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Natural gas — Determination of mercury

Gaz naturel — Détermination de la teneur en mercure

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Foreword

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

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 6978 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Sub-Committee SC 1, *Analysis of natural gas*.

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Natural gas — Determination of mercury

WARNING — Mercury presents a health hazard if incorrectly handled. Avoid prolonged inhalation of the vapour. Spillages of mercury should be removed immediately, even from places which are difficult to access.

1 Scope

This International Standard specifies two methods, A and B, for the determination of mercury, including elemental mercury, dimethyl mercury and diethyl mercury, in natural gas.

Method A prescribes sampling at atmospheric pressure, using absorption in potassium permanganate solution followed by reduction of mercury ions and subsequent analysis by flameless atomic absorption spectrometry. The lower detection limit is $0,05 \mu\text{g}/\text{m}^3$ for a sampling time of 2 h. Aromatic hydrocarbons may interfere. If aromatic hydrocarbons are present, method B is recommended.

Method B prescribes sampling at atmospheric or higher pressure using adsorption of mercury on silver/gold followed by desorption and subsequent analysis by flameless atomic absorption spectrometry. The lower detection limit is $3 \times 10^{-4} \mu\text{g}/\text{m}^3$ at a minimum pressure of 3 MPa (30 bar) and for a sampling time of 2 h.

Method A is recommended for natural gases with a high mercury content ($> 0,5 \mu\text{g}/\text{m}^3$) while method B is preferred for lower mercury concentrations ($10^{-3} \mu\text{g}/\text{m}^3$ to $1 \mu\text{g}/\text{m}^3$).

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 641:1975, *Laboratory glassware — Interchangeable spherical ground joints.*

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

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

3 Principle

3.1 Method A: Determination of mercury by sampling at atmospheric pressure

The gas is passed through a gas washing bottle filled with a potassium permanganate-sulfuric acid solution. The mercury present in the gas is oxidized to mercury(II) ions. The excess of permanganate is reduced by a hydroxylamine hydrochloride solution, and the mercury(II) ions are reduced by a tin(II) chloride solution to form elemental mercury which is drawn into nitrogen stream. The nitrogen stream is passed through an absorption cell (optical path length 175 mm) which is placed in an atomic absorption spectrometer. The mercury is determined by measuring the absorbance of the mercury resonance line at 253,7 nm.

3.2 Method B: Determination of mercury by sampling at atmospheric or high pressure

The gas is passed through a silica tube containing silver lint placed in a stainless steel high-pressure vessel. Mercury present in the gas is quantitatively trapped by the silver and is subsequently released by heating the tube in an oven at 850 °C whilst passing a stream of air. The mercury vapour is trapped in a second silica tube filled with gold thread, whilst hydrocarbons and other contaminants are oxidized and passed through. The tube contain-

ing gold thread is heated in an oven at 850 °C and, by means of an air stream, the mercury vapour is passed through an absorption cuvette and determined by flameless atomic absorption spectrometry at a wavelength of 253,7 nm.

4 Method A: Determination of mercury by sampling at atmospheric pressure

4.1 Reagents and materials

All reagents shall be of recognized analytical grade and have a mercury content as low as possible. For all purposes where water is mentioned, water of a suitable purity shall be used; various types of water are described in ISO 3696.

4.1.1 Aqua regia, cleaning solution

Mix 3 volumes of concentrated hydrochloric acid ($\rho_{20} = 1,19$ g/ml) with 1 volume of concentrated nitric acid ($\rho_{20} = 1,40$ g/ml).

4.1.2 Sulfuric acid solution, 65 % (m/m).

Cautiously add 1 volume of concentrated sulfuric acid ($\rho_{20} = 1,84$ g/ml) to 1 volume of water.

4.1.3 Potassium permanganate, solution, 4 % (m/m).

Dissolve 40 g of potassium permanganate in 1 litre of water and decant the clear liquid. Add 5 g of manganese dioxide. Shake this solution vigorously for 30 min. Allow the solution to stand overnight and remove the manganese dioxide by centrifuging. Store in a brown flask.

4.1.4 Potassium permanganate absorption solution.

Mix 1 volume of the potassium permanganate solution (4.1.3), 1 volume of the sulfuric acid solution (4.1.2) and 2 volumes of water.

4.1.5 Tin(II) chloride solution, 10 % (m/m).

Dissolve 20 g of tin(II) chloride dihydrate in 40 ml of warm concentrated hydrochloric acid. Strip the solution with mercury-free nitrogen or air at a rate of about 50 l/h for 5 min and dilute to 200 ml with water.

NOTE 1 The stripping procedure is intended to remove any traces of mercury from the tin(II) chloride solution.

4.1.6 Hydroxylamine chloride, solution, 10 % (m/m).

Dissolve 10 g of hydroxylamine chloride in water and dilute to 100 ml.

WARNING — Hydroxylamine chloride attacks the skin and may cause dermatitis. Prevent contact with the skin and eyes.

4.1.7 Mercury standard solution, 1,0 g/l.

Dissolve 1,353 g of mercury(II) chloride (HgCl_2) in water, add 5 ml of nitric acid and dilute with water to 1 000 ml in a volumetric flask.

NOTE 2 Alternatively the solution can be prepared with mercury(II) nitrate.

