INTERNATIONAL STANDARD

Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Hydrogen peroxide/barium perchlorate/Thorin method

Émissions de sources fixes — Détermination de la concentration en masse de dioxyde de soufre — Méthode au peroxyde d'hydrogène/perchlorate de baryum/Thorin

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7934 was prepared by Technical Committee ISO/TC 146, *Air quality.*

Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Hydrogen peroxide/barium perchlorate/Thorin method

1 Scope

This International Standard specifies a hydrogen peroxide/barium perchlorate/Thorin [1] method for the determination of the mass concentration of sulfur dioxide emitted from combustion facilities and technical processes with negligible amounts of sulfur trioxide and sulfuric acid. It is applicable from a minimum of 30 mg/m^3 sulfur dioxide by reference to sampling periods of normally 30 min.

At mass concentrations of sulfur dioxide greater than 2 000 mg/m^3, the volume of the waste gas under investigation passed through the sampling train is 30 litres.

Substances, which, if contained in the waste gas under investigation and thus in the waste gas sample, are known to have an effect on the titration reading, are given in 7.4. Information on performance characteristics is given in 8.2.

At mass concentrations of sulfur dioxide less than 30 mg/m^3, a sampling period greater than that specified in this International Standard is used.

All concentrations are based on dry gas at a temperature of 273,1 K and a 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 valid International Standards.

ISO 3696 : 1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 6879 : 1983, *Air quality — Performance characteristics and related concepts for air quality measuring methods.*

3 Principle

Absorption of the sulfur dioxide present in the waste gas sample passing through a hydrogen peroxide solution within a specified period, resulting in the formation of sulfuric acid solution.

Adjustment of the pH of the sample solution to pH 3,5 with sodium hydroxide solution or perchloric acid solution as required. Determination of the mass concentration of sulfate ions present in the treated sample solution by titration with a barium perchlorate solution using Thorin as indicator and calculation of the mass concentration of sulfur dioxide.

4 Reagents

During the analysis use only reagents of recognized analytical grade and only water of at least grade 3 purity according to ISO 3696.

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

4.1 Propan-2-ol [CH$_3$CH(OH)CH$_3$].

4.2 Absorption solution.

Place 100 ml of a 27 % (*m/m*) to 30 % (*m/m*) solution of hydrogen peroxide (H$_2$O$_2$) into a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Prepare this solution on the day of use.

4.3 Barium perchlorate, standard volumetric solution, $c[Ba(ClO_4)_2] = 0,005$ mol/l.

Use a commercially available barium perchlorate solution of defined concentration or, if this is not possible, prepare for example as follows.

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1) Thorin is also known as Thoron or Thoronol, the sodium salt of 4-[(2-arsonophenyl)-azo]-3-hydroxy-2,7-naphthalene-disulfonic acid.

Dissolve 1,7 g of anhydrous barium perchlorate [Ba(ClO$_4$)$_2$] in about 200 ml of water in a 1 000 ml one-mark volumetric flask. Make up to the mark with propan-2-ol (4.1) and mix well.

Standardize this solution accurately by titration against a 0,005 mol/l standard volumetric sulfuric acid solution.

1 ml of exactly 0,005 mol/l barium perchlorate solution is equivalent to a mass of sulfur dioxide of 0,320 33 mg.

4.4   Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,1 mol/l.

4.5   Perchloric acid, standard volumetric solution, c(HClO$_4$) = 0,1 mol/l.

4.6   Thorin, {4-[2-arsonophenyl]-azo]-3-hydroxy-2,7-naphthalene-disulfonic acid disodium salt} 2 g/l solution.

Dissolve 0,2 g of Thorin in water in a 100 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Store this solution in a bottle made of fused silica or polyethylene.

5   Apparatus

Ordinary laboratory apparatus and

5.1   Sampling equipment as specified in 5.1.1 to 5.1.13.

5.1.1   Sampling probe

Borosilicate glass or fused silica tube with a spherical ground joint at one end, of a suitable length to reach the representative measurement point(s) in the measurement plane of the waste gas flue and encircled by a heating jacket capable of producing a temperature of at least 200 °C.

