pressure correction using the equation given in B.1.

NOTE The nominal sample uptake rate given by a manufacturer[23] of diffusive badges is 20,0 $ml \cdot min^{-1}$ at a temperature of 20 °C and a pressure of 101,3 kPa.

12.1.2 Pumped sampling

Calculate the mean volumetric flow rate by averaging the measurements taken at the start and end of the sampling period. If appropriate, (see 10.2.2), calculate the mean atmospheric temperature and pressure by averaging the measurements taken at the start and end of the sampling period and apply a temperature and pressure correction to the mean volumetric flow rate. Follow the guidance given in B.2. Then calculate the volume of the air sampled, in litres, by multiplying the mean volumetric flow rate, in litres per minute, by the duration of the sampling period, in minutes.

12.2 Calculation of mercury in air concentrations

12.2.1 Calculate the mass concentration of mercury in the air samples at ambient conditions, using the equation:

$$\rho_{Hg} = \frac{\left[\left(\rho_{Hg,1} \times V_1 \times F\right) - \left(\rho_{Hg,0} \times V_0\right)\right] \times 1000}{V}$$

where

ρ_{Hg} is the calculated mass concentration of mercury in the air sample, in milligrams per cubic metre, at ambient conditions;

$\rho_{Hg,0}$ is the mean mass concentration of mercury in the blank test solutions, in micrograms per litre (see 11.5.6.7);

$\rho_{Hg,1}$ is the mass concentration of mercury in the sample test solution, in micrograms per litre (see 11.5.6.3);

V is the volume, in litres, of the air sample (see 12.1);

V_0 is the volume, in millilitres, of the blank test solutions (see 11.3.1.5 or 11.4.1.7);

V_1 is the volume, in millilitres, of the sample test solution (see 11.3.1.5 or 11.4.1.7); and

F is the dilution factor used in 11.5.6.6 ($F = 1$ in the absence of dilution).

12.2.2 If it is necessary to recalculate mercury in air concentrations to reference conditions (see 10.2.3), calculate the mean atmospheric temperature and pressure by averaging the measurements taken at the start and end of the sampling period and apply a temperature and pressure correction to mercury in air concentrations calculated in 12.2.1 using the equation given in B.3.

13 Method performance

13.1 General

The method performance data given in this clause relate to the particular commercially available diffusive badges[22],[23] and sorbent tubes[24],[25] that were evaluated in the method validation work[4]. Other diffusive badges and sorbent tubes could have different performance characteristics.

13.2 Detection and quantification limits

13.2.1 Sampling with diffusive badges and analysis by cold-vapour atomic absorption spectrometry

Using flow injection CVAAS, the method detection limit and quantification limit for mercury, defined as three times and ten times the standard deviation of a blank determination, respectively, have been determined[4] to be 0,012 µg and 0,040 µg for samples of mercury vapour collected using a diffusive badge. For the minimum sampling time of 6 h (equivalent to an air sample volume of 7,2 l), this corresponds to mercury-in-air concentrations of 0,002 mg·m^{-3} and 0,006 mg·m^{-3}, respectively.

13.2.2 Sampling with pumped sorbent tubes and analysis by cold-vapour atomic absorption spectrometry

Using flow injection CVAAS, the method detection limit and quantification limit for mercury, defined as three times and ten times the standard deviation of a blank determination, respectively, have been determined[4] to be 0,009 µg and 0,030 µg for samples of mercury vapour collected on sorbent tubes containing 200 mg of

Anasorb and 0,010 µg and 0,033 µg for samples of total inorganic mercury (mercury vapour and particulate inorganic mercury compounds) collected on sorbent tubes containing 200 mg of Anasorb with quartz-fibre prefilters. For the minimum air sample volume of 12 l, this corresponds to mercury-in-air concentrations of 0,001 $mg \cdot m^{-3}$ and 0,003 $mg \cdot m^{-3}$, respectively, in both cases.

