INTERNATIONAL STANDARD

ISO 11632

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Stationary source emissions — Determination of mass concentration of sulfur dioxide — Ion chromatography method

Émission de sources fixes — Détermination de la concentration en masse de dioxyde de soufre — Méthode par chromatographie ionique

Contents

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.

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.

International Standard ISO 11632 was prepared by Technical committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Annex A of this International Standard is for information only.

Introduction

For determining the mass concentration of sulfur dioxide in waste gas of stationary emissions sources, several integrated sampling and analysis methods exist. These include methods for independent manual sampling [ISO 7934] and for automated measuring systems [ISO 7935]. The latter have found a greater usage since a continuous measurement of sulfur dioxide, often specified by environmental authorities, can be obtained. The manual methods are required however, in calibrating automated measuring instruments.

This International Standard offers an alternative method to ISO 7934, replacing the Thorin method for analysing sulfate ions by a method based on ion chromatography. In addition, this International Standard is intended to apply to a lower emission range than ISO 7934.

Stationary source emissions — Determination of mass concentration of sulfur dioxide — Ion chromatography method

1 Scope

This International Standard specifies a method for the determination of the mass concentration of sulfur dioxide emitted from combustion facilities and technical processes, and defines the most important performance characteristics.

The method described in this International Standard has been tested for a sulfur dioxide concentration range of 6 mg/m^3 to 333 mg/m^3 with sampling periods of 30 min. It is applicable to mass concentrations of sulfur dioxide exceeding this range by carrying out an appropriate dilution of the sample solutions prior to the analysis or by using larger volumes of absorption solution, and to sulfur dioxide concentrations below this range by extending the sampling period.

This International Standard is applicable to the analysis of samples containing negligible levels of sulfur trioxide and volatile sulfates (< 5 % of the expected sulfur dioxide concentration), and ammonia (< 5 mg/m^3).
All concentrations are based on dry gas at a temperature of 273,2 K and pressure of 101,3 kPa.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently available valid International Standards.

ISO 6879:1995, *Air quality — Performance characteristics and related concepts for air quality measuring methods.*

ISO 7934:1989, *Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Hydrogen peroxide/barium perchlorate/Thorin method.*

ISO 7935:1992, *Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Performance characteristics of automated measuring methods.*

ISO 10396:1993, *Stationary source emissions — Sampling for the automated determination of gas concentrations.*

ISO Guide 25:1990, *General requirements for the competence of calibration and testing laboratories.*

3 Principle

A representative sample of waste gas is extracted via a temperature-controlled probe, filtered and drawn through a hydrogen peroxide solution for a specified time and flow rate. The sulfur dioxide in the waste gas sample is absorbed by the solution and sulfate anions are formed. The mass concentration of sulfate in the absorption solution is subsequently determined using ion chromatography.

4 Reagents

During the analysis, use only reagents of recognized analytical grade. The sulfate-free water shall have an electrical conductivity of < 0,01 mS/m and shall not contain particulate matter of a particle size > 0,45 µm. Normal, accepted laboratory safety practices should be followed during reagent preparation.

4.1 Absorption solution, 3 % H_2O_2

Pipette 100 cm³ of a 27 % (mole fraction) to 30 % (mole fraction) solution of hydrogen peroxide (H_2O_2) into a 1000 cm³ one-mark volumetric flask. Make up to the mark with water and mix well. Prepare this solution if possible on the day of use.

4.2 Eluent solution

The choice of eluent depends on the manufacturer's separator column and detector. For the exact composition of the eluent, refer to the instructions given by the manufacturer.

NOTE For an ion chromatograph using the suppressor technique, a typical eluent is a solution of $1,7 \times 10^{-3}$ mol/l $NaHCO_3$ and $1,8 \times 10^{-3}$ mol/l Na_2CO_3.

4.3 Standard sulfate stock solution, $10,4 \times 10^{-3}$ mol/l SO_4^{2-}

Dissolve 1,8141 g of analytical grade potassium sulfate (K_2SO_4) in reagent water and dilute to 1 l using a 1000 cm³ one-mark volumetric flask. 1 cm³ of stock solution corresponds to 1 mg of SO_4^{2-}.

NOTE Standard sulfate stock solution is stable for at least 28 days when stored at 277 K. Calibration standards are prepared by diluting the standard stock solution with the absorption solution as specified in 7.4.2.

4.4 Regeneration solution for suppressor

For the exact composition of the suppressor regeneration solution, refer to the instructions given by the manufacturer of the suppressor.

NOTE An example is a solution of $12,5 \times 10^{-3}$ mol/l H_2SO_4.

5 Apparatus

5.1 Sampling equipment

5.1.1 General

Alternative variations of the sampling equipment fulfilling the specified performance requirements for each component may be used. The performance characteristics set out in clause 9 refer, however, to the examples of sampling equipment described in 5.1.1 to 5.1.16. It is important that all parts of the sampling equipment upstream of the first absorber are heated and that the components shall not react with or absorb SO_2.

