BRITISH STANDARD

BS EN
13211:2001

Air quality — Stationary source emissions — Manual method of determination of the concentration of total mercury

The European Standard EN 13211:2001 has the status of a British Standard

ICS 13.040.40

National foreword

This British Standard is the official English language version of EN 13211:20001.

The UK participation in its preparation was entrusted by Technical Committee EH/2/, Air quality, to subcommittee EH/2/1, Stationary source emissions, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

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

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled "International Standards Correspondence Index", or by using the "Find" facility of the BSI Standards Electronic Catalogue.

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This British Standard, having been prepared under the direction of the Health and Environment Sector Committee, was published under the authority of the Standards Committee and comes into effect on 15 August 2001

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EUROPEAN STANDARD

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English version

Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury

Qualité de l'air - Emissions de sources fixes - Méthode manuelle de détermination de la concentration en mercure total

Luftqualität - Emissionen aus stationären Quellen - Manuelles Verfahren zur Bestimmung der Gesamtquecksilber-Konzentration

This European Standard was approved by CEN on 6 January 2001.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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EUROPÄISCHES KOMITEE FÜR NORMUNG

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Contents

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by July 2001, and conflicting national standards shall be withdrawn at the latest by July 2001.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European standard specifies a manual reference method for the determination of the mass concentration of mercury in exhaust gases from ducts or chimneys. This European standard is validated for the determination of the mass concentration of total mercury in exhaust gases from the incineration of waste for the concentration range of total mercury from 0,001 mg/m^3 to 0,5 mg/m^3[1)]. The method may be applicable for exhaust gases from other sources with the following typical composition:

total suspended matter	from 0 mg/m^3 to 20 mg/m^3
C_xH_y	from 0 mg/m^3 to 10 mg/m^3
HCl	from 0 mg/m^3 to 50 mg/m^3
HF	from 0 mg/m^3 to 10 mg/m^3
SO_2	from 0 mg/m^3 to 250 mg/m^3
CO	from 0 mg/m^3 to 250 mg/m^3
NO_x	from 0 mg/m^3 to 500 mg/m^3
CO_2	from 0 % (volume fraction) to 15 % (volume fraction)
H_2O (g)	from 2 % (volume fraction) to 25 % (volume fraction) (actual)
O_2	from 8 % (volume fraction) to 15 % (volume fraction) (dry, actual)
temperature	from 60 °C to 140 °C

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 1483	Water quality — Determination of mercury.
prEN 13284-1:1998	Stationary source emissions — Determination of low range mass concentrations of dust — Part 1: Manual gravimetric method.

3 Terms and definitions

For the purpose of this European Standard, the following terms and definitions apply:

3.1
mercury
mercury and mercury in its compounds

3.2
total mercury
sum of the mercury in exhaust gas independent from the state (gaseous, solved in droplets, solid, absorbed on particles)

3.3
representative sampling
isokinetic, flow equivalent sampling at the required minimum number of sampling points in the sampling plane as stated in the prEN 13284-1:1998

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1) m^3 expressed as m^3 under dry conditions, normalized to 0 °C and 101,325 kPa and at 11 % (volume fraction) O_2 (unless otherwise stated).

3.4
absorber
a device in which gaseous mercury (and mercury attached to small particles that are not filtered) is absorbed into an absorption solution

3.5
gas divider, impingers or fritted bubblers
a part in the absorber bottle which divides the gas stream in small bubbles into the absorption liquid

4 Principle

A sample stream of flue gas is extracted representatively from a duct or chimney over a certain period of time with a controlled flow and known volume. Dust in the sampled gas stream is collected on a filter whereafter the gas stream is passed through a series of absorbers, which contain an appropriate absorption solution for collecting gaseous mercury.

At the end of the sampling period the filter and absorption solution are collected to be taken to the laboratory.

The collected dust on the filter is digested in such a way that the mercury contained in the dust fraction is dissolved in a liquid. This liquid is then analyzed.

The absorption solution from the absorbers is prepared for analysis and analyzed.

The data from the sampling and analysis are combined and the results are expressed in milligrams of total mercury per cubic meter (mg/m^3) of flue gas.

The analysis of mercury is performed according to EN 1483.

5 Sampling equipment

5.1 Conditions for isokinetic and non-isokinetic sampling

Although mercury is mainly present in the gaseous form, it can also be found in the dust phase as well as in droplets which can be present after wet scrubbers. Therefore isokinetic sampling is necessary in order to collect dust and droplets correctly.

When sampling has to be performed isokinetically then both dust and droplets, as well as flue gas, shall be sampled in one and the same equipment. This approach is necessary, due to the delicate gaseous/solid/droplet partitioning of mercury.

NOTE 1 As the total mercury content is to be determined, a shift in the equilibrium within a single sampling system does not influence the measurement of the total amount of mercury.

If the sum of the mercury content in the dust phase and droplets corresponds to less than 1 $\mu g/m^3$, then gaseous mercury can be sampled non-isokinetically.

NOTE 2 An estimate of the amount of mercury in droplets may be determined on basis of the mercury content in the wet scrubber solution and the droplet content in the flue gas.

In the case that no droplets are present non-isokinetic sampling can also be performed when the ratio between the highest and lowest velocity at any point in the sampling plane is less or equal to a factor of 1,2.

5.2 General requirements

The sampling equipment consists of

— a probe with an entry nozzle and a temperature controlled tube;

— a filter housing with a filter support and a filter;

— a series of absorbers;

— suction unit(s) with gas metering device(s) and flow regulator(s).

The filter housing may be located:

— in the duct or chimney mounted directly behind the entry nozzle (in-stack filtration);

— outside the duct or chimney directly behind the suction tube (out-stack filtration).

In the latter case (out-stack filtration) the filter housing shall be temperature controlled.

NOTE The filter can also be placed semi-outstack, in the probe after a short piece of gas preheated suction tube.

5.3 Isokinetic sampling equipment

Reference is made to prEN 13284-1:1998 for the specific details about the requirements of the sampling equipment, including the equipment for the determination and maintaining of isokinetic conditions.
In this present standard only specific requirements for the sampling of mercury (gaseous, dust and droplets) are stated, additional to those specified in prEN 13284-1:1998.

NOTE 1 The geometrical dimensions of glass nozzles will deviate from those specified in prEN 13284-1:1998, but the deviations can be decreased so that the remaining differences will not have a significant influence on the result.