NOTES

1   The heating jacket also serves as a protective tube to the gas sampling probe. The gas sampling probe should, therefore, always be used encircled by the heating jacket.

2   A stop valve before the first absorber is necessary to prevent loss of agents when sampling in flues under suction conditions.

5.1.2   Particle filter

Borosilicate glass or fused silica tube glass tube ends with spherical ground joints, packed in a progressive manner with chemically pure quartz wool. As an example, a particle filter that has proven suitable is shown in figure 1.

5.1.3   Absorbers

Absorption bottles of the Drechsel type, nominal capacity 100 ml or 250 ml as required (see table 1) equipped with an absorption bottle insert having a sintered filter (see figure 2), the porosity of which shall be fine enough to enable an absorption efficiency of at least 0,95 to be obtained. Sintered filters having pore diameters between 40 μm and 90 μm are suitable.

The absorption efficiency of each individual absorber should be tested twice a year as specified in 7.1.

NOTE — Impingers may be used if it is proven that absorption efficiency of at least 0,95 can be achieved.

5.1.4   Heating bandage, capable of producing a temperature of at least 200 °C.

5.1.5   Voltage regulator.

5.1.6   Trap

Absorption bottle of the Drechsel type, equipped with an absorption bottle insert not having a sintered filter.

5.1.7   Sampling pump, capable of drawing waste gas at a volume flow rate 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.

5.1.8   Regulating valve

Needle valve capable of adjusting a waste-gas flow rate within the range 0,02 m^3/h to about 0,2 m^3/h.

5.1.9   Gas metering device

Wet-gas meter (or dry gas meter with a drying tube upstream) capable of use at a waste-gas volume flow rate within the range 0,02 m^3/h to about 0,2 m^3/h, limits of error < 2 %, equipped with a thermometer (5.1.11).

Test the limits of error twice a year, for example by means of an appropriate soap bubble meter.

5.1.10   Connecting tubing of different lengths and of different internal diameters, made of polyethylene, silicone rubber or polytetrafluorethylene.

5.1.11   Thermometer, measuring range − 5 °C to + 50 °C, limits of error < ± 0,2 °C.

5.1.12   Barometer capable of measuring the atmospheric pressure present at the sampling location, limits of error approximately ± 1 % of the upper limit of measurement.

5.1.13   Stop watch.

5.2   Direct reading pH meter, preferably equipped with temperature compensation, measuring range 0 to 14, limits of error around pH 3,5 : < 0,2.

Calibrate the direct reading pH meter in accordance with the manufacturer's instructions using an appropriate buffer solution, the pH of which shall be accurately known at a given temperature. After calibration, rinse the electrodes thoroughly before use.

6 Sampling

6.1 Depending on in which of the ranges given in table 1 the expected mass concentration of sulfur dioxide lies, place, for example by pipette or dispenser, either 40 ml of the absorption solution (4.2) into each of the two 100 ml absorbers (5.1.3), or 80 ml of the absorption solution into each of the two 250 ml absorbers (5.1.3). Assemble the absorbers used and the apparatus specified in 5.1.1 to 5.1.2 and 5.1.6 to 5.1.11, to obtain a sampling train in accordance with the examples schematically represented in figure 3. Use spherical ground glass joints upstream of the second absorber.

6.2 Plug the intake of the sampling probe (5.1.1), switch on the sampling pump (5.1.7) and leak test the sampling train following normal laboratory practice.

Carefully release the sampling probe intake plug and switch off the sampling pump.

6.3 Insert the sampling probe into the access hole in the wall of the waste gas flue and place the tip of the sampling probe at the representative measurement point(s) in the measurement plane of the waste gas flue. Fill the resultant space between the sampling probe and the access hole in the wall of the waste gas flue with an appropriate sealing material such that ambient air does not reach the measurement point(s) nor waste gas escape to any great degree.

6.4 Take necessary measures to stop ambient air entering the waste gas flue through the space between the sampling probe and the heating jacket, thus causing a local cooling of the sampling probe and altering the sample composition.

Wrap the particle filter (5.1.2) in the heating bandage (5.1.4). Switch on the heating system and adjust the voltage regulator (5.1.5) to give a temperature at each point within the heated zone at which, during the sampling period, the formation of condensate will not be possible.