NOTE In special cases an unheated gas connector line may be used between the heated filter and first absorber, but this must be thoroughly rinsed with absorption solution after sampling and the washings combined with the sample.
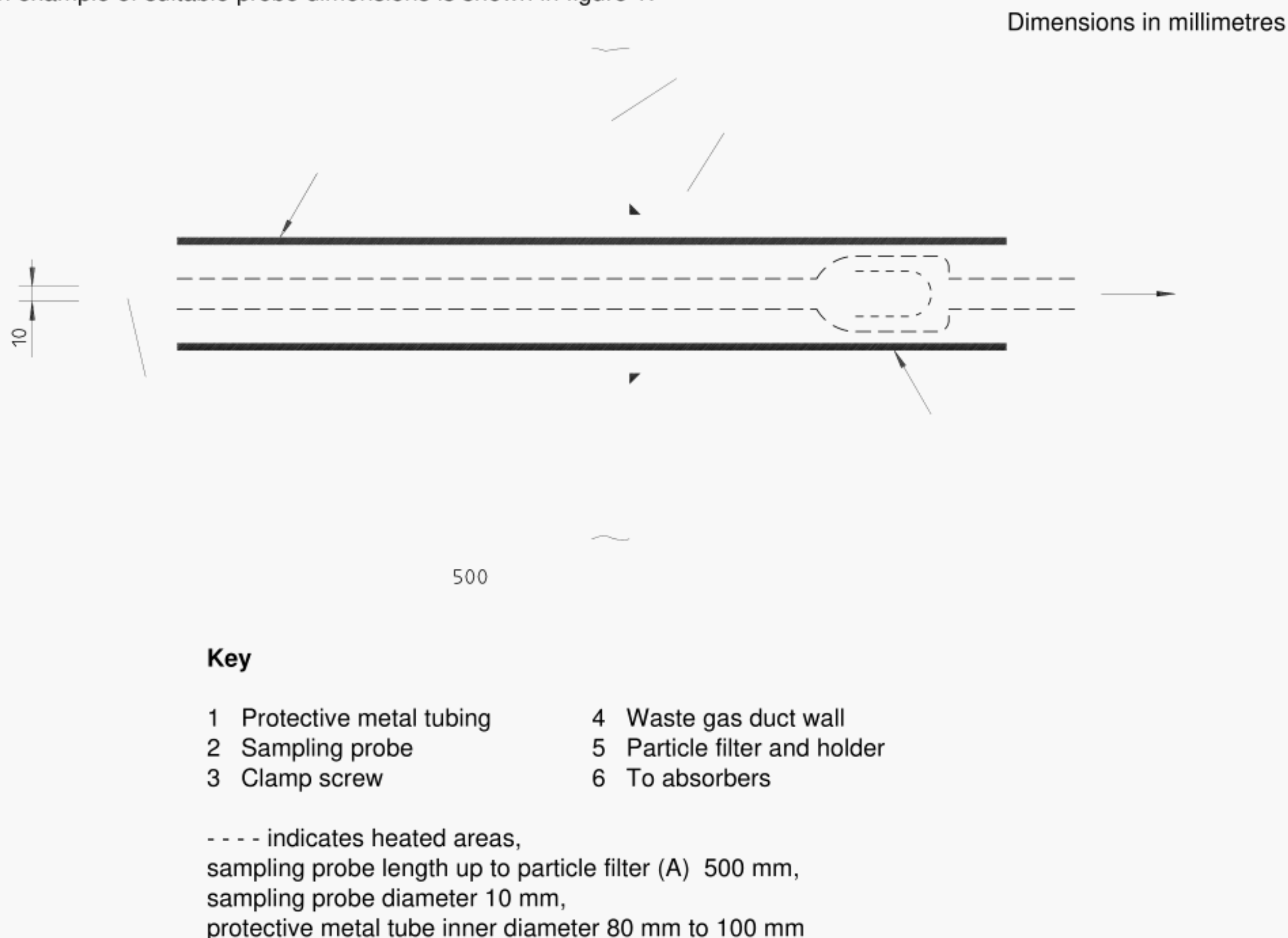
5.1.2 Sampling probe

The probe shall be of borosilicate glass or fused silica tube with a spherical ground joint at one end. Alternative probes of different lengths and inner diameters may be used, but the residence time of the sample gas in the probe shall be minimized. The sampling probe, which is surrounded by a heating jacket, shall be protected and positioned

using a metal outer tube. A clamp screw shall be used to adjust the probe length to reach the representative measurement point in the measurement plane of the waste gas duct.

NOTE An example of suitable probe dimensions is shown in figure 1.

Dimensions in millimetres

Key

1	Protective metal tubing	4	Waste gas duct wall
2	Sampling probe	5	Particle filter and holder
3	Clamp screw	6	To absorbers

- - - - indicates heated areas,
sampling probe length up to particle filter (A) 500 mm,
sampling probe diameter 10 mm,
protective metal tube inner diameter 80 mm to 100 mm

Figure 1 — Positioning of sampling probe, filter holder and protective tube

5.1.3 Filter holder

The filter holder shall be of borosilicate glass or fused silica glass with tube ends of spherical ground joints. The filter holder, which is encircled by the heating jacket, shall be connected to the sampling probe and housed within the protective metal tubing as shown in figure 1. The temperature after the filter holder is verified using a thermocouple.

NOTE 1 In special cases where the waste gas temperature is > 473 K, the heating jacket around the sampling probe, filter holder and connector line may be omitted. The temperature in the sampling line before the first absorber, however, should not fall below the acid dew point temperature of the waste gas.

NOTE 2 An example of suitable filter holder dimensions is shown in figure 2.
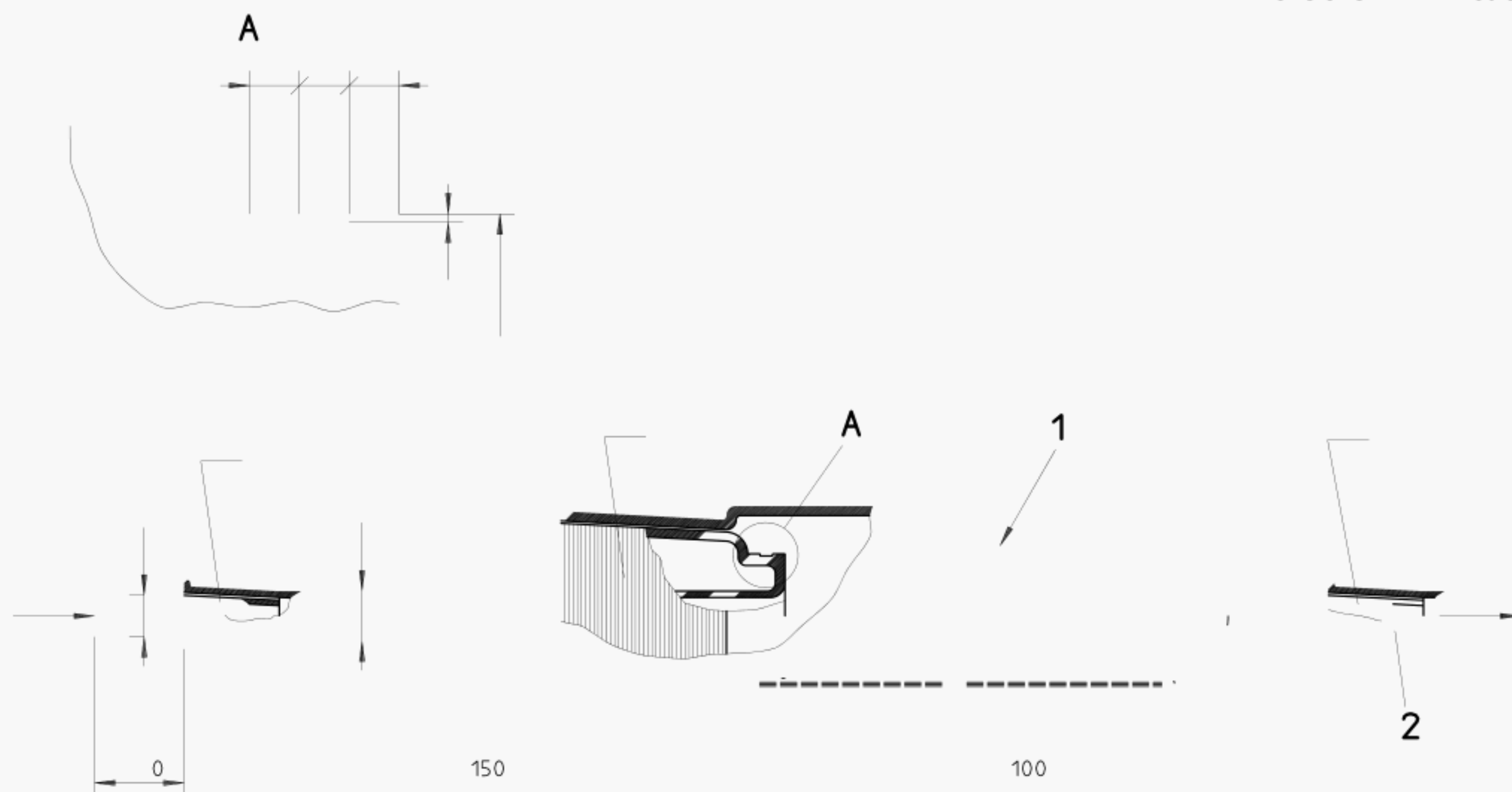
5.1.4 Particle filter