Depending upon the type of absorbers used (see 5.5) two different sampling arrangements may be employed; a so-called ‘main-stream arrangement’ or a ‘side stream arrangement’.
In the main-stream arrangement all the sampled flue gas is passed through the absorbers, but in the side-stream arrangement only a part of the sampled flue gas is passed through the absorbers.
Figures of both arrangements of the isokinetic sampling equipment for total mercury are given in Annex A.

The sampling probe shall be temperature controlled. If an out-stack filter is employed then this shall also be temperature controlled.

NOTE 2 In cases of wet flue gases containing droplets or saturated flue gases it is advised to use out-stack filtration.

NOTE 3 In the case of the side-stream arrangement the connection to the T-piece and the T-piece itself shall be temperature controlled. Insulation of these parts, without additional heating, is not allowed.

NOTE 4 The heat input from the sampled gas is insufficient to compensate for the thermal losses even with insulation.

The parts of the equipment that are in contact with the sampled flue gas shall be made of specific materials which are prescribed in 5.9.

5.4 Non-isokinetic sampling equipment

In general the non-isokinetic sampling equipment is assembled according to the main-stream arrangement. Depending upon the gas flow employed, different types of absorbers (see 5.5) may be used.

A figure of the non-isokinetic sampling equipment is given in Annex A.

The sampling probe shall be temperature controlled. If an out-stack filter is employed then this shall also be temperature controlled.

The parts of the equipment that are in contact with the sampled flue gas shall be composed of specific materials which are prescribed in 5.9.

5.5 Absorbers

For efficient collection two absorbers shall be placed in series.

Downstream of these absorbers an extra empty absorber may be used as a liquid trap and as a protection for the downstream equipment.

The amount of mercury collected in the second absorber shall correspond to less than 5 % of the total amount of mercury in both absorbers or less than 2 $\mu g/m^3$, whichever is the greatest.

Impingers or fritted bubblers can be used (figures of absorbers are contained in Annex B).

NOTE 1 Impingers have the advantage that they can be employed under high flow rate conditions. The disadvantage is the larger amount of (corrosive) absorption solution compared to that employed by fritted bubblers.

NOTE 2 Typical flow rates for impingers are in the range from 1 m^3/h to 2 m^3/h (17l/min to 33 l/min).

NOTE 3 This standard is not validated for impingers.

NOTE 4 The advantage of fritted bubblers is a good absorption efficiency with a smaller amount of absorption solution than that employed by impingers. The disadvantage is that normally only a limited gas flow rate can be used (from about 0,06 m^3/h (1 l/min) to approximately 0,18 m^3/h (3 l/min)). If these bubblers are used in isokinetic sampling equipment a secondary sampling line (a side-stream arrangement) is needed.

5.6 Filter

5.6.1 Filter collection efficiency

For the filter collection efficiency the same specifications as in prEN 13284-1:1998 are required. This efficiency shall be certified by the supplier.

The filter material shall have an efficiency of 99,5 % on a test aerosol with a maximum abundance at a particle diameter of 0,3 μm at the maximum flow rate anticipated, (or 99,9 % on a test aerosol of 0,6 μm mean diameter), see prEN 13284-1:1998.

5.6.2 Filter material

The filter may be of any shape (flat, thimble or wool). The filter material shall be applicable up to the maximum temperature anticipated. The filter material shall have a blank value for mercury (calculated in units of $\mu g/m^3$ of sampled flue gas) of less than 0,1 $\mu g/m^3$.

The filter material may consist of glass fibre, quartz fibre or polytetrafluoroethylene (PTFE), see 5.9.

When using filters with organic binders precautions shall be taken to ensure, that during digestion all mercury attached to the filter material will be dissolved. The organic binders or the reaction products from these binders after digestion shall not influence the analysis.

5.7 Connections

The choice of materials for the connections between the different parts of the sampling equipment are given in 5.9 and shall be employed to those parts which are in contact with the mercury containing flue gas.

For the main-stream arrangement these materials shall be employed from the nozzle to the last absorber.

For the side-stream arrangement these materials shall be employed from the nozzle to the last absorber in the side-stream.

The total length of unheated connections (such as tubing) from the sampling probe to the absorbers shall be as short as possible but less than 1 m.

The use of silicone tubing is limited in relation to the sampled gas flow rate; the total inner surface of all silicone tubing in the sampling equipment shall be less than 0,0033 m^2 per m^3/h (2 cm^2 per litre/min).

NOTE 1 Laboratory tests have shown severe losses in silicone tubing for Hg^{2+} if the surface to gas flow ratio is higher than 2 cm^2 per l/min.

NOTE 2 As an example of how this restriction may be applied: the total length of tubing with an inner diameter of 6 mm and a sampling gas flow of 1,5 l/min is limited to 1,6 cm.

5.8 Storage bottles and containers

The material of the storage bottles for the absorption solutions is prescribed in 5.9.

The storage bottles for the permanganate/sulphuric acid solution (2 % *m/m* $KMnO_4$/10 % *m/m* H_2SO_4, see 6.2) shall be darkened or stored in a dark place to avoid enhanced formation of MnO_2.

The material of the filter storage containers is prescribed in 5.9.

5.9 Choice of materials for the sampling equipment

The parts of the sampling equipment in contact with the mercury containing flue gas, or with liquids containing mercury, shall be made of the materials shown in table 1. The different parts are described in 5.3 to 5.8.

Table 1 — Materials for the sampling equipment

Equipment part	Material	Remark
Nozzle	Standard laboratory glass Borosilicate glass Quartz glass PTFE Titanium	
Sampling probe (inner suction tube)	Standard laboratory glass Borosilicate glass Quartz glass PTFE Titanium	
Filter housing Filter support	Standard laboratory glass Borosilicate glass Quartz glass PTFE Titanium	
Filter material	Flat filter: - quartz fibre - glass fibre - PTFE Thimble filter: - quartz fibre - glass fibre Wool filter: - quartz fibre - glass fibre	Efficiency see 5.6.1
Absorbers	Standard laboratory glass Borosilicate glass Quartz glass	
Connection fittings	Standard laboratory glass Borosilicate glass Quartz glass Titanium PTFE	Also the T-piece for the side-stream arrangement of the equipment (see also 5.7) Ball joints of the stated materials with PTFE lined seals are also allowed
Connection tubing	PTFE Silicone (with a total inner surface of less than 2 cm^2 per l/min)	Use of silicone tubing is restricted (see 5.7)
Storage bottles	Standard laboratory glass Borosilicate glass Quartz glass Polypropylene (PP) Polyethylene (PE)[1)]	For solutions and samples
Cap of storage bottles	PTFE, PFA, FEP Polypropylene (PP) Uncoloured polyethylene (PE)[1)]	Caps of other materials are allowed as long as they have an insert of an allowed material
Filter storage container	Standard laboratory glass Borosilicate glass Quartz glass Polypropylene (PP) Polyethylene (PE) PTFE Titanium	
1) Only high density polyethylene (HDPE) shall be used.		