13.2.3 Sampling with pumped sorbent tubes and analysis by cold-vapour atomic fluorescence spectrometry

Using discrete injection CVAFS, the method detection limit and quantification limit for mercury, defined as three times and ten times the standard deviation of a blank determination, respectively, have been determined[4] to be 0,002 µg and 0,008 µg for samples of mercury vapour collected on sorbent tubes containing 200 mg of Anasorb. For the minimum air sample volume of 12 l, this corresponds to mercury-in-air concentrations of 0,000 2 $mg \cdot m^{-3}$ and 0,000 7 $mg \cdot m^{-3}$, respectively.

13.2.4 Sampling with inhalable samplers and analysis by cold-vapour atomic absorption spectrometry

Using flow injection CVAAS, the method detection limit and quantification limit for mercury, defined as three times and ten times the standard deviation of a blank determination, respectively, have been determined[4] to be 0,003 µg and 0,009 µg for samples of particulate inorganic mercury compounds collected on quartz-fibre filters. For the minimum air sample volume of 30 l, this corresponds to mercury-in-air concentrations of 0,000 1 $mg \cdot m^{-3}$ and 0,000 3 $mg \cdot m^{-3}$, respectively.

13.3 Upper limits of the analytical range

13.3.1 The upper limit of the useful analytical range is determined by the linear dynamic range of the spectrometer.

13.3.2 Using a flow injection CVAAS system with a 0,5 ml sample injection volume, the calibration obtained[4] was significantly curved at mercury concentrations above 0,1 $mg \cdot l^{-1}$. This is equivalent to 2,5 µg of mercury for the 25 ml sample solution volume used for diffusive badges or 5 µg of mercury for the 50 ml sample solution volume used for pumped samplers. If greater amounts of mercury are collected, dilution of sample solutions or the use of a smaller sample loop is required.

13.3.3 Using discrete injection CVAFS, the calibration obtained[4] was close to linear over a much greater concentration range, and mercury concentrations up to at least 10 $mg \cdot l^{-1}$ could be measured without dilution of the sample. This is equivalent to 250 µg of mercury for the 25 ml sample solution volume used for diffusive badges or 500 µg of mercury for the 50 ml sample solution volume used for pumped samplers.

13.4 Blank values

Anasorb used in diffusive badge sorbent capsules and sorbent tubes contains trace amounts of mercury. Laboratory experiments[4] have established that the 800 mg of Anasorb used in sorbent capsules typically has a mercury blank of 0,08 µg, whilst the 200 mg of Anasorb used in standard sorbent tubes typically contains 0,02 µg of mercury.

NOTE The blank due to mercury impurities in the Anasorb has much more influence on the accuracy of analysis of diffusive badges than on that of pumped sorbent tubes. This is because the quantity of Anasorb is four times greater and because the sampling rate is 10 times lower. The net effect is to make the blank 40 times greater compared with the mass of mercury sampled. Technically, both methods do not meet the EN 838[11] and EN 1076[12] requirement that the blank value should not exceed 1/3 of the mass of analyte collected at 1/10 of the limit value for the minimum sampling time. However, the consistency of the mercury blanks within batches of sorbent capsules and sorbent tubes is such that conformity with the overall performance requirements of the standards is nevertheless achieved using both sampling methods.

13.5 Bias and precision

13.5.1 Analytical bias

Laboratory experiments have shown that the analytical method does not exhibit significant bias. The mean analytical recovery has been determined[4] to be 97,4 % for sorbent tubes containing 200 mg of Anasorb dosed in the range 0,15 µg to 4,8 µg of mercury, 96,2 % for quartz-fibre prefilters and sorbent tubes containing 200 mg of Anasorb dosed with 2,4 µg mercury and 93,3 % for quartz-fibre filters dosed with 2,4 µg mercury.