Alternative particle filters and filter holders of different designs may be used, but the residence time of the sample gas should be minimized. The filter material (quartz fibre or quartz wool packed progressively) shall have an efficiency better than 99,9 % for particles of cut-off diameter 0,6 μm for the actual sampling flow.

NOTE 1 An example of a suitable quartz-fibre particle filter of the "thimble" variety is shown in figure 2. The filter is held in position in the filter holder by stainless steel wire.

NOTE 2 In certain cases, a check on the possibility of a reaction between SO_2 in the sampled gas and particles retained on the filter may be warranted. This can be performed by comparing sulfate analyses on the particle fractions obtained from (i) the

filter used when sampling according to this International Standard, and (ii) particles obtained from another source at the site, e.g. cyclone.

Dimensions in millimetres

1 Quartz fibre particle filter ('thimble variety') 90 mm × 30 mm inner diameter
2 Thermocouple

Figure 2 — Example of a particle filter and filter holder

5.1.5 Absorbers

Two absorption bottles with spherical ground glass joints and equipped with an absorption bottle insert having a sintered filter. Alternative absorber sizes and configurations may be used, provided that the absorption efficiency criteria specified in 7.1 are met.

NOTE As an example, two 125 cm^3 size absorption bottles of the Drechsel type with pore diameters in the sintered filter between 40 μm and 90 μm may be used (see figure 3).
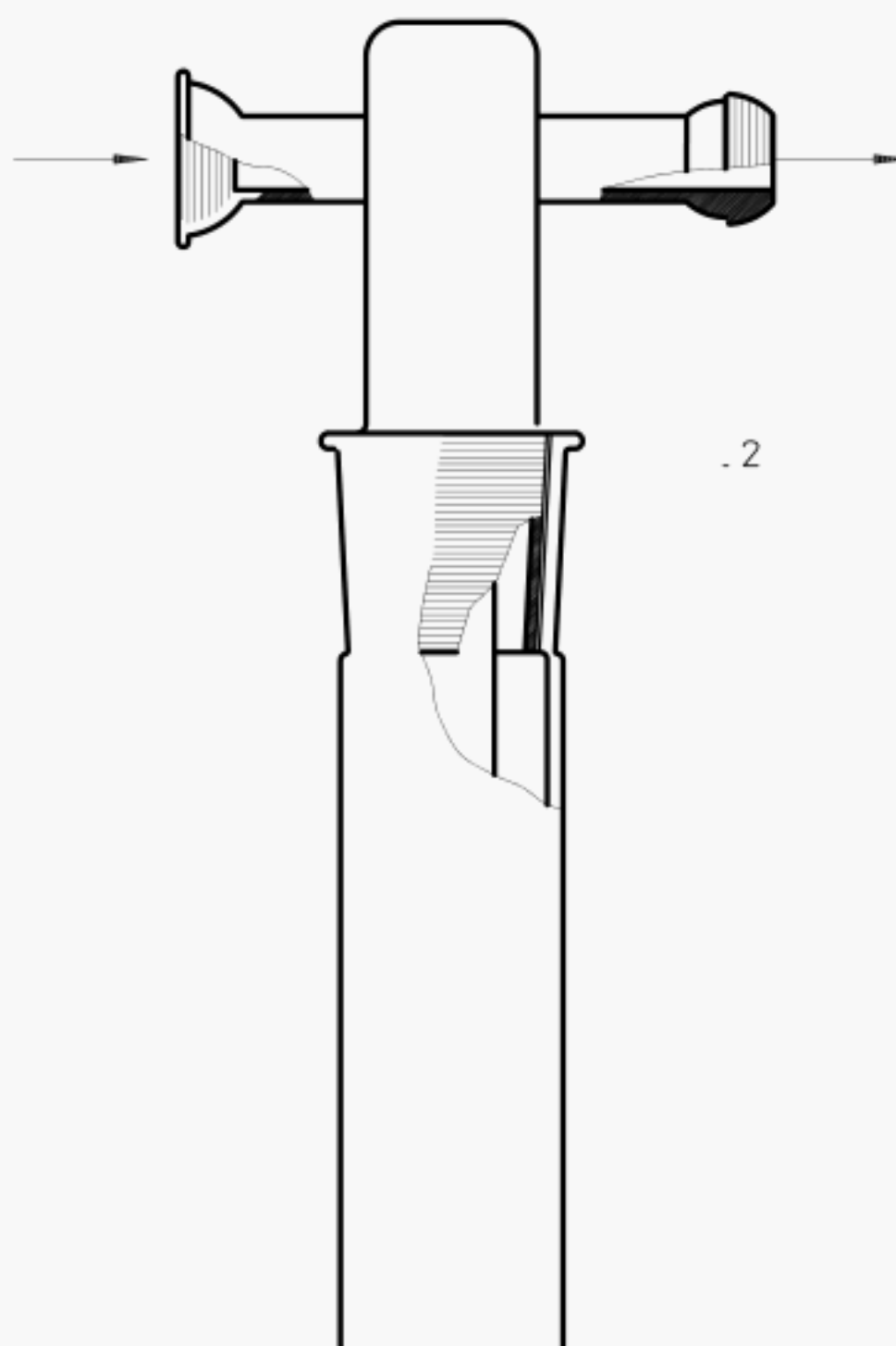
5.1.6 Heating jacket

Heating jacket or bandage capable of producing a temperature of at least 473 K.