5.10 Suction unit

Depending on the arrangement of the sampling equipment (see 5.3 and 5.4) two suction units may be required for one sampling system.

Suction-units shall be gas tight (see 7.3.4) and capable of extracting at least the desired gas flow rates from the duct. Wide adjustments of the sample flow rates shall be facilitated using regulating and/or by-pass valves. Shut-off valve(s) for stopping the gas flow, or back flow due to low pressure in the duct, shall also be used.

NOTE Measures for the protection of the suction unit(s) such as filters, water-traps, etc. may be useful.

Flow meters (variable area meter, orifice plate etc.) are strongly recommended in order to monitor the flow rate. The flow meters shall be leak tested.

5.11 Gas volume metering device

Two kinds of systems may be used to measure the gas volume:

— flow rate measurements on a dry basis;

— flow rate measurements on a wet basis.

The requirements for the flow rate measurements on a dry basis are:

— condensor and/or gas drying tower providing a residual humidity less than 10 g/m^3 at the maximum flow rate;

— gas-tight pump;

— flowmeter, in order to facilitate the flow rate adjustment, calibrated against the dry gas volumeter;

— dry gas volumeter (uncertainty less than 2 % at the anticipated flow rate) with associated absolute pressure and absolute temperature measurement (uncertainty less than 1 %).

The requirements for the flow rate measurements on a wet basis are:

— insulated or heated tubing, in order to prevent upstream condensation of the sample gas;

— heated orifice plate or equivalent device (flow meter), calibrated within 2 % of the anticipated flow rate; the uncertainty of temperature, pressure (absolute and differential) measurement shall be less than 1 %;

— suction device (such as compressed air ejector, pump, etc.);

— barometer.

5.12 Additional equipment

If sampling is to be performed under isokinetic conditions then additional measurement equipment is needed in order to maintain the isokinetic conditions. For the description of this equipment and the associated specific requirements reference is made to prEN 13284-1:1998.

6 Reagents

6.1 General

Use only reagents of recognized analytical grade and distilled or de-ionized water, all with the lowest possible mercury content.

WARNING Use the reagents in accordance with the appropriate health and safety regulations.

6.2 Reagents for precleaning the sampling equipment

Use appropriate reagents for precleaning the sampling equipment (see 7.2).

6.3 Choice of absorption solutions

6.3.1 General

One of the two following solutions shall be chosen for the absorption of gaseous mercury:

I. Potassiumpermanganate/sulphuric acid solution (2 % *m/m* $KMnO_4$/10 % *m/m* H_2SO_4);
II. Potassiumdichromate/nitric acid solution (4 % *m/m* $K_2Cr_2O_7$/20 % *m/m* HNO_3).

The maximum storage time of the absorption solution shall be one week.

WARNING Do not mix these solutions because a combination of nitric and sulphuric acid can cause gas release in the bottle which results in high pressure and possible explosion of the bottle.

NOTE The absorption efficiency of the two solutions was tested in laboratory tests.

6.3.2 Absorption solution I (2 % *m/m* $KMnO_4$/10 % *m/m* H_2SO_4)

Slowly add 60 ml of H_2SO_4 (ρ =1,84 kg/l, 95 % *m/m* to 97 % *m/m*) to 800 ml of distilled or de-ionized water. Weigh 22 g of $KMnO_4$, gradually mix with the H_2SO_4 solution and stir until $KMnO_4$ is dissolved. Fill up to about 980 ml with water and mix. Add 2 ml HCl (1 mol/l), make up to 1000 ml with water and mix. Store in the dark.

6.3.3 Absorption solution II (4 % *m/m* $K_2Cr_2O_7$/20 % *m/m* HNO_3)

Slowly add 250 ml of HNO_3 (ρ = 1,41 kg/l, 65 % *m/m*) to 700 ml of distilled or de-ionized water. Weigh 46 g of $K_2Cr_2O_7$, gradually mix with the HNO_3 solution and stir until $K_2Cr_2O_7$ is dissolved. Make up to 1000 ml with water and mix.

6.4 Reagents for rinsing the sampling equipment after sampling

6.4.1 HNO_3 solution, 5 % *m/m*

Obtain or prepare a HNO_3 solution of about 5 % *m/m*.

NOTE This solution is used for:
1. the rinsing of the nozzle, probe (inner tube) and filter housing;
2. the rinsing of the absorbers filled with absorption solution II.

6.4.2 Rinsing solution for absorbers with absorption solution I

Choose one of the two following rinsing solutions for the absorbers with absorption solution I:

A. Hydrogen peroxide (H_2O_2) solution, 3 % *m/m*
Prepare a fresh solution of H_2O_2 of about 3 % *m/m* in a sufficient quantity.
or:
B. Hydroxylammoniumchloride ($HONH_3Cl$) solution, 10 % *m/m*
Prepare a fresh solution of $HONH_3Cl$ of about 10 % *m/m* in a sufficient quantity.

WARNING Follow the health and safety requirements for the use of hydroxylammoniumchloride.

6.4.3 Acetone

Acetone (of analytical grade) may be used for quick drying purposes after rinsing.

6.4.4 Reagents for digestion of the filter

6.4.4.1 Hydrofluoric acid

HF, 40 % *m/m,* ρ_4^{20}=1,16 kg/l

6.4.4.2 Water

H_2O, doubly distilled or of the same quality, specific conductivity $\rho < 10\ \mu Sm^{-1}$ (i.e. specific resistance $\kappa > 0{,}1\ M\Omega m$).

6.4.4.3 Boric acid solution

H_3BO_3, to obtain a cold saturated boric acid, 5 % *m/m,* dissolve 55 g of boric acid in 1000 ml warm water (6.4.4.2) and let cool down to room temperature.

6.4.4.4 Dilute nitric acid

HNO_3, 5 % *m/m,* for digestion. Thoroughly mix about 75 ml of HNO_3 (65 % *m/m*; ρ_4^{20}=1,40 kg/l) with 500 ml of water (6.4.4.2) and make up to 1 l with water (6.4.4.2).