13.5.2 Analytical precision

The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), is dependent on a number of factors, including the analytical instrumentation used, and is at a minimum when the concentration of mercury in the test solution is in the mid-range of the calibration. Laboratory experiments have been carried out to obtain figures of merit for CV(analysis). Using flow injection CVAAS, CV(analysis) has been determined[4] to be 0,7 % for sorbent tubes containing 200 mg of Anasorb dosed with 2,4 µg of mercury, 3,9 % for sorbent tubes containing 200 mg of Anasorb with quartz-fibre prefilters dosed with 2,4 µg of mercury and 2,2 % for quartz-fibre filters dosed with 2,4 µg of mercury. Using discrete injection CVAFS, CV(analysis) has been determined[4] to be 4,1 % for sorbent tubes containing 200 mg of Anasorb dosed with 2,4 µg of mercury

13.5.3 Overall bias of sampling and analysis methods

Laboratory experiments have been performed[4] to determine the overall bias of the combined sampling and analysis methods. These experiments were carried out by sampling mercury vapour generated at concentrations between 0,002 5 $mg \cdot m^{-3}$ and 0,05 $mg \cdot m^{-3}$ at a temperature of 20 °C and a relative humidity of 50 %, and comparing results with an independently calibrated method. An average recovery of 91,8 % was obtained for sorbent tubes containing 200 mg of Anasorb, referenced against direct analysis using gold trapping thermal desorption atomic fluorescence spectrometry. The two methods agreed to better than $\pm$ 10 % and it was therefore concluded that the sorbent tube method exhibits no significant bias. An average recovery of 92,4 % was obtained for diffusive badges when compared with measurements made using the sorbent tubes containing 200 mg of Anasorb. This result, which is consistent with a systematic bias of $-$ 7 % reported by OSHA[5], can be attributed to a small error in the nominal uptake rate of the diffusive badges given by the manufacturer[23].

13.5.4 Overall precision of sampling and analysis methods

Laboratory experiments have been performed[4] to determine the overall coefficient of variation, CV(overall), of the combined sampling and analysis methods. These experiments were carried out by sampling mercury vapour generated at concentrations between 0,002 5 $mg \cdot m^{-3}$ and 0,05 $mg \cdot m^{-3}$ at a temperature of 20 °C and a relative humidity of 50 %. The average CV(overall) determined using flow injection CVAAS was 3,7 % for samples collected on sorbent tubes containing 200 mg of Anasorb at 200 $ml \cdot min^{-1}$ for sampling periods ranging from 1 h to 8 h and 6,3 % for samples collected on diffusive badges for sampling periods ranging from 2 h to 8 h.

13.6 Overall uncertainty of sampling and analysis methods

13.6.1 Laboratory experiments have been performed[4] in accordance with the procedures given in EN 838[11] to assess whether the diffusive badge method for measurement of mercury vapour meets the general performance requirements specified in EN 482[14] for the overall uncertainty of measurements made for comparison with limit values. The results demonstrated that, for measurements made for comparison with a limit value of 0,025 $mg \cdot m^{-3}$, the method meets the overall uncertainty requirements for sampling times close to 8 h, but not for sampling times as short as 4 h.

NOTE EN 482[14] provides general requirements for the performance of procedures for the measurement of chemical agents in workplace atmospheres. Upper limits of acceptability for overall uncertainty have been specified for a number of measurement tasks and these are used as a guideline for the purposes of this International Standard. EN requirements

are less stringent for screening measurements than for measurements for comparison with limit values; and they are less stringent for measurements for comparison with limit values when these are made in the range 0,1 to 0,5 times the exposure limit value (overall uncertainty < 50 %) than when they are made in the range 0,5 to 2,0 times the exposure limit value (overall uncertainty < 30 %).