5.1.7 Temperature regulator

Temperature regulator suitable for use with the heating jacket or bandage.

Figure 3 — Example of an absorption bottle

5.1.8 Trap

Absorption bottle equipped with an absorption bottle insert not having a sintered filter. This bottle is connected after the second absorber and collects possible splashes of absorption solution.

NOTE The use of the trap is optional.

5.1.9 Drying tube

Glass tube or absorption bottle packed with drying agent to dry the sample gas and protect the gas metering device and pump.

NOTE As an example, silica gel (1 mm to 3 mm particle size) previously dried at 448 K for at least 2 h may be used.

5.1.10 Sampling pump

Leak-free diaphragm pump capable of drawing sample gas at a flowrate within the range 0,02 m^3/h to about 0,2 m^3/h during the sampling period against a pressure of -10 kPa to -30 kPa. A small surge tank between the pump and rotameter may be used to eliminate the pulsation effect of the diaphragm pump on the rotameter.

5.1.11 Rotameter

Flowmeter or rotameter capable of measuring the selected sample gas flow with limits of error $< \pm 2$ % of the upper limit of measurement.

5.1.12 Regulating valve

Needle valve capable of adjusting the sample gas flowrate within the range 0,02 m^3/h to 0,2 m^3/h.

5.1.13 Gas metering device

Dry-gas meter capable of use at a sample gas flowrate within the range 0,02 m^3/h to about 0,2 m^3/h, limits of error $< \pm 2$ % of the measured volume, and equipped with a thermometer (5.1.14).

5.1.14 Connecting tubing

Connecting tubing in a range of lengths and internal diameters. All parts of the sampling train upstream of the first absorber shall be of a material which does not react with or absorb SO_2. The requirements are less stringent for parts of the sampling system downstream of the absorbers but corrosion resistant materials are recommended.

NOTE Examples of convenient materials are borosilicate glass, fused silica and polytetrafluoroethylene (upstream of the absorbers) and polyethylene and silicone rubber (downstrean of the absorbers).

5.1.15 Thermometer

Thermometer with measuring range 268 K to 323 K, limits of error $< \pm 2$ % of the upper limit of measurement.

5.1.16 Barometer

Barometer capable of measuring the atmospheric pressure (kPa) present at the sampling location, limits of error $< \pm 1$ % of the upper limit of measurement.

5.1.17 Stopwatch

5.2 Analysis equipment

5.2.1 Analytical balance

Analytical balance capable of weighing to the nearest 0,0001 g.

5.2.2 Ion chromatograph

Analytical system, complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gases, detector and recording device. The essential minimum requirements for an ion chromatograph system for the scope of this International Standard are as follows (see figure 4):

a) **Sample injection system.** An automated constant-volume injection system may be used.

b) **Anion separator column.** This column produced the separation of anions in the sample, enabling a clear measurement of the sulfate anion peak area and height. Other anions which may be present in the sample solution include F^-, Cl^- and NO_3^-. The resolution power of the separator column shall be sufficient so that the peak resolution (Rs) shall not fall below 1,3 where:

$$Rs = \frac{2(t_2 - t_1)}{(w_1 + w_2)}$$
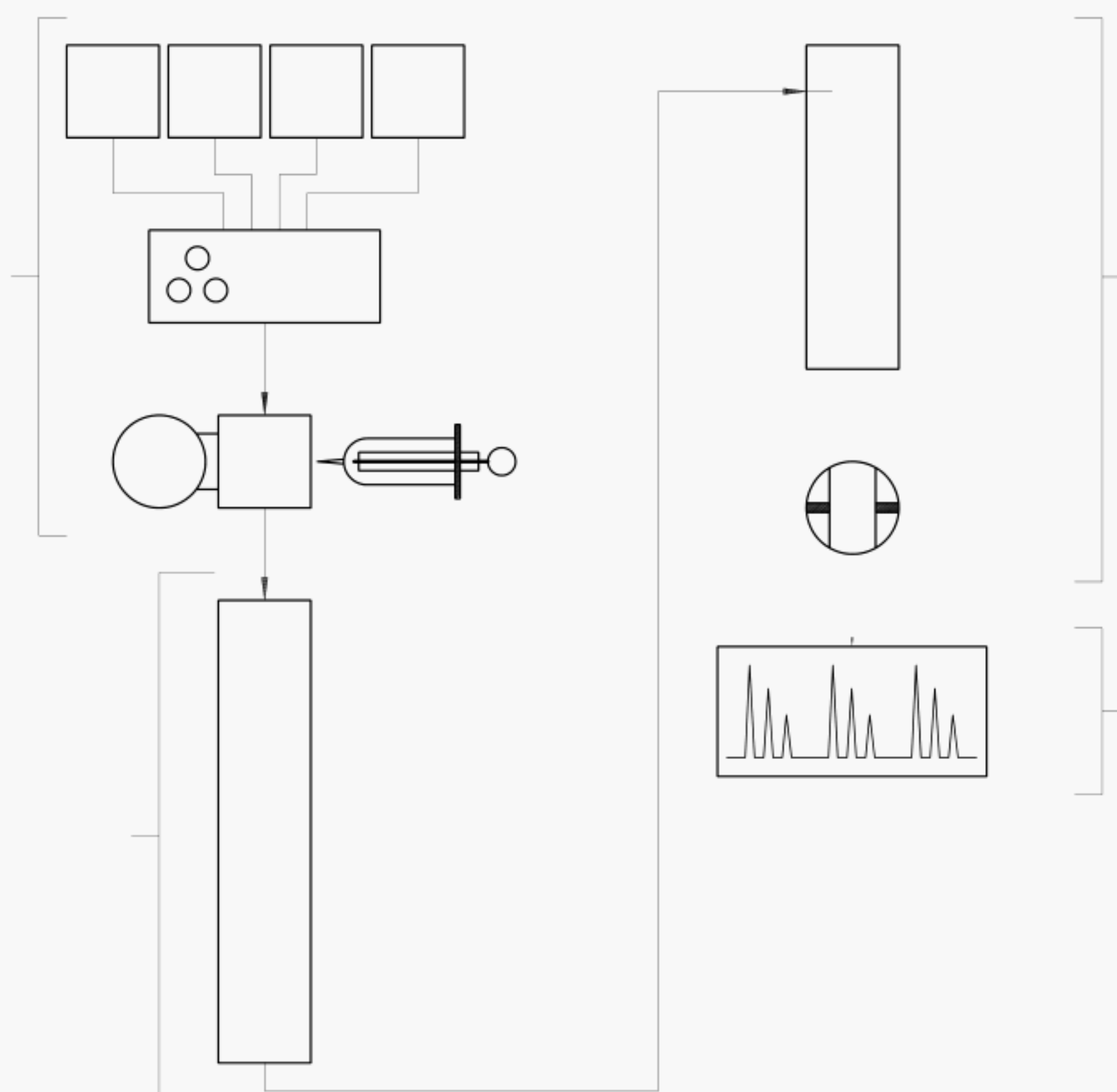
Key