NOTE — The temperature of the heating bandage may be checked with a thermocouple.

At the end of the heating up period (about half an hour) record the reading on the gas meter (5.1.9) and the time, start the sampling pump and adjust the regulating valve (5.1.8) to give the desired waste gas-volume flow rate within the range of 0,03 m³/h to 0,2 m³/h.

6.5 Normally, the sampling period is 30 min. Record the reading on the gas meter thermometer (5.1.11), θ_i, and the reading on the barometer (5.1.12). The waste-gas volume flow rate selected shall be approximately constant.

NOTE — The sample flow rate is derived from the information given on the sample volume of waste gas given in table 1, and the normal sampling period (i.e. 30 min).

6.6 At the end of the sampling period, switch off the sampling pump, record the time and the reading on the gas meter. Remove the absorbers from the sampling train and transfer quantitatively both sample solutions into a sample bottle of suitable capacity. Rinse the absorption bottle including the absorption bottle inserts with water and force the wash water through the sintered filters using a pressure bulb. Add the wash water to the combined sample solution in the sample bottle.

6.7 Adjust, using the direct reading pH meter (5.2), the pH of the combined sample solution to pH 3,5 by adding the appropriate volume of the standard volumetric sodium hydroxide solution (4.4) or the standard volumetric perchloric acid solution (4.5) as required to the combined sample solution. Transfer the resultant combined sample solution into a one-mark volumetric flask of suitable nominal capacity (see table 1). Make up to the mark with water and mix well.

6.8 To take further waste gas samples, place into each of the two absorbers the appropriate volume of absorption solution, replace the absorbers and proceed as specified above. In such cases ensure that greater volumes of ambient air do not enter the particle filter or the sampling probe when the absorbers are disconnected from the sampling train.

NOTES

1 Experience shows that a temperature in the particle filter within the range 150 °C to 200 °C is sufficient.

Table 1 — Variation of the volume of waste gas to pass through the sampling train, joint sample solution of portion of the treated joint sample solution to be titrated and the resultant volume of Ba(ClO₄)₂ solution related to the range of mass concentration of sulfur dioxide

Expected mass concentration of sulfur dioxide mg/m³	Capacity of the absorbers ml	Volume of absorption solution to be placed into each of two absorbers ml	Volume of the waste gas to pass through the sampling train m³	Volume of the treated joint sample solution ml	Portion of the treated joint sample solution to be titrated ml	Volume of Ba(ClO₄)₂ solution used for the titration of the portion ml
30 to 100	100	40	0,100	100	20	1,875 to 6,25
100 to 500	100	40	0,060	100	20	3,75 to 18,75
500 to 1 000	250	80	0,060	250	20	7,5 to 15,0
1 000 to 2 000	250	80	0,030	250	20	7,5 to 15,0
2 000 to 5 000	250	80	0,030	250	20	15 to 37,5
2 000 to 5 100	250	80	0,030	250	10[1]	7,5 to 18,75
1) The portion of the joint sample solution to be titrated is diluted to 20 ml with distilled water.						

2 If a wet-gas meter is used in the sampling train, prior to sampling a volume of the waste gas under investigation should be passed through the sampling train that contains a mass of carbon dioxide (CO_2) greater than that needed to saturate the sealing liquid in the wet-gas meter with carbon dioxide. Experience shows that a volume of waste gas under investigation within the range 0,05 m^3 and 0,1 m^3 is sufficient. Furthermore, the temperature of the sealing liquid in the wet-gas meter should not significantly differ from the gas passing through.

7 Procedure

7.1 Test of absorption efficiency

Place the appropriate volume of absorption solution (see table 1) into each of two identical absorbers. Assemble the apparatus specified in 5.1 to obtain a sampling train. Use spherical ground glass joints upstream of the second absorber.

By reference to table 1 use a sampling period that results in the absorption of about 0,5 mg of sulfur dioxide per 1 ml of the absorption solution in the first absorber. Carry out sampling as specified in clause 6.

Calculate the absorption efficiency by dividing the volume of the standard volumetric barium perchlorate solution (4.3) used for titration of the sample solution in the first absorber by the sum of the volumes of the standard volumetric barium perchlorate solution (4.3) used for titration of the sample solutions in the first and second absorbers.