13.6.2 Laboratory experiments have been performed[4] in accordance with the procedures given in EN 1076[12] to assess whether the pumped sorbent tube method for measurement of mercury vapour meets the general performance requirements specified in EN 482 for the overall uncertainty of measurements made for comparison with limit values. The results demonstrated that, for measurements made for comparison with a limit value of 0,025 $mg \cdot m^{-3}$ using a sorbent tube containing 200 mg of Anasorb at a sampling rate of 200 $ml \cdot min^{-1}$, the method meets the overall uncertainty requirements for sampling times in the range 1 h to 8 h.

13.6.3 Laboratory experiments have been performed[4] in accordance with the procedures given in EN 13890[34] to assess whether the pumped sampling methods for measurement of particulate inorganic mercury compounds meet the general performance requirements specified in EN 482[14] for the overall uncertainty of measurements made for comparison with limit values. The results demonstrated that, for measurements made for comparison with a limit value of 0,025 $mg \cdot m^{-3}$ using a sorbent tube containing 200 mg of Anasorb with a quartz-fibre prefilter at a sampling rate of 200 $ml \cdot min^{-1}$, the method meets the overall uncertainty requirements for sampling times in the range 1 h to 8 h. For measurements made for comparison with a limit value of 0,025 $mg \cdot m^{-3}$ using a quartz-fibre filter mounted in an inhalable sampler used at a typical sampling rate of 2 $l \cdot min^{-1}$, the method meets the overall uncertainty requirements for sampling times as short as 15 min.

13.6.4 Flow injection CVAAS was used for measuring mercury in all the experiments referred to in 13.6.1 through 13.6.3. However it was demonstrated[4] that equally good performance could be obtained using discrete injection CVAFS.

13.7 Effects on sampler performance

13.7.1 Effect of exposure concentration and time on sampler performance

13.7.1.1 Laboratory experiments have been performed[4] in accordance with the procedures given in EN 838[11] to determine the effect of exposure concentration and time on the performance of the diffusive badges. These experiments were carried out by sampling mercury vapour generated at concentrations between 0,002 5 $mg \cdot m^{-3}$ and 0,05 $mg \cdot m^{-3}$ at a temperature of 20 °C and a relative humidity of 50 %. Results demonstrated that the effect of exposure concentration is negligible for sampling periods close to 8 h.

13.7.1.2 Laboratory experiments have been performed[4] in accordance with the procedures given in EN 1076[12] to determine the effect of exposure concentration and time on the performance of sorbent tubes containing 200 mg of Anasorb. These experiments were carried out by sampling mercury vapour generated at concentrations between 0,002 5 $mg \cdot m^{-3}$ and 0,05 $mg \cdot m^{-3}$ at a temperature of 20 °C and a relative humidity of 50 %. Results demonstrated that the effect of exposure concentration and time is negligible for sampling periods up to 8 h.

13.7.2 Effect of atmospheric temperature, pressure and humidity on sampler performance

13.7.2.1 Laboratory experiments have been performed[4] in accordance with the procedures given in EN 838[11] to determine the effect of atmospheric temperature and humidity on the performance of the diffusive badges. These experiments were carried out by sampling mercury vapour at a concentration of 0,05 $mg \cdot m^{-3}$ at temperature extremes of 5 °C and 40 °C and relative humidity extremes of 20 % and 70 %. Results showed that the method complies with the performance requirements of EN 482 within these extremes of temperature and humidity. However, they also indicated that the use of a temperature-corrected uptake rate could significantly improve accuracy at the extremes of the temperature range tested (see 10.2.1).

13.7.2.2 Laboratory experiments have been performed[4] in accordance with the procedures given in EN 1076[12] to determine the effect of atmospheric temperature and humidity on the performance of sorbent tubes containing 200 mg of Anasorb. These experiments were carried out by sampling mercury vapour at a concentration of 0,05 $mg \cdot m^{-3}$ at temperature extremes of 5 °C and 40 °C and relative humidity extremes of

20 % and 70 %. Results demonstrated that the effect of temperature and humidity is negligible within these extremes.