1	Eluent reservoirs	7	Recorder, integrator, computer
2	Pump	8	Eluent/sample delivery
3	Sample injector	9	Analyte separation
4	Separator column	10	Analyte detection
5	Suppressor device	11	Data output
6	Detector cell		

Figure 4 — Example of an ion chromatograph

where

t_1 = retention time of the first peak, in seconds;

t_2 = retention time of the second peak, in seconds;

w_1 = peak width, in seconds on the time axis, of the first peak;

w_2 = peak width, in seconds on the time axis, of the second peak.

In general it is recommended to use a pre-column or anion guard column to protect the anion separator column. If this is omitted from the system, the retention times will be shorter. Two different types can be used: those containing the same substrate as the separator column, and those packed with a macroporous polymer.

c) **Detector**. The method of detection should rely on a measurement of the electrical conductivity with or without a suppressor device and be capable of providing the data as required in 7.5.

d) **Recording device**. A system using a strip chart recorder and integrator or other computer-based data system enabling the requirements in 7.5 to be fulfilled.

6 Sampling

6.1 It is necessary to ensure that the gas concentrations measured are representative of the average conditions inside the waste gas duct [ISO 10396]. The sampling location should be free from any obstructions which will seriously disturb the gas flow in the duct. Usually the cross-sectional concentration of gaseous pollutants is uniform because of diffusion and turbulent mixing. In addition, the sampling location shall be chosen with regard to safety of the personnel, accessibility and availability of electrical power.

6.2 Assemble the apparatus specified in 5.1 to obtain a sampling train in accordance with the example schematically represented in figure 5. The clearance or dead volume in the sampling probe, filter holder and tubing up to the first absorber should be minimized. Use sparingly greased spherical ground-glass joints and clamps upstream of the second absorber. Fill each of the two absorbers (5.1.5) with 80 cm^3 of the absorption solution (4.1).

6.3 Plug the intake of the sampling probe (5.1.2), switch on sampling pump (5.1.10) and leak test the sampling train following normal laboratory practice. Carefully release the sampling probe intake plug and switch off the sampling pump.

6.4 Wrap the sampling probe (5.1.2), particle filter holder (5.1.3) and connector tubing up to the first absorber with the heating jacket (5.1.6). Switch on the heating system and adjust the temperature regulator (5.1.7) so that during the sampling period the temperature in the heated zone is well above the acid dew-point temperature of the waste gas.

NOTE The temperature after the particle filter is checked with a thermocouple. Experience shows that a temperature of 448 K is usually sufficient.

6.5 Insert the sampling probe into the access hole in the wall of the waste gas duct and place the tip of the sampling probe at the representative measurement point in the measurement plane of the waste gas duct.

Secure the probe and protective metal tube using the clamp screw. Fill in the resultant space between the sampling probe and the access hole in the wall of the waste gas duct with an appropriate sealing material such that ambient air does not reach the measurement point nor waste gas escape. During the heating period (about half an hour), care shall be taken, in cases with large pressure differences between the ambient air and waste gas, that the absorption solution does not leave the absorbers.

6.6 At the end of the heating period, record the reading (V_1) on the gas meter (5.1.13), start the sampling pump (5.1.10) and stopwatch (5.1.17), and adjust the regulating valve (5.1.12) to give the desired sample gas flowrate of 0,06 m^3/h.

NOTE Higher flowrates may be used provided that the absorption efficiency specified in 7.1 can be verified.

6.7 The sampling period is normally 30 min. Record the reading (T) on the gas meter thermometer (5.1.15), and the reading (P) on the barometer (5.1.16). The sample gas flowrate selected shall be as constant as possible.

NOTE Where the expected mass concentration of sulfur dioxide is < 6 mg/m^3, the sampling period should be extended so that a sulfate concentration of > 1 mg/l is obtained in the final sample solution in 6.7.

6.8 At the end of the sampling period, switch off the sampling pump, record the time on the sto watch and the reading (V_2) on the gas meter. Remove the absorbers from the sampling train and transfer quantitatively both sample solutions into a 250 cm^3 size sample bottle. Clean glass or polyethylene sample bottles should be used. Rinse the absorption bottles, including the absorption bottle inserts, with absorption solution and force the solution

through the sintered filters using a pressure bulb. If used, the trap should also be rinsed and combined with the washings. Add the wash solution to the combined sample solution in the sample bottle.

Samples shall be stored as soon as possible in a refrigerator prior to analysis. 28 days shall be the maximum holding time for sulfate anions stored at 277 K.

NOTE In cases when low sulfur dioxide concentrations are expected, when the absorption solution is suspected to have a high background sulfate concentration or when a large quantity of condensate is collected in the absorbers, the absorption solutions from each absorber and the wash solution should be kept separate in three sample bottles and analysed individually.

6.9 To take additional waste gas samples, place into each of the two absorbers 80 cm^3 of absorption solution, replace the absorbers and proceed as specified above. By taking into account the total volume of waste gas sampled for all samples, the expected particle concentration of the waste gas, and any reductions in the sample gas flowrate during sampling, the operator should assess whether a change of particle filter is necessary.