6.4.4.5 Rinsing acid

HNO_3, 25 % *m/m*, for rinsing the digestion equipment. Thoroughly mix about 275 ml of HNO_3 (65 % *m/m*; *ρ_4^{20}=1,40 kg/l)* with 300 ml of water (6.4.4.2) and make up to 1 l with water (6.4.4.2).

7 Procedure

7.1 General requirements

For the case of isokinetic sampling (see 5.1), sampling shall be performed according to prEN 13284-1:1998. This includes the procedure for representative grid sampling and for maintaining isokinetic conditions.

Sampling may be simplified and carried out at only one point of the duct section in the case of highly homogeneous flow stream, when the preliminary survey measurements show that the following criteria are met:

— standard deviation of velocities is less than 10 % of the mean velocity value;

— local temperatures differences vary by less than 10 °C;

— standard deviation of O_2 concentration is less than 10 % of the mean O_2 concentration value (or other pertinent tracer equivalent criterion).

The sampling point shall be located near the middle of the duct.

When the sampling is carried out under these conditions at least 0,1 D away from the wall, this choice shall be justified in the test report , and supported by the results of preliminary survey measurements.

The sampling probe and the out-stack filter shall be maintained at a temperature of at least 20 °C above flue gas temperature. When using titanium equipment the temperature shall be maintained at 180 °C or higher.

NOTE 1 Lower temperatures may result in the condensation of mercury salts or adsorption of mercury on to the inner walls of the probe and filter housing. This will result in an under estimation of the mercury concentration.

The sampling time shall meet legal or other regulations and requirements.

NOTE 2 If it is known from previous measurements that the mercury content of the dust corresponds to less than 2 $\mu g/m^3$ for one sampling period, several samplings may be performed with the same filter.

7.2 Precleaning of the equipment

All parts of the sampling equipment in contact with the mercury shall be cleaned prior to sampling.
The following parts shall be cleaned: nozzle, probe (inner tube), filter housing, filtersupport, T-piece (if employed), absorbers, connection tubing, storage bottles and containers.

In Annex C some cleaning procedures are given as examples, but any other good laboratory practice cleaning procedure may be used.

The quality of the reagents used shall be according to clause 6.

7.3 Preparation and installation of equipment

7.3.1 Nozzle installation

In the case of isokinetic sampling has to be performed the appropriate nozzle diameter shall be determined according to prEN 13284-1:1998.
Attach the nozzle to the probe.

NOTE If non-isokinetic sampling will be performed then a nozzle is not necessary.

7.3.2 Filter installation

Install the filter in the filter housing and attach it to the probe. Care shall be taken in handling the filter in order to avoid contamination of the filter by mercury containing deposits or dusts.

NOTE If a number of filter housings are available the filters may be already installed in the filter housings in a laboratory. Consequently at the sampling site only the filter housings have to be changed.

7.3.3 Installation of absorbers

Charge two absorbers with an appropriate amount of absorption solution (see 6.3) such that sufficient gas/liquid contact is guaranteed in both absorbers. Place the charged absorbers in series and connect them to the probe. An empty absorber shall be added behind the second absorber as a protection for the downstream suction equipment.

It shall be proven at least once per measuring campaign for each duct or chimney that the amount of mercury in the second absorber is less than 5 % of the total amount of mercury in both absorbers or corresponds to less than 2 $\mu g/m^3$, whichever is the greatest.

WARNING As the absorption solutions are highly corrosive care and safety measures have to be taken in order to avoid injury to persons and/or damage to equipment in the case of breakage or leakage of the absorbers.

NOTE 1 If a sufficient number of absorbers are available the absorbers may already be charged and capped in a laboratory. Consequently at the sampling site only the absorbers have to be changed after rinsing the tubing to the absorbers (see 7.6.3).

NOTE 2 Absorbers may be used again during the same measurement campaign, provided that the prescribed cleaning procedure for the absorbers (see 7.6.3) has been followed.

7.3.4 Leak test

The complete equipment shall be leak tested before each sampling by sealing the nozzle and starting the suction unit(s). After having reached minimum pressure the leak flow rate shall be less then 2 % of the nominal sampling flow rate.

7.3.5 Installation of equipment at the sampling location

Install the complete assembled sampling equipment at the sampling location and place the sampling probe into the sampling port at the chimney or flue gas duct. Avoid any unintended gas flow through the sampling equipment of absorption solution into the sampling equipment, prior to sampling in the case of low pressure in the chimney or duct.

WARNING In cases where high pressure exists in the chimney or duct care and safety measures shall be taken because hot fumes may escape from the sampling port.

Avoid contamination of the interior part of the nozzle with dust during insertion of the sampling probe into the sampling port.

7.4 Sample blanks

In order to check the complete procedure sample blanks shall be taken depending on the required quality level of the measurement by following the procedure prescribed in 7.3 and 7.6 except that no flue gas is extracted.

7.5 Performance of the sampling

Re-assemble the equipment and check for air leakage. Heat the probe before insertion in the duct.

Record the gas meter readings and ambient pressure. Start the suction unit(s), set the sampling flow rate and extract flue gas from the duct.

Record the temperature and the pressure in the gas meter(s) at the start and at least every 10 minutes.

For the case of isokinetic sampling check that isokinetic conditions are being maintained at each sampling point and adjust if necessary.
Perform grid sampling according to prEN 13284-1:1998.

After the required sampling time stop the extraction of flue gas. Record the gas meter readings, the ambient pressure and the temperature in the gas meter(s).

If absorption solution I ($KMnO_4/H_2SO_4$) has been discoloured during sampling, the sampling is invalid.

7.6 Disassembling the equipment

7.6.1 General

In case of in-stack filtration, remove the sampling probe from the sampling port.

WARNING In cases where high pressure exists in the chimney or duct care and safety measures shall be taken because hot fumes may escape from the sampling port.

7.6.2 Disassembling of the filter housing

Open the filter housing at an appropriate place where contamination of the filter can be avoided. Place the filter in an identifiable and marked container.

NOTE If a sufficient number of filter housings are available then opening of the housing at the sampling site is not necessary as this operation may be performed at the laboratory.

7.6.3 Rinsing of the unheated connection tubing to the first absorber

Rinse the connection tubing to the first absorber after each measurement.

a) For the absorbers containing absorption solution I (permanganate/sulphuric acid solution):
Rinse the connection tube to the first absorber with H_2O_2-solution or hydroxylammoniumchloride solution into the first absorber.