The absorption efficiency shall be at least 0,95. Absorbers that do not fulfil these requirements shall not be used.

7.2 Determination

Transfer the portion of the treated combined sample solution specified in table 1 into a conical flask of suitable nominal capacity and add 80 ml of propan-2-ol (4.1) plus four drops of the Thorin solution (4.6) and mix well. Record the ratio, f_V, of the volume of the treated combined sample solution to the volume of the portion taken.

Titrate the solution obtained with the standard volumetric barium perchlorate solution (4.3) to the change in colour from orange-yellow to permanent light pink, using either a burette with a spindle-valve or an automatic titrator, and record the volume needed for titration of this solution. Repeat this procedure and, if either end-point is indistinct, a third time and calculate the mean, V_1, of these values.

NOTE — In some types of light, in which the change in colour from orange-yellow to permanent light pink is very difficult to observe, as for example in fluorescent lighting and direct sunlight, titration should be carried out under a daylight lamp or, preferably, using a photometer with a glass fibre-optic light guide capable of measuring the transmission of liquids at a wavelength of 520 nm, and an automatic titrator.

7.3 Preparation of blank solution

Prepare a blank solution by adding 80 ml of propan-2-ol (4.1) and four drops of the Thorin solution (4.6) to a portion of the absorption solution, the volume of which corresponds to the volume of the selected portion of the treated joint sample solution, and proceed as specified above. The blank value, V_2, shall usually be evaluated each time the absorption solution is prepared.

NOTE — If the mass concentration of sulfur dioxide present in the waste gas under investigation is much greater than the detection limit of the method (see 8.2.1), then the evaluation of the blank values may be dispensed with.

7.4 Interferents

7.4.1 Sulfur trioxide

Sulfur trioxide (SO_3) is absorbed in the absorption solution resulting in the formation of sulfuric acid. In many of the waste gases under investigation, however, sulfur trioxide is present in small quantities and, in such circumstances, regard the effect on the titration reading of sulfur trioxide as negligible. For example, in waste gases from combustion facilities the mass concentration of sulfur trioxide is smaller than 0,05 times the mass concentration of sulfur dioxide.

In cases in which the mass concentration of sulfur dioxide is to be determined separately from the mass concentration of sulfur trioxide present in the waste gases under investigation use a method other than that specified in this International Standard.

7.4.2 Volatile sulfates

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

7.4.3 Anions

Anions that are absorbed by the absorption solution and that also form sparingly soluble salts with barium ions at pH 3,5 can interfere.

NOTE — Interferences by inorganic gaseous chlorine and fluorine compounds and stable oxides are not expected in normal flue gases. In exceptional cases (extremely high flue-gas temperature) interferences by volatile sulfates and volatile salts of polyvalent metal cations can take place.

7.4.4 Volatile salts of polyvalent metal cations

Those which respond to the indicator Thorin. The metal cations, however, can be removed from the treated joint sample solution by percolating the latter through a cation exchanger. (See note to 7.4.3.)

8 Expression of results

8.1 Calculation

Calculate the mass concentration of sulfur dioxide $\varrho(SO_2)$, expressed in milligrams per cubic metre, present in the waste gas sample at the state defined by $p_r = 101,3$ kPa and $T_r = 273,1$ K, related to the dry waste gas, by using the equation

$$\varrho(SO_2) = f_A \times f_V \times \frac{V_1 - V_2}{V_3} \times \frac{101,3 \times (273,1 + \theta_i)}{273,1 \times (p - p_{H_2O})}$$

where

f_A is the sulfur dioxide equivalent, in micrograms per millilitre, of the barium perchlorate solution used;

f_V is the ratio of the volume of the treated joint sample solution to the volume of the portion titrated;

p is the atmospheric pressure, in kilopascals, at the sampling stage;

p_{H_2O} is the partial pressure of water vapour, in kilopascals, at the Celsius temperature θ_i; if a dry gas meter is used, the partial pressure of water is 0;

V_1 is the mean, in millilitres, of the values of the volume of the standard volumetric barium perchlorate solution (4.3) used for titrating the portion (see table 1) of the treated joint sample solution;

V_2 is the mean, in millilitres, of the values of the volume of the standard volumetric barium perchlorate solution (4.3) used for titrating the blank solutions;

V_3 is the volume, in cubic metres, of the waste gas simple;

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

8.2 Performance characteristics

8.2.1 Lower detection limit[1]

The lower detection limit of the method is 0,72 mg/m^3, when passing the volume of 0,09 m^3 of the waste gas under investigation through the sampling train and selecting the portions specified in table 1.