6.10 Prepare a field-zero sample by adding approximately 100 cm^3 of absorption solution to a sample bottle.

6.11 If no prior experience is available which verifies the absorption efficiency of the absorbers for the sampling equipment and conditions, the procedure specified in 7.1 shall be followed at the measurement site.

7 Analytical procedure

7.1 Test of absorption efficiency

Place 80 cm^3 of absorption solution (4.1) into each of the two absorbers, where the first absorber is denoted A and the second absorber B (5.1.5). Assemble the apparatus specified in 5.1 to obtain a sampling train as illustrated in figure 5.

In consideration of the expected mass concentration of sulfur dioxide, choose a suitable sampling period that results in the absorption of about 0,45 mg of sulfur dioxide in the first absorber A, (corresponding to a sulfate concentration in A of 8,4 mg/l). Carry out sampling as specified in 6.1 to 6.6. At the end of the sampling period, switch off the sampling pump, record the time and reading (V_2) on the gas meter.

Remove the absorbers from the sampling train and transfer the sample solutions from absorbers A and B into two separate sample bottles. If a trap is used, its contents should be combined with sample bottle B. Rinse each absorber separately with absorption solution and add the washings to the appropriate sample bottle. Divide the two sample solutions into four approximately equal aliquots, denoted A1, A2, B1 and B2, using two additional empty sample bottles. Determine the volume of the four solutions, V_{A1}, V_{A2}, V_{B1} and V_{B2}. Combine solutions A1 and B1, mix well and label as (A1 + B1).

Analyse samples (A1 + B1) and A2 as in 7.2 and determine the sulfate concentrations, $C_{(A1 + B1)}$ and C_{A2}. Calculate the absorption efficiency of absorber A as the fraction of the mass of sulfate absorbed in absorber A, to the total mass of sulfate absorbed in A and B, as below:

$$\text{Absorption efficiency of A} = \frac{C_{A2} \times (V_{A1} + V_{A2})}{C_{(A1+B1)} \times (V_{A1} + V_{A2} + V_{B1} + V_{B2})}$$

Repeat 7.1 and determine the absorption efficiency of the second absorber by interchanging the absorber positions in the sampling train.

The absorption efficiency of both absorbers shall be at least 0,95.

7.2 Analysis

Start up the ion chromatograph in accordance with the manufacturer's instructions and confirm the readiness for operation (e.g. stable baseline). Check system calibration daily and, if necessary, recalibrate as described in 7.4.
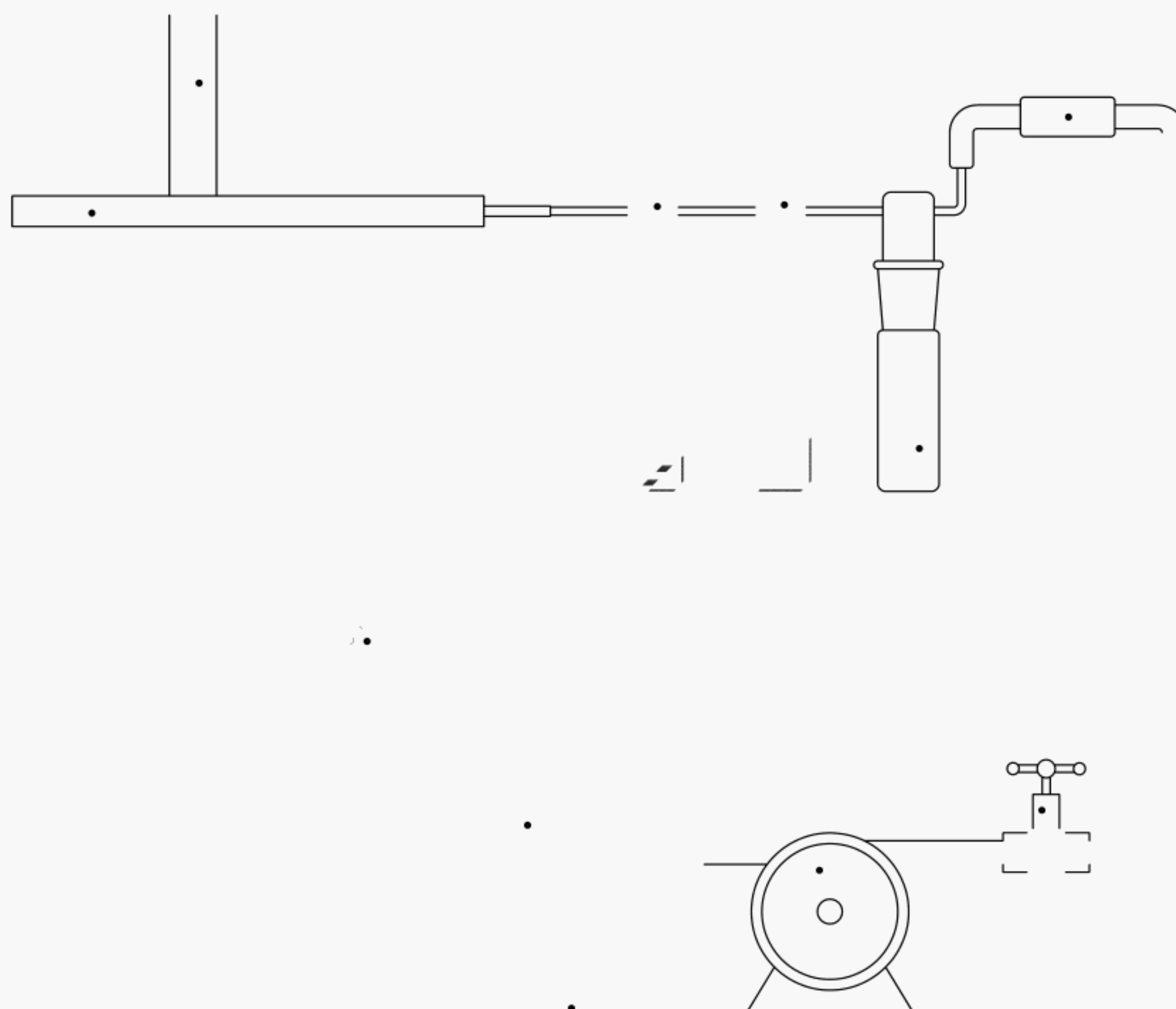
Key

1	Waste gas duct wall	7	Pump
2	Sampling probe and particle filter	8	Surge tank (optional)
3	Absorbers containing 3 % H_2O_2 solution	9	Rotameter
4	Trap (optional)	10	Thermometer
5	Drying tube	11	Dry gas meter
6	Regulating valve		

Figure 5 — Sampling system

Before each sample injection, determine the total volume of sample solution (V_s) using a graduated measuring cylinder (accurate to 1 cm^3).