13.7.2.3 In accordance with 5.6.2 of ISO 16107:1999[35], no laboratory experiments were performed to assess the effect of pressure on the performance of the diffusive badges, because there is no reason to suspect that use of the formula given in B.1 will lead to error in the corrected sample uptake rate.

13.7.2.4 Similarly, no laboratory experiments were performed to assess the effect of pressure on the performance of sorbent tubes, because there is no reason to suspect that use of an appropriate correction factor, where necessary (see B.2), will lead to error in the corrected air sample volume.

13.7.3 Effect of air velocity on performance of diffusive badges

The manufacturer's literature[22],[23] states that the uptake rate of the diffusive badge remains more or less constant for wind speeds in the range 7,5 $m \cdot min^{-1}$ to 230 $m \cdot min^{-1}$. However, in still air conditions (below about 7,5 $m \cdot min^{-1}$) the uptake rate can drop by up to 30 % and in very high wind speeds (in excess of about 230 $m \cdot min^{-1}$) erratic increases in sampling rate can occur. Similar data have been obtained in laboratory experiments carried out by OSHA[5]. The observed face velocity effects have implications for the field of application of diffusive badges (see A.1.2).

13.8 Sample uptake rate and sampling capacity of diffusive badges

13.8.1 The sample uptake rate of the diffusive badge given by the manufacturer[23] is 20,0 $ml \cdot min^{-1}$ at 20 °C and a pressure of 101,3 kPa. This compares with an uptake rate of 18,5 $ml \cdot min^{-1}$ determined by OSHA[5] and an uptake rate of 18,6 $ml \cdot min^{-1}$ determined by HSL[4] in laboratory experiments carried out in accordance with the procedures given in EN 838[11] at a temperature of 20 °C and a relative humidity of 50 %. Despite the close agreement between these two sets of experimental data, it is recommended that the 20,0 $ml \cdot min^{-1}$ nominal uptake rate given by the manufacturer is used to calculate the concentration of mercury in air. Although this appears to introduce a sampling bias of – 7 %, the overall uncertainty requirements of EN 482 were nevertheless found to be met (see 13.6.1).

13.8.2 Laboratory experiments carried out by OSHA with diffusive badges have shown[5] that mercury vapour concentrations of 0,21 $mg \cdot m^{-3}$ can be sampled for up to 120 h without a decrease in uptake rate. This indicates that the sampling capacity of the 800 mg of Anasorb contained in the diffusive badges is at least 30 µg of mercury vapour.

13.9 Collection efficiency, breakthrough volume and sampling capacity of sorbent tubes

Laboratory experiments have shown[4] that the collection efficiency of sorbent tubes is close to 100 %. Breakthrough was found to be less than 0,5 % when sampling mercury vapour at a concentration of 0,05 $mg \cdot m^{-3}$ for 24 h using an elevated flow rate of 500 $ml \cdot min^{-1}$ at a temperature of 20 °C and a relative humidity of 50 %. The breakthrough volume is therefore greater than 720 l for mercury vapour at a concentration of 0,05 $mg \cdot m^{-3}$. This corresponds to a sampling capacity of at least 36 µg of mercury vapour.

13.10 Storage stability

Laboratory experiments have shown[5] that samples of mercury vapour collected using diffusive badges are stable for at least one month when the sorbent capsules are sealed in the plastic pouches in which they were supplied, and that samples of mercury vapour collected using pumped sorbent tubes are stable for at least one month when the tubes are sealed with their plastic caps.

NOTE Anecdotal evidence suggests that samples are stable for periods much longer than one month.

13.11 Mechanical strength

Mechanical strength tests specified, such as those in EN 838[11], have not been carried out on the diffusive badges. However, it has been observed[4] that Anasorb granules can be pulverized somewhat when a sorbent capsule is loaded into a diffusive badge and rapped repeatedly. As a result, Anasorb can escape from the

sorbent capsule and contaminate the gauze discs used in the sampler. A significant proportion of the mercury sampled could be trapped on contaminated gauze and therefore not enter the sorbent capsule. It is therefore possible that the diffusive badge would not pass the mechanical strength test. Consequently, it is recommended that the diffusive badge be regarded as unsuitable for personal sampling of workers carrying out vigorous tasks in which it is inevitable that the diffusive badges will be repeatedly knocked.