8.2.2 Standard deviation under repeatable conditions

Based on the mass concentrations of sulfur dioxide found to be present in identical volumes, for one and the same interval of time, of a waste gas from much the same measurement point, the standard deviations under repeatable conditions given in table 2 have been evaluated:

Table 2 — Standard deviation under repeatable conditions

Mean of mass concentration of sulfur dioxide mg/m^3	Number n of pairs of values	Standard deviation of the series of measurements based on n pairs of values mg/m^3
16	10	4,4
221	35	7,1
470	10	17
2 000	28	74

9 Test report

The test report shall include at least the following information:

a) reference to this International Standard;

b) identification of the sample;

c) 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 operations during sampling, for example burner changes;

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

i) the test result;

j) date and time of sampling.

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1) For definition see ISO 6879.
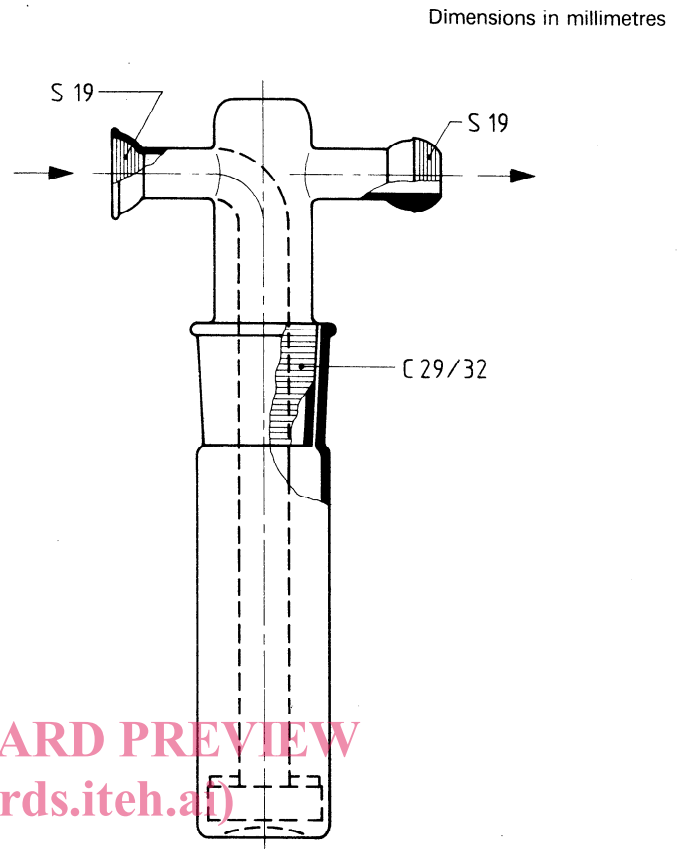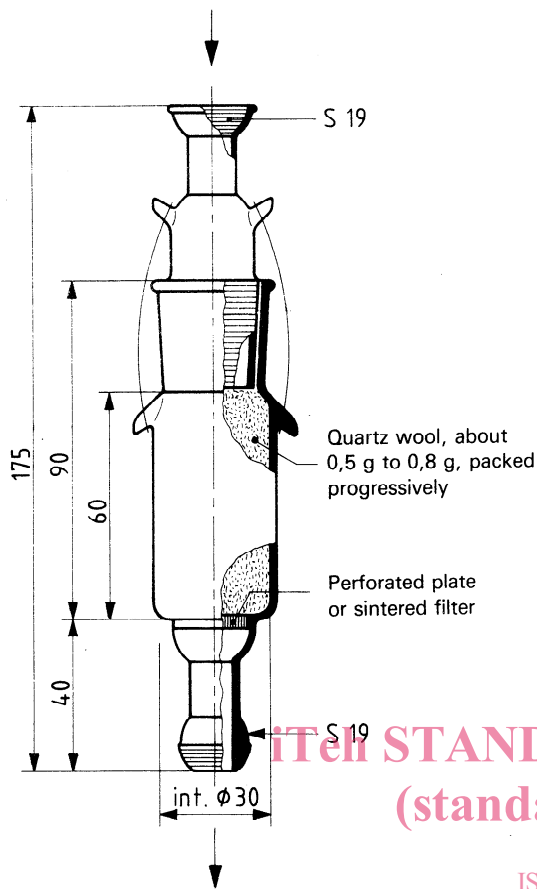
Dimensions in millimetres