NOTE Before this rinsing, a rinsing with absorption solution I is allowed.

Be careful not to use too much rinsing solution. If the absorption solution now becomes discoloured, the sampling is still valid as the oxidation capacity of the solution is maintained by the presence of H_2O_2.

WARNING Do not use HNO_3 (6.4.1) as a rinsing solution as the combination of nitric acid and sulphuric acid can cause gas release which can result in high pressure and explosion of the bottle or blow out of the absorption solution.

b) For the absorbers containing absorption solution II (potassiumdichromate/nitric acid solution):
Rinse the connection tube to the first absorber with HNO_3 (6.4.1) into the first absorber.

7.6.4 Collection of the absorption solutions from the absorbers

If a number of absorbers are available the absorbers may be already charged and capped in a laboratory, so that at the sampling site only the absorbers have to be changed. Consequently the following procedure can be performed in the laboratory. In that case the absorber is the storage bottle.

If the absorption efficiency has to be determined, treat both absorbers separately. In other cases the absorption solutions may be combined in the same storage bottle.

If separate storage bottles are used, then pour out the absorption solutions from the absorbers into marked and identified storage bottles.

a) For the absorbers which contained absorption solution I (permanganate/sulphuric acid solution):
Rinse the absorbers with H_2O_2-solution or hydroxylammoniumchloride-solution and add the solutions to the storage bottles.

Use just enough H_2O_2-solution or hydroxylammoniumchloride to collect the remaining absorption solution and any MnO_2-deposits.
If the absorption solution now becomes discoloured, the sampling is still valid as the oxidation capacity of the solution is maintained by the presence of H_2O_2.
Special care shall be taken during the rinsing of absorbers employing frits, because these devices are not easily rinsed.

b) For the absorbers which contained absorption solution II (potassiumdichromate/nitric acid solution):
Rinse the absorbers with HNO_3 (6.4.1) and add the solutions to the storage bottles.
Special care shall be taken during the rinsing of absorbers employing frits, because these devices are not easily rinsed.

WARNING Do not blow out the rinsing solution from the fritters by mouth, but use a handpump or a peleus ball.

7.6.5 Rinsing of the sampling equipment

Rinse the nozzle, probe (inner tube) and filter housing after each series of measurement at each duct or chimney. Rinse first with a HNO_3 solution and then with water. Take care that a sufficient amount of rinsing solution is used to wet the total inner surface of the mentioned parts.

Store the rinsing solution in a marked and identified storage bottle.

Rinse the nozzle, probe (inner tube) and filter housing with acetone and let them dry.

In case of absorption solution I, the rinsing solution shall not be added to the first absorber (see also the warning in 7.6.3).

7.7 Requirements for storage of the samples

Samples (liquids and filters) in PP or PE bottles or containers shall be stored at a temperature of below 6 °C (refrigerator).
Samples in glass or quartz glass bottles or containers may be stored at room temperature.

WARNING If stored warm, post digestion may cause leaks, exploding bottles or acid droplets in eyes or on skin when opening.

The samples shall be analyzed within two weeks after sampling.

7.8 Pre-treatment before analysis

7.8.1 General

Before the different samples can be analyzed some pre-treatment is necessary. This pre-treatment is described in 7.8.2 to 7.8.4. The concentrations of the necessary reagents are prescribed in EN 1483.

7.8.2 Digestion of the filter

7.8.2.1 Pre-cleaning of the digestion equipment

The digestion equipment shall be pre-cleaned to avoid contamination of the samples. This can be performed by precleaning (e.g. in a laboratory dishwasher), and additional cleaning by submersion in rinsing acid (6.4.4.5) for 24 h. Afterwards the equipment is rinsed with water.

Any other good laboratory practice procedure may be applicable.

7.8.2.2 Filter treatment

The sampling filter shall be digested in a closed vessel at increased temperature and pressure; PTFE filters are treated in the same way without dissolution of the filter material. This procedure describes how a sampling filter is dissolved by digestion with a mixture of HNO_3 and HF. After the digestion boric acid is added to the liquid to form complexes with excess fluoride, at the same time the boric acid dissolves insoluble fluorides by complexation.

The methods given are valid for plane filters of approx. 100 mg per filter, and a maximum of 10 mg of particulate matter collected on the filter. If the actual figures differ significantly from these values, the amounts of acids have to be changed proportionally.

In every series of analyses, at least one blank value shall be determined for the filter and all the reagents by digesting an unused filter from the same batch.

NOTE If there is any elementary carbon present at the filter, this will not be digested by this method. If that is the situation the liquid has to be filtered before analysis. This shall be stated in the final measurement report.

7.8.2.2.1 Method blank

The method blank is determined by treatment and analysis of an unused filter from the same batch as the used filters as said in 7.8.2.2. The method blank gives the blank values for the filter and treatment only. This value can be subtracted from the analytical value. The method blank is not the same as sampling blank.

7.8.2.2.2 General procedure

— Transfer the filter from the transport case to the PTFE vessel. For this procedure a plastic coated pair of tweezers shall be used. The filters may be folded some times to fit in the vessel. In the case of PTFE filters be sure that the filter is submersed completely by the digestion liquid.

— Record the filter identification number and the vessel identification number on a working sheet. Note other relevant information as well.

— Clean the transport case with 1,5 ml of HNO_3 (6.4.4.4), and add it to the vessel.

— Add additional 1,5 ml of HNO_3 (6.4.4.4) to the vessel.

— Add 2,0 ml of HF (6.4.4.1) to the vessel. The filter has to be totally wetted.

— Assemble the vessel, as described in the manufacturer's instructions.

If a oven or a heating plate are used as heating source, continue with 7.8.2.2.3. If a microwave oven is used go to 7.8.2.2.4.

7.8.2.2.3 Heating in oven or heating plane

— Place the closed vessel in the oven, kept at a temperature of at least 160 °C for at least 8h.

— Take out the vessel, and let it cool to room temperature. Open the vessel carefully, and add 20 ml of water (6.4.4.2) and 20 ml of H_3BO_3 (6.4.4.3).

— Place the vessel into the oven at 150 °C for 2 h.

— Take out the vessel, and let it cool to room temperature. Open carefully the vessel. Transfer the liquid quantitatively into a 100 ml volumetric flask.

— Wash the inside of the vessel several times with water and add it to the volumetric flask. Fill up with water and mix well.

NOTE For expected low concentrations in the filter a 50 ml volumetric flask may be used instead of a 100 ml flask.

— (O*ptional*) Transfer the digestion to a 100 ml storage bottle.