13.12 Interferences

13.12.1 In the chloralkali process, mercury vapour commonly co-exists in the atmosphere with chlorine. Chlorine can react with mercury vapour in the air to form particulate mercuric chloride[26] and therefore diffusive badges are unsuitable for measuring mercury in air concentrations in chloralkali works. However, chlorine does not interfere with the sampling process using sorbent tubes. This is because the particulate mercuric chloride formed is trapped on the glass wool retaining plugs or on the prefilter, if used, and it is subsequently analysed together with mercury vapour collected on the sorbent.

13.12.2 No data are available concerning whether gaseous organomercury compounds are collected by Anasorb and neither the diffusive badge method nor the pumped sorbent tube method has been assessed to establish whether it collects and measures organomercury compounds. If present and collected, these compounds could cause a positive interference.

13.12.3 If organomercury compounds contained within or adsorbed onto airborne particles are present in the test atmosphere, they will be collected on filters along with particulate inorganic mercury compounds. The effectiveness of the sample dissolution method described has not been assessed for organomercury compounds, but, if present, they could cause a positive interference in the measurement of particulate inorganic mercury compounds.

13.12.4 Any compound with the same absorption wavelength as mercury (253,7 nm) can cause interference in CVAAS. Some volatile organic compounds (e.g. benzene, toluene, acetone and carbon tetrachloride) absorb at this wavelength and are considered analytical interferences. These compounds are not expected to be retained on Anasorb during sample collection, but they can occur as contaminants in the reagents used during sample dissolution. However, such analytical interferences are rendered insignificant by using organic-free deionized water and reagent grade chemicals or by blank subtraction. CVAFS does not suffer from interference by volatile organic compounds that absorb at 253,7 nm, since they do not re-emit at this wavelength[36].

14 Test report

14.1 Test record

A comprehensive record of the test performed shall be maintained, including the following information:

a) a statement to indicate the confidentiality of the information supplied, if appropriate;

b) a complete identification of the air sample, including

   1) the date of sampling,

   2) the place of sampling,

   3) the type of sample (personal or static),

   4) either the identity of the individual whose breathing zone was sampled (or other personal identifier) or the location at which the general occupational environment was sampled (for a static sample),

   5) a very brief description of the work activities that were carried out during the sampling period,

   6) a unique sample identification code;

c) a reference to this International Standard;

d) the make and type of diffusive badge or sorbent tube and/or sampler used;

e) the make, type and diameter of filter used, if appropriate;

f) for pumped sampling, the make and type of sampling pump used and its identification;

g) for pumped sampling, the make and type of flowmeter used, the primary standard against which the calibration of the flowmeter was checked, the range of flow rates over which the calibration of the flowmeter was checked and the atmospheric temperature and pressure at which the calibration of the flowmeter was checked, if appropriate;

h) the time at the start and at the end of the sampling period and the duration of the sampling period in minutes;

i) for pumped sampling, the mean flow rate during the sampling period, in litres per minute;

j) the mean atmospheric temperature and pressure during the sampling period, if appropriate;

k) the volume of air sampled, in litres, at ambient conditions;

l) the name of the person who collected the sample;

m) the time-weighted average mass concentration of mercury vapour and/or particulate inorganic mercury compounds, or total inorganic mercury (mercury and particulate inorganic mercury compounds) found in the air sample (in $mg \cdot m^{-3}$), at ambient temperature and pressure or, if appropriate, adjusted to reference conditions;

n) the analytical variables used to calculate the result, including the concentrations of mercury in the blank and sample test solutions, the volumes of the blank and sample test solutions and the dilution factor, if applicable;