Load and inject a fixed amount of well-mixed and filtered (0,45 µm membrane filter) sample solution. Flush the injection loop thoroughly between each sample run using the eluent solution. Use the same size loop for calibration standards and samples. Record the resulting output signal, i.e. sulfate peak size, in units of area or height.

The width of the retention-time window used to make identifications should be based upon measurements of actual retention-time variations of calibration standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size. However, the experience of the analyst should weigh heavily in the interpretations of the chromatograms.

If the output signal exceeds the calibrated working range of the system, dilute the sample with an appropriate amount of absorption solution and reanalyse. If the resulting chromatogram fails to produce adequate resolution, or if identification of the sulfate peak is questionable, fortify the sample with an appropriate amount of standard and reanalyse.

NOTE Retention time is inversely proportional to concentration, and sulfate anions are particularly sensitive. In some cases this peak migration may produce poor resolution or identification.

Compute sample sulfate concentration in mg/l (C_s) by comparing sample output signal with the sulfate calibration curve, taking into account any dilution made.

Similarly, determine the sulfate concentration of the field-zero sample (C_b).

7.3 Interferences

7.3.1 Sulfur trioxide

Sulfur trioxide (SO_3) (normally present as a fine mist of liquid sulfuric acid or gaseous sulfuric acid at high temperatures) is absorbed into the absorption solution, resulting in the formation of sulfate anion which is determined by the ion chromatograph. In many of the waste gases under investigation, however, sulfur trioxide is present only in small quantities and may then be considered negligible. For example, the mass concentration of sulfur trioxide is usually smaller than 0,05 times the mass concentration of sulfur dioxide. In cases where the mass concentration of sulfur dioxide is to be determined separately from the mass concentration of sulfur trioxide present in the waste gas under investigation, use a method other than that specified in this International Standard.

7.3.2 Volatile sulfates

Volatile sulfates that, under the conditions of sampling, form sulfate ions in the absorption solution can interfere.

7.3.3 Ammonia

Ammonia in the waste gas can lead to the formation of fine particles of ammonium sulfites and sulfates which may pass through the absorption solution resulting in a negative interference. In cases where excessive ammonia levels exist, that is, > 5 mg/m^3, use a method other than that specified in this International Standard.

7.3.4 Contaminants

Interference may be caused by contaminants in the reagent water and in other sample-processing apparatus that lead to discrete artefacts or elevated baseline in ion chromatograms.

7.4 Calibration

7.4.1 Establish ion chromatographic operating parameters equivalent to those given in the manufacturer's instructions.

7.4.2 Prepare calibration standards at a minimum of three concentration levels and a zero sample (absorption solution) over a chosen working range. If the calibrated working range exceeds the linear range of the system, a sufficient number of calibration standards must be analysed to allow an accurate calibration curve to be established. One of the calibration standards should be at a concentration near, but above, the detection limit if the system is operated on a number of attenuator ranges. The other calibration standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, i.e. ± 2%, each range shall be calibrated individually.

NOTE 1 A calibration standard consists of a sulfate solution prepared in the laboratory from the stock standard solution and accurately diluted as needed with absorption solution to calibrate the output signal with respect to sulfate concentration.

NOTE 2   As an example, for sulfur dioxide concentrations in the range 6 mg/m^3 to 333 mg/m^3, a working range for sulfate concentrations between 0,1 mg/l and 9 mg/l is suitable (64 is the molecular weight of sulfur dioxide and 96 is the molecular weight of sulfate ion).

7.4.3   inject an amount, depending on the injection loop volume, of the first calibration standard and tabulate the output signal against concentration. Flush the injection loop with eluent solution and repeat for the other calibration standards and zero sample. The results are used to prepare a sulfate calibration curve. Record the retention times during this procedure.

7.4.4   Verify the calibration curve each working day, whenever the anion eluent is changed or after every 20 samples. If the retention time varies from the expected values by more than ± 10 %, repeat the test using fresh calibration standards. If the results are still more than ± 10 %, prepare a new sulfate calibration curve.

7.4.5   Non-linear response within the range of the detector can result when the separator column capacity is exceeded (overloaded). The output signals for a sample when diluted 1 to 10 and when not diluted should be compared. If the calculated sulfate concentrations of the sample are the same, samples with this sulfate concentration need not be diluted.

7.5   Quality control

The analysis method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting chromatograms. Each laboratory shall demonstrate the ability to generate acceptable results with this method and have a formal certified quality control programme which is consistent with that described in ISO Guide 25. An example of a suitable quality control programme is given in annex A.

8   Expression of results

Calculate the mass concentration of sulfur dioxide (C_m) in mg/m^3 present in the waste gas sample at the state defined by $P = 101,3$ kPa and $T = 273,2$ K, related to the dry gas, using the equation:

$$C_m = \frac{64}{96} \times \frac{(C_s \times V_s) - (C_b \times V_{s'})}{(V_2 - V_1)} \times \frac{(273 + T)}{273,2} \times \frac{101,3}{P}$$

where,

C_b is the field-zero sample sulfate concentration, in mg/l;

C_s is the sample sulfate concentration, in mg/l;

T is the temperature, in degrees Celsius, of the volume of the waste gas under investigation passing through the gas meter;

V_s is the sample solution volume, in litres;

$V_{s'}$ is the absorption solution volume, in litres, in the sample solution;

V_1 is the volume reading, in cubic metres, of the dry gas meter at the start of sampling;

V_2 is the volume reading, in cubic metres, of the dry gas meter at the end of sampling; and

P is the atmospheric pressure, in kPa, at the sampling point.

NOTE 1   In cases where large clearance volumes exist or where the sampling volume is reduced and the clearance volume contains ambient air, the clearance volume should be estimated and subtracted from (V_2 - V_1) in the equation above.