— Mark the bottle with the filter identification number etc.

The digestion is now ready for analysis.

7.8.2.2.4 Heating in a microwave oven

For digestion in microwave oven several individual procedures may be used by the laboratories. This subclause gives the minimum requirements to ensure a complete filter digestion.

The minimum requirements are based on one vessel in the microwave oven at the time. If two or more vessels are placed in the same oven, the procedure has to be changed accordingly, and as described by the manufacturer of the microwave oven.

— Place the closed vessel in the microwave oven, and heat it according to the internal heating program, which should fulfil the minimum requirements given below:

  — minimum power used (in any part of the procedure): 200 W

  — minimum duration (excluded are time without heating): 20 min

  — minimum average power (time weighted): 300 W

  — minimum total energy produced by the microwave oven: 500 kJ

NOTE 1 The minimum total energy produced by the microwave oven as required is calculated by multiplying the power (W) given by the microwave oven in a certain period with the length of that period(s). The different periods are summarised.

— Take out the vessel, and let it cool to room temperature. Open the vessel carefully, and add 20 ml of water (6.4.4.2), and 20 ml of H_3BO_3 (6.4.4.3).

— Place the closed vessel in the microwave oven and heat it for at least 20 min in total with a total energy dispatch W during this period of at least 500 kJ.

— Take out the vessel, and let it cool to room temperature. Open the vessel carefully. Transfer the liquid quantitatively to a 100 ml volumetric flask.

— Wash the inside of the vessel several times with water, and add it to the volumetric flask. Make up with water and mix well.

NOTE 2 For expected low concentrations in the filter a 50 ml volumetric flask can be used instead of a100 ml flask.

— (*Optional*) Transfer the digestion to a 100 ml storage bottle.

— Mark the bottle with filter identification number etc.

The digestion is now ready for analysis.

7.8.3 Absorption solution

a) Absorption solution I (permanganate/sulphuric acid solution):

Add hydroxylammoniumchloride solution gently to the whole sample until the solution is just discoloured to avoid that no gaseous mercury (Hg^0) will escape from the reaction vessel prior to analysis. Make sure that no MnO_2 is present in the solution or on storage container walls. Determine and record the weight or volume of this solution.

Take a subsample for analysis and analyze immediately.

b) Absorption solution II (potassiumdichromate/nitric acid solution):

Determine and record the weight or volume of the absorption solution. Take a subsample for analysis and analyze immediately.

7.8.4 Rinsing solution

Determine and record the weight or volume of the liquid.
Take a subsample and analyze immediately.

7.9 Analysis

The analysis of the solutions obtained in 7.8.2 to 7.8.4 shall be performed according to EN 1483.

The described digestion step for the liquid solutions in EN 1483 is unnecessary and shall be omitted. After pre-treatment of the solutions they shall be analyzed immediately.

The analysis can be performed using Tin(II)chloride ($SnCl_2$) or Sodium tetrahydroborate ($NaBH_4$) as a reduction agent. The described manual method in EN 1483 may be used as well as a flow injection analysis system for both reduction agents.

All other necessary steps shall be carried out according to EN 1483.

8 Expression of results

8.1 Calculation

8.1.1 Total mercury content

The total mercury content in the flue gases is calculated as mass concentration as given below.

For the side-stream arrangement of the sampling equipment:

$$C_{Hg} = \left(\frac{m_{filter} + m_{rinse}}{V_{main} + V_{side}} + \frac{m_{absorber}}{V_{side}} \right) \times \frac{1}{1000} \quad (1)$$

For the main-stream arrangement of the sampling equipment:

$$C_{Hg} = \frac{m_{filter} + m_{rinse} + m_{absorber}}{V_{main} \times 1000} \quad (2)$$

where
C_{Hg} is the total mercury concentration in mg/m^3 [2)] ;
m_{filter} is the mass of mercury on the filter in μg;
m_{rinse} is the mass of mercury in the rinsing solution in μg;
$m_{absorber}$ is the total mass (sum) of mercury in both absorbers in μg;
V_{main} is the gas volume through the main sampling line in m^3;
V_{side} is the gas volume through the side-stream (absorbers) in m^3.

8.1.2 Gas volume at standard conditions

The calculation of the gas volume to standard conditions is performed by:

$$V = V_{meas} \times \frac{273{,}15}{(273{,}15 + \vartheta)} \times \frac{P}{101{,}325} \quad (3)$$

where
V is the dry gas volume in m^3;
V_{meas} is the measured dry gas volume in m^3, at actual conditions, in the case of wet gas meters recalculate the measured wet gas volume to dry conditions;
ϑ is the average temperature in the gas meter in °C;
P is the pressure in the gas meter in kPa (1 kPa = 10 mbar).

8.1.3 Total mercury content at a reference O_2-concentration

The total mercury content at a reference O_2-concentration (e.g. 11 % (volume faction) O_2) is calculated by

$$C_{Hgatref.O_2\%} = C_{Hg} \times \frac{21 - O_{2,ref}}{21 - O_{2,meas,dry}} \quad (4)$$

where
$C_{Hg\ at\ ref.\ O2\%}$ is the total mercury content in mg/m^3 at the reference O_2-concentration;
C_{Hg} is the total mercury content in mg/m^3 (8.1.1);
$O_{2,ref}$ is the reference O_2-concentration (e.g. 11 % (volume fraction) O_2);
$O_{2,meas,\ dry}$ is the measured O_2-concentration in the flue gas at dry conditions.

8.1.4 Absorption efficiency

$$Eff. = \left(1 - \frac{m_{abs2}}{(m_{abs1} + m_{abs2})}\right) \times 100 \quad (5)$$

where
$Eff.$ is the absorption efficiency in %;
m_{abs1} is the mercury content in μg or μg/m^3 in the first absorber;
m_{abs2} is the mercury content in μg or μg/m^3 in the second absorber.

8.2 Performance characteristics

8.2.1 Introduction

This European Standard has been validated during two intercomparison tests at two different waste incinerators. In these tests several teams from different European countries performed measurements according to this standard. In these tests probes with inner suction tubes made of glass or titanium were used. When titanium was employed, the temperature was maintained above 180 °C. Some teams used absorption solution I (permanganate/sulphuric acid solution) and some used absorption solution II (potassiumbichromate/nitric acid solution).

NOTE Definitions of repeatability and reproducibility can be found in ISO 5725-1.

[2)] m^3 expressed as m^3 under dry conditions, normalized to 0 °C and 101,325 kPa (unless otherwise stated).