NOTE If the necessary data (e.g. the volume of air sampled) are not available to the laboratory for the above calculations to be carried out, the laboratory report may contain the analytical result in micrograms of mercury per sample.

o) the type(s) of instrument(s) used for sample preparation and analysis and unique identifier(s);

p) the estimated instrumental detection limit, method detection limit and quantification limit under the working analytical conditions; the measurement uncertainty determined in accordance with the GUM[17]; and, if requested by the customer, quality control data;

q) any operation not specified in this International Standard, or regarded as optional;

r) the name of the analyst(s) or other unique identifier(s);

s) the date of the analysis; and

t) any inadvertent deviations, unusual occurrences, or other notable observations.

14.2 Laboratory report

The laboratory report shall contain all information required by the end user, regulatory authorities and accreditation organizations.

Annex A
(informative)
Guidance on selection of a sampling method for mercury vapour

A.1 Advantages and disadvantages of diffusive sampling

A.1.1 Diffusive badges used for collection of mercury vapour are small, lightweight and require no sampling pump. Samples are stable for at least 30 days if the sorbent capsules are stored in the plastic pouches in which they are supplied. Sampling can therefore be carried out with the minimum of equipment and samples can easily be sent for analysis by mail. Also, the sampler is reusable, so that consumable costs are kept to a minimum.

A.1.2 Whilst eminently suitable for sampling throughout the entire working period, the diffusive badge method is not suitable for sampling periods $<$ 6 h.

A.1.3 The diffusive badge method is not suitable for measuring particulate inorganic mercury compounds.

A.1.4 The uptake rate of diffusive badges is dependent upon face velocity (see 13.7.3). In particular, the uptake rate drops off in still air conditions. For personal sampling this is not a problem, since body movements and convection currents due to body heat provide sufficient air movement. However, diffusive badges should be used with caution for static (area) sampling (see 10.3.3.2.2). At very high wind speeds, erratic increases in sampling rate can occur and additional shielding is necessary (see 10.3.3.2.2).

A.1.5 Diffusive badges are not suitable for use if they could become contaminated with liquid mercury, or if the badges could be subject to frequent knocks or vibration which might pulverise the sorbent, allowing it to escape from the capsules.

A.2 Advantages and disadvantages of pumped sampling

A.2.1 An advantage of pumped sampling is that mercury vapour and particulate may be collected simultaneously for comparison with a limit value for mercury and inorganic compounds. This can be achieved by sampling with a sorbent tube alone when particulate mercury compounds are present in the air at low concentrations, e.g. in chloralkali processes. However, when high concentrations of particulate mercury compounds could be present, it is necessary to use a quartz-fibre prefilter and analyse it together with the contents of the sorbent tube to obtain a total mercury-in-air concentration.

A.2.2 When it is known that all the airborne mercury is present in particulate form, sampling may be carried out using a quartz-fibre filter alone. This is analysed using an analytical technique that is essentially identical with that described for sorbent tube samples.

A.2.3 Pumped sampling can be used for sampling times as short as 1 h using the 200 mg sorbent tube, or 15 min using the 500 mg sorbent tube. It can be used in still air and windy conditions since the sampling rate is independent of air speed.

Annex B
(informative)

Temperature and pressure corrections

B.1 Temperature and pressure corrections for the sample uptake rate of diffusive badges

The sample uptake rate of diffusive badges is dependent on temperature and pressure. If desired (see 10.2.1), calculate a temperature- and/or pressure-corrected sample uptake rate using the following equation:

$$U_{\text{corr}} = U \times \left(\frac{T_1}{T_2}\right)^{1,5} \times \left(\frac{p_2}{p_1}\right)$$

where

U_{corr} is the calculated temperature-corrected sample uptake rate, in millilitres per minutes;