Figure 1 — Example of a particle filter
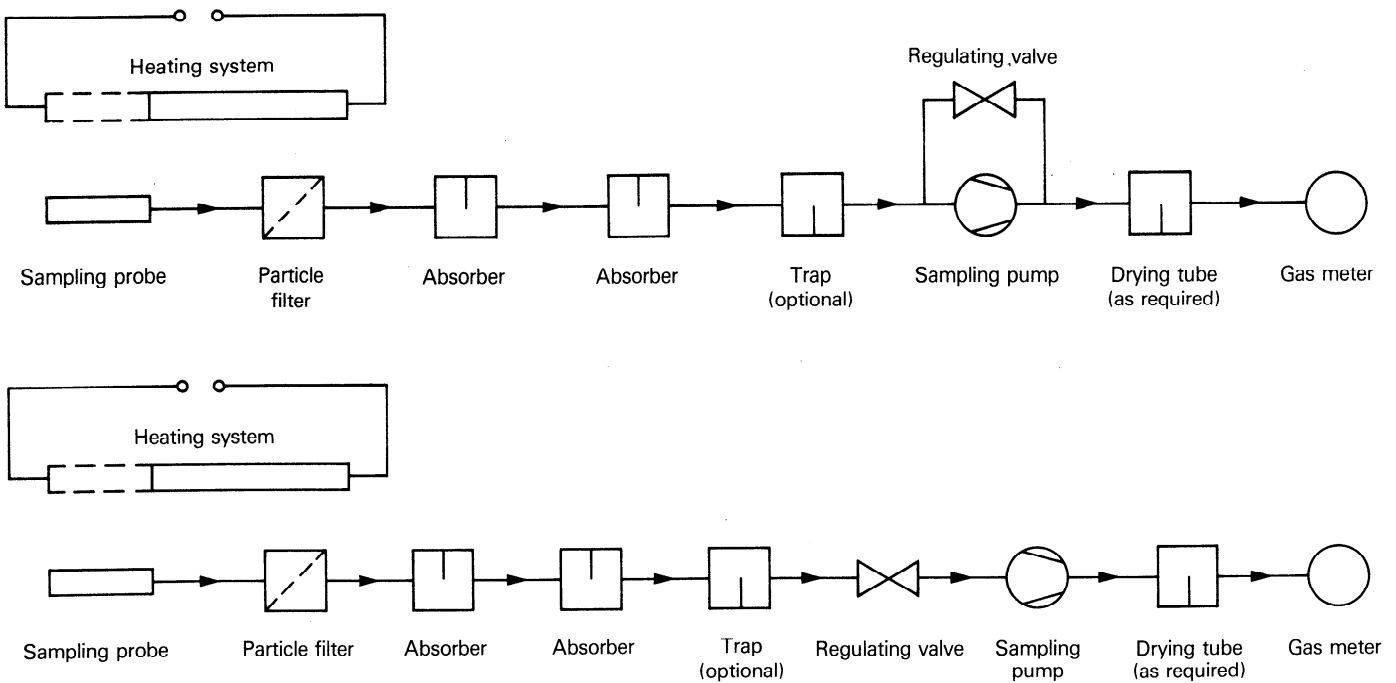
Figure 2 — Absorption bottle

Figure 3 — Schematic representation of sampling trains for the determination of the concentration of sulfur dioxide
in waste gases from stationary sources