8.2.2 Lower detection limit

The lower detection limit strongly depends on the quality of the chemicals used, the sampled gas volume, the volume of the absorption solutions and the analytical method. The detection limit for mercury in the absorption solutions has been determined during a laboratory test with absorption solution I (permanganate/sulphuric acid solution). The results are stated in table 2.

Table 2 — Detection limit based on 30 measurements with absorption solution I

Parameter	absolute detection limit (μg)	relative detection limit* (μg/m^3)
Average concentration of the blank ($\bar{y}_{\beta=0}$)	0,05	0,9
Standard deviation of the blank ($S_{\beta=0}$)	0,03	0,6
Detection limit ($\underline{Y} = \bar{y}_{\beta=0} + 3S_{\beta=0}$)	0,13	2,6
* calculated for a nominal sampled gas volume of 0,05 m^3		

8.2.3 Repeatability

The values for the repeatability of the method described in this European Standard are given in Table 3.

Table 3 — Repeatability

Concentration		Number of teams	Number of double measurements	Repeatability standard deviation	95% Confidence level for a single measurement	Repeatability	
Range μg/m^3	Average μg/m^3			μg/m^3	μg/m^3	μg/m^3	%
4 to 10	6	4	23	0,6	1,2	1,7	30
40 to 100	100	3	30	6,3	13	18	18

8.2.4 Reproducibility

The values for the reproducibility of the method described in this European Standard are given in Table 4.

Table 4 — Reproducibility

Concentration		Number of teams	Number of parallel measurements	Reproducibility standard deviation	95% Confidence level for a single measurement	Reproducibility	
Range	Average						
$\mu g/m^3$	$\mu g/m^3$			$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	%
4 to 10	6	4	12	1,2	2,5	3,5	62
40 to 100	100	3	11	12,5	26	36	36

9 Test report

The test report shall include at least the following information:

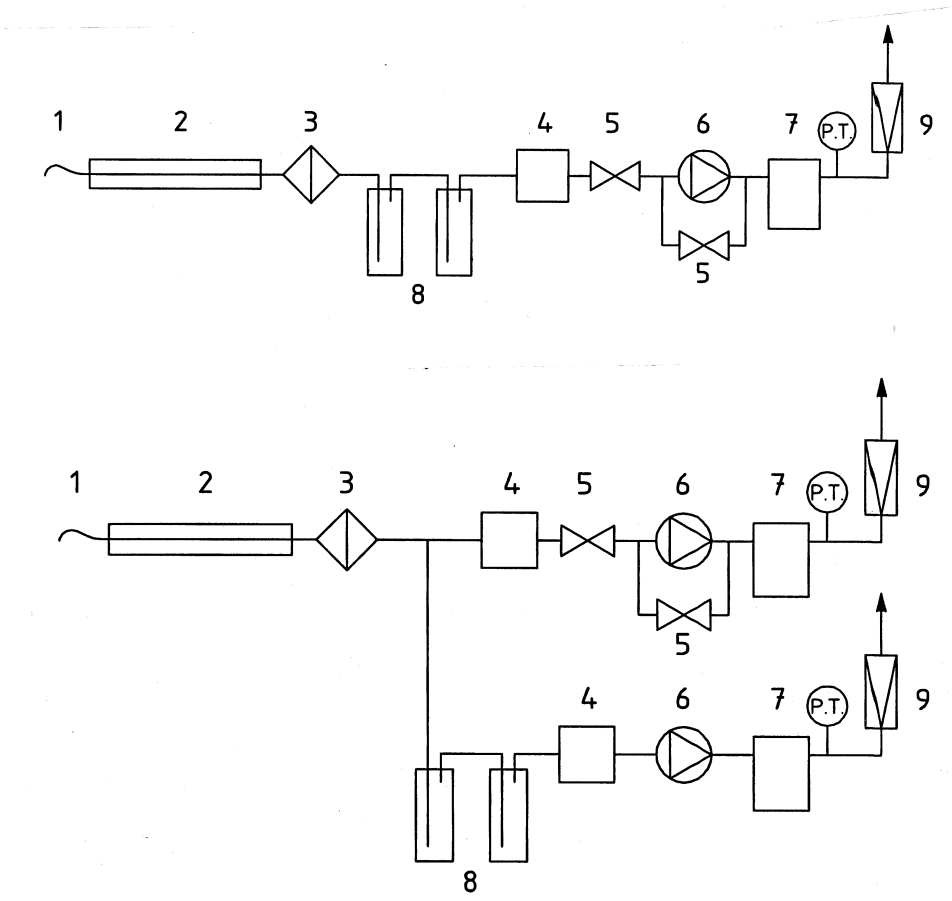
a) reference to this European Standard;
b) identification and number of sample(s);
c) description of the plant and process;
d) plant operating conditions;
e) location of the sampling points;
f) number of sampling points in the sampling plane in the duct or chimney;
g) isokinetic/non-isokinetic sampling;
h) sampling time;
i) sampling volume(s);
j) value of the sampling blank;
k) actual isokinetic conditions;
l) type of absorbers;
m) type of absorption solution;
n) analysis procedure (reduction agent, manual or flow injection);
o) total mercury content as mass concentration;
p) any deviations from this standard.

Annex A
(informative)

Examples of isokinetic and non-isokinetic equipment

a)

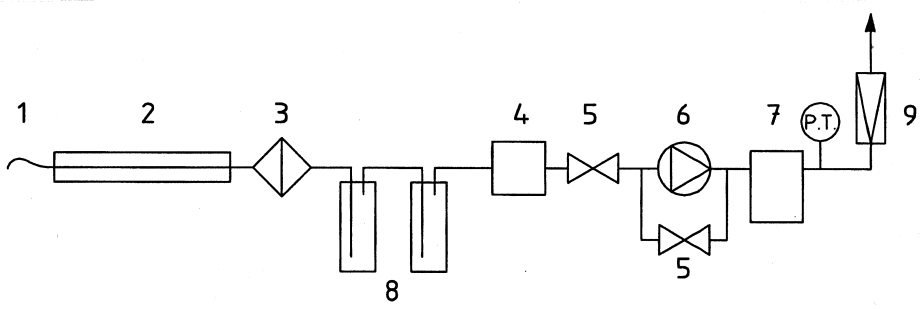
b)



Key

1 nozzle
2 probe
3 filter
4 dryer
5 flow control valve
6 suction unit
7 gas volume meter
8 absorber
9 gas flow meter
a) main stream
b) side stream
p. pressure
T. Temperature