NOTE 2   In most cases $V_{s'}$ can be assumed to equal to V_s. When low sulfur dioxide concentrations are expected, when the absorption solution is suspected to have a high background sulfate concentration or when a large quantity of condensate is collected in the absorbers, however, the solution from each absorber (A and B) and the washings are analysed individually

(see 6.7). If the concentrations and volumes of these solutions are denoted as C_{sA}, C_{sB}, C_w, V_{sA}, V_{sB}, and V_w respectively, then in the calculation above, $V_{s'} = V_w + 0,16$ and the term $(C_s \cdot V_s)$ is replaced by $[(C_{sA} \cdot V_{sA}) + (C_{sB} \cdot V_{sB})]$.

9 Performance characteristics

9.1 Detection limit

The detection limit of the test method can be estimated to be 6 mg/m^3 when passing the volume of 0,03 m^3 of the waste gas under investigation through the sampling train. This is based however on a detection limit of a sulfate concentration of 1,0 mg/l in the ion chromatography analysis.

NOTE 1 The detection limit refers to the value at which 50% of measured values exceed the detection limit [ISO 6879].

NOTE 2 This detection limit can be improved by modifications during sampling (e.g. increasing sampling time) and in the ion chromatograph system used (e. g. altering the working range).

9.2 Standard deviation under repeatability conditions

The performance criteria shown below have been obtained using two sampling trains and the method described in this International Standard. Based on the mass concentrations of sulfur dioxide found to be present in identical volumes, sampled simultaneously, of a waste gas from the same measurement point, the standard deviations under repeatability conditions given in table 1 have been obtained.

Table 1 — Standard deviations under repeatability conditions

Mean of mass concentration of sulfur dioxide mg/m^3	Number n of pairs of values	Standard deviation of series of measurements based on n pairs of values mg/m^3
6	7	1,7
22	6	1,8
123	6	7,4
211	5	7,2
333	6	15,0

In certain cases, it may be appropriate to modify the sampling train specified in 5.1, for example use of a longer sampling probe or alternative filter arrangement. In these cases, the operator should validate the modified method so that its performance does not deviate from the data shown above.

An interlaboratory test involving eight samples (sulfate concentrations of 2,7 mg/l to 7,0 mg/l) distributed to 13 laboratories gave an average relative standard deviation of 16 % for the ion chromatographic analysis method.

10 Test report

The test report shall include at least the following information:

a) reference to this International Standard;

b) identification code of the sample;

c) brief description of plant and process;

d) plant operating conditions;

e) location of the measurement plane;

f) location of the measurement point in the measurement plane;

g) changes in the plant operation during sampling, for example burner changes;

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

i) the test results;

j) date and time of sampling;

k) identification of test participants.

Annex A

(informative)

Example of a quality control programme

NOTE As the following is an example, the annex is informative. However, a quality control programme is mandatory and the wording of the example therefore takes a normative form.

A.1 Each laboratory using this analysis method shall have a formal quality control programme. The minimum requirements of this programme consist of initial demonstration of laboratory capability (A.2) and the analysis of fortified samples as ongoing confirmation of performance. The laboratory should maintain performance records to define and document the quality of data that are generated.

A.1.1 In recognition of the rapid advances in ion chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made, the analyst is required to repeat the procedure specified in A.2.

A.1.2 The laboratory should fortify and analyse a minimum of 10 % of all samples to monitor continuing laboratory performance. Field and laboratory duplicates shall also be analysed.

NOTE 1 A laboratory fortified sample matrix (LFM) is an aliquot of an environmental sample to which known quantities of sulfate (in the range 0,5 to 2,5 times the estimated true value) are added in the laboratory. The LFM is analysed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the sulfate in the sample matrix are determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

NOTE 2 Laboratory duplicates (LD) are two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures but not the sample collection, preservation, or storage procedures.

NOTE 3 Field duplicates (FD) are two samples taken at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage as well as with laboratory procedures.

A.2 Before performing any analyses, the analyst shall demonstrate the ability to generate acceptable accuracy and precision with this method, using a laboratory performance evaluation (LPE) sample.

NOTE An LPE sample is a sulfate solution distributed by a Quality Assurance Research Division (QARD) to several laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analysed with the procedures used for samples. Results of the analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. The true sulfate concentration values are unknown to the analyst.

A.2.1 Select a representative check concentration (LPC). Using the standard stock solution, prepare a concentrate in reagent water 100 times more concentrated than the selected check concentration.

NOTE An LPC (laboratory performance check) sample is prepared in the laboratory by adding appropriate volumes of standard stock solutions to reagent water and is used to evaluate the instrument system with respect to a defined set of method criteria.

A.2.2 Using a pipette, add $1,00 \text{ cm}^3$ of the LPC sample (A.2.1) to each of a minimum of four 100 cm^3 aliquots of reagent water. Analyse the mixed aliquots according to the procedure in 7.2.

A.2.3 Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), i.e. operator precision, for the results. If these values are outside those specified, review potential problem areas and repeat the test.

A.3   The analyst shall calculate method performance criteria and define the performance of the laboratory for each spike concentration of sulfate measured. The upper and lower control limits for method performance are calculated as follows:

$$\text{Upper Control Limit (UCL)} = R + 3s$$

$$\text{Lower Control Limit (LCL)} = R - 3s$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

A.4   The laboratory should develop and maintain separate accuracy statements of laboratory performance for each matrix being analysed by the laboratory. An accuracy statement for the method is defined as $R \pm s$. Develop the accuracy statement by the analyses of four aliquots of water or waste water as described in A.2.2, followed by the calculation of R and s.

A.5   Before processing any samples, the analyst shall demonstrate through the analysis of an aliquot of water that any contamination introduced via glassware and reagents is known. The result shall be recorded in the test report. Each time there is a change in reagents, a laboratory reagent blank shall be processed, as a safeguard against laboratory contamination.

A.6   It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are the most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates (A.1.2) shall be analysed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification shall be used. Whenever possible, the laboratory shall perform analyses of quality control samples and participate in relevant performance evaluation sample studies.

NOTE A quality control sample (QCS) is a sulfate solution of known concentration prepared by a laboratory other than the laboratory performing the analysis. The analysing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method.

A.7   To verify that standards have been prepared correctly, perform a reference standard check using a standard of known concentration prepared by an independent source.

A.8   With each batch of samples processed, analyse a single laboratory fortified blank (LFB) (A.1.2) containing sulfate at a concentration at or near 0,02 mg/l. If more than 20 samples are run in batch, analyse one LFB for every 20 samples. Evaluate the accuracy as in A.2.3. If acceptable data cannot be obtained, locate the problem and correct it.

A.9   At least quarterly, analyse replicates of LFBs to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.