U is the nominal sample uptake rate, in millilitres per minutes, given by the manufacturer of the diffusive badge (see Note in 12.1.1);

T_1 is the mean atmospheric temperature, in kelvin, during the sampling period (see 12.1.1);

T_2 is the temperature, in kelvin, at which the sample uptake rate given by the manufacturer of the diffusive badge applies [normally 293 K (see Note in 12.1.1)];

p_1 is the mean atmospheric pressure, in kilopascals, during the sampling period (see Note in 12.1.1); and

p_2 is the pressure at which the sample uptake rate given by the manufacturer of the diffusive badge applies, in kilopascals, 101,3 kPa (see Note in 12.1.1);

A theoretical calculation shows that a 5 % deviation in the sample uptake rate occurs at 96,2 kPa and 106,4 kPa. Both these values are within normal weather conditions at sea level (although unusual) and this pressure difference corresponds to an altitude change of about 400 m (−0,1 kPa corresponds to an increase in altitude of approximately 8 m) at normal atmospheric pressure (101,3 kPa at sea level). Similarly, a 5 % deviation in the sample uptake rate occurs at 284 K and 303 K.

B.2 Temperature and pressure corrections for the indicated volumetric flow rate of flowmeters

B.2.1 Bubble flowmeters are preferred for measuring the volumetric flow rate because the readings they give are independent of temperature and pressure. For other flowmeters, it might be necessary to apply a correction to the indicated volumetric flow rate if the temperature and pressure at the time of measurement is different to when the calibration of the flowmeter was checked.

B.2.2 A typical example of the need for a temperature and pressure correction is when a constant pressure drop, variable area, flowmeter is used to measure the volumetric flow rate. In this instance, use the following equation to calculate a corrected air sample volume:

$$V_{\text{corr}} = q_V \times t \times \sqrt{\frac{p_1 \times T_2}{p_2 \times T_1}}$$

where

V_{corr} is the calculated corrected air sample volume, in litres;

q_V is the mean volumetric flow rate, in litres per minute (see 12.1.2);

t is the duration of the sampling period, in minutes;

p_1 is the atmospheric pressure, in kilopascals, during calibration of the flowmeter (see 8.2.8);

p_2 is the mean atmospheric pressure, in kilopascals, during the sampling period (see 12.1.2);

T_1 is the temperature, in kelvin, during calibration of the flowmeter (see 8.2.8);

T_2 is the mean temperature, in kelvin, during the sampling period (see 12.1.2).

A theoretical calculation shows that a 5 % deviation in the air sample volume occurs at 91,9 kPa and 112,2 kPa. Both these values are outside the normal weather conditions at sea level, but this pressure difference corresponds to an altitude change of about 800 m (−0,1 kPa corresponds to approximately 8 m increase in altitude) at normal atmospheric pressure (101,3 kPa at sea level). Similarly, a 5 % deviation in the air sample volume occurs at 264 K and 323 K.

B.2.3 Any other flowmeter can also require a correction for variation in pressure and temperature. Follow the manufacturer's instructions for such corrections.

B.3 Recalculation of mercury-in-air concentrations to reference conditions

If necessary (see 10.2.3) to recalculate mercury-in-air concentrations to reference conditions (e.g. 293 K and 101,3 kPa), using the following equation:

$$\rho_{\text{Hg, corr}} = \rho_{\text{Hg}} \times \frac{(101{,}3 \times T_2)}{(p_2 \times 293)}$$

where

$\rho_{\text{Hg, corr}}$ is the corrected concentration of mercury in the air sample, in milligrams per cubic metre, at reference conditions;

ρ_{Hg} is the concentration of mercury in the air sample, in milligrams per cubic metre, at ambient conditions;

T_2 is the mean temperature, in kelvin, during the sampling period;

p_2 is the mean atmospheric pressure, in kilopascals, during the sampling period;

293 is the reference temperature, in kelvin; and

101,3 is the reference atmospheric pressure, in kilopascals.

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