Figure A.1 - Examples of isokinetic sampling equipment



Key

1 nozzle
2 probe
3 filter
4 dryer
5 flow control valve
6 suction unit
7 gas volume meter
8 absorber
9 gas flow meter

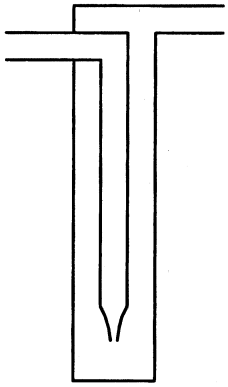
p. Pressure
T. Temperature

Figure A.2 - Example of non-isokinetic sampling equipment

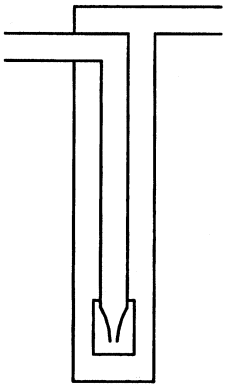
Annex B
(informative)

Examples of impingers and fritted bubblers

Examples of impingers and fritted bubblers



a) Midget impinger



b) Greenburg-Smith impinger

Figure B.1 - Example of an impinger (1 m^3/h to 2 m^3/h, equivalent to 17 l/min to 33 l/min)

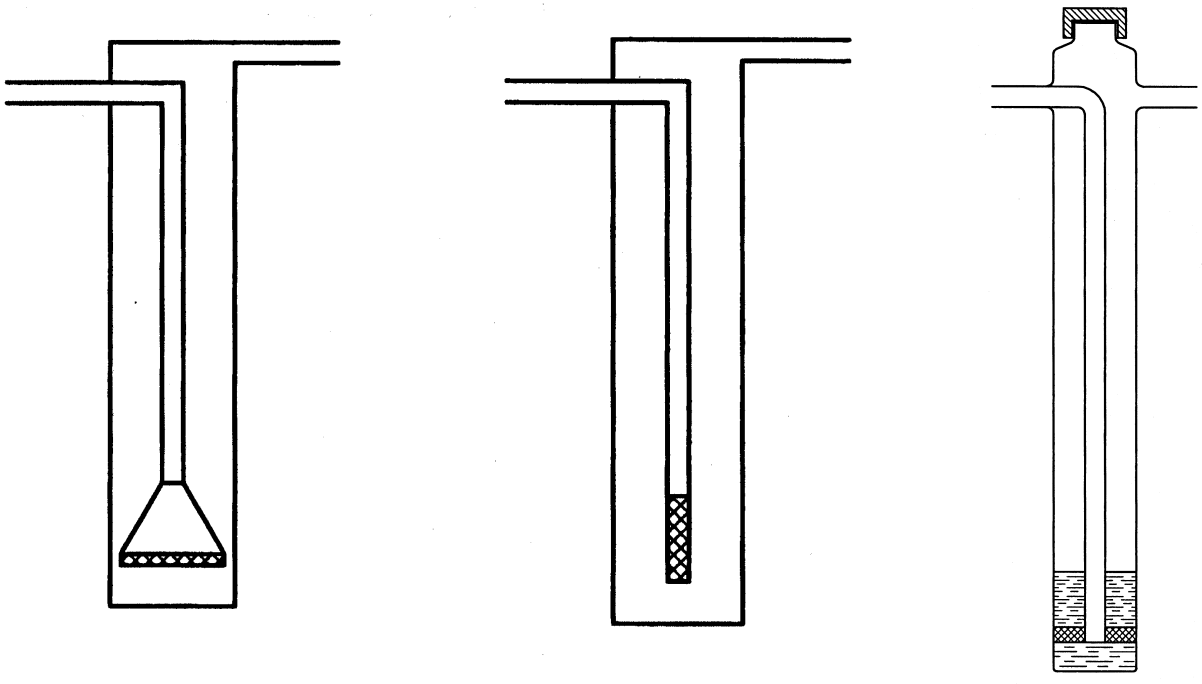


Figure B.2 - Examples of fritted bubblers (0,06 m^3/h to 0,18 m^3/h, equivalent to 1 l/min to 3 l/min)

NOTE For a high absorption efficiency it is advised to distribute the gas stream in the absorption solution homogeneously and to maximize the contact time between gas and liquid. The absorption solution should not be transferred to the next absorber by the gas stream. In practice a sufficient free space in the absorber above the solution shall be present to avoid solution transfer. This free space will also break down any foam which may be formed while the gas is bubbling through the liquid.

Annex C
(informative)

Precleaning procedures of the sampling equipment (at the laboratory)

C.1 General

The precleaning shall be performed in the laboratory according to good laboratory practice. In this Annex some options are given for the cleaning of equipment, absorbers and storage bottles.

C.2 Equipment

C.2.1 Option A

The nozzle, probe (inner tube) and the filter housing are cleaned by circulating 5% m/m HNO_3 through these parts for about 15 minutes at room temperature.

C.2.2 Option B

Filter housing

- Coarse cleaning, if necessary in ultrasonic bath, followed by drying
- Rinse with 10 % m/m HNO_3 and H_2O, then dry

Probe, nozzle

- Circulate 10 % m/m HNO_3 for 1 hour at room temperature and 10 min at 60 °C
- Rinse with H_2O
- Dry with clean particle free air

C.2.3 Option C

Any other good laboratory practice cleaning procedure.

C.3 Absorbers and storage bottles

C.3.1 Option A

The absorbers and storage bottles are rinsed with a 3 % *m/m* H_2O_2 solution and treated in an ultrasonic bath if necessary.

C.3.2 Option B

- Coarse cleaning and rinsing with H_2O
- Fill the absorbers and storage bottles with half concentrated aqua regiae (HCl/HNO_3 3:1) and leave them for a day
- Pour out the aqua regiae and fill the absorbers and storage bottles with H_2O
- Decant, and rinse the absorbers and storage bottles with H_2O
- Dry the absorbers and storage bottles

C.3.3 Option C

- Machine washed absorbers and storage bottles are charged with 38 % *m/m* HNO_3 (Hg-free)
- Shake the absorbers and storage bottles
- Leave overnight at room temperature
- Shake the absorbers and storage bottles again
- Rinse the absorbers and storage bottles with water
- Repeat this procedure once
- Dry the absorbers and storage bottles in an oven at 110 °C

C.3.4 Option D

Any other good laboratory practice cleaning procedure.

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