4.1.8 Mercury standard solution, 1 mg/l.

Pipette 10 ml of the mercury standard solution (4.1.7), into a 1 000 ml one-mark volumetric flask, add 5 ml of nitric acid and dilute with water to the mark. Pipette 10 ml of this solution into a 100 ml one-mark volumetric flask, add 5 ml of nitric acid, and dilute with water to the mark.

Prepare a fresh solution every week.

4.1.9 Nitrogen, pure.

4.2 Apparatus

4.2.1 Atomic absorption spectrometer.

Any flameless atomic absorption spectrometer can be used if a suitable gas absorption cell can be maintained, providing it can measure at 253,7 nm in the range 0, to 100 μm^3 in the purging gas stream.

NOTE 3 Mercury vapour monitors, specially suited for this method, are commercially available.

4.2.2 Recorder or electronic integrator, suitable for the atomic absorption spectrometer (4.2.1).

4.2.3 Two gas washing bottles, of capacity 100 ml, with a sintered glass filter P 160 (100 μm to 160 μm , see ISO 4793), heatable if they are to be used at a temperature below 10 °C.

4.2.4 Two heated valve assemblies, stainless steel (see figure 1).

4.2.5 Two flowmeters, capable of measuring air flow rates up to 150 l/h.

4.2.6 Gas meter, wet type, 1 litre per revolution.

4.2.7 Gas meter, dry type, of capacity 2,5 m^3/h , including a thermometer.

4.3 Sampling and analysis

Any connection of sampling equipment to the sampling point shall be of stainless steel, as short as

possible and preferably be heated to the pipeline temperature.

Whenever the distance from sampling point to sampling equipment is too long, special care shall be taken (e.g. the use of a by-pass fast loop).

Clean all glassware to be used with aqua regia (4.1.1). Check the glassware, air, nitrogen and reagents for mercury contamination by making frequent blank tests.

Check the breakthrough of mercury through the potassium permanganate solution in the gas washing bottle regularly, especially in the case of gases which have been processed. Do this by connecting two gas washing bottles in series and checking the mercury content of the second bottle.

WARNING — Ascertain that the sampling procedure complies with local safety regulations.

4.3.1 Assembly apparatus

Place 40 ml of potassium permanganate solution (4.1.4) in the gas washing bottle (4.2.3) and assemble the apparatus as shown in figure 1. Place the valve assembly (B) in a suitable container filled with hot water (> 80 °C) and connect valve (A) to the sampling point.

NOTES

4 Alternatively, the valve assemblies can be heated by other means (trace heating, etc.).

5 If the pressure of the gas is less than 1 MPa (10 bar) the heated valve assembly (B) may be omitted.

4.3.2 Absorption of mercury

Open valve (A) completely and adjust valve (B) to give a sample flow rate of 50 l/h to 140 l/h. Pass a measured amount of gas through so as to absorb approximately 0,1 µg to 5 µg of mercury. If the solution is no longer violet after absorption, repeat the test using a smaller volume of gas or more absorption solution. Read the volume passed through the gasmeter and measure the temperature.

4.3.3 Spectrometric measurement

Transfer an aliquot of the solution obtained in 4.3.2 to a gas washing bottle, then add hydroxylamine chloride solution (4.1.6) drop by drop until all the potassium permanganate is reduced. Dilute to 40 ml with water, add 2 ml of tin(II) chloride solution (4.1.5) and mix by giving the bottle one swirl. Connect the bottle to the spectrometer as shown in figure 2. Strip the mercury from the solution with a nitrogen stream at a flowrate of 75 l/h and record the peak height or area.

4.3.4 Calibration

NOTE 6 To improve the accuracy of the method, it is recommended that the amount of mercury in the test solution be as close as possible to the amount of mercury in the mercury standard solution (4.1.8). In this respect, multi-level calibration can be advantageous.

Disconnect the washing bottle filled with potassium permanganate solution as specified in 4.3.1, and add 100 µl of mercury standard solution (4.1.8), equivalent to 0,1 µg of mercury, to the contents of the bottle.

Add hydroxylamine chloride solution (4.1.6) drop by drop until all the potassium permanganate is reduced, then proceed as indicated in 4.3.3.

NOTE 7 Alternatively, a standard addition procedure may be used.

4.3.5 Blank test

Carry out a blank test using the same amounts of reagents and water as used for the determination in 4.3.3. Measure the peak height or area.

NOTE 8 The blank test on 10 ml of the absorption liquid should give a result equivalent to less than 5 ng of mercury. If the result of the blank test is higher, the glassware or the reagents may be contaminated. In this case, clean again with aqua regia and investigate for reagent contamination if necessary.

4.3.6 Expression of results

4.3.6.1 Calculate the volume V of gas passed through the absorber, in cubic metres at 0 °C and 101,325 kPa (1 013,25 mbar), by means of the following equation:

$$V = V_1 \times \frac{273,15}{273,15 + t} \times \frac{p}{101,325}$$

where

V_1 is the gas volume, in cubic metres, read from the gasmeter;

t is the temperature, in degrees Celsius, of the gas at the gasmeter;

p is the barometric pressure, in kilopascals.

4.3.6.2 Calculate the mercury content ρ_{Hg} of the gas, in micrograms per cubic metre of gas at 0 °C and 101,325 kPa (1 013,25 mbar) by means of the following equation:

$$\rho_{\text{Hg}} = \frac{h_s - h_b}{h_c \cdot V} \times F \cdot m$$

where

h_s	is the peak height or area of the sample, in scale divisions;
h_b	is the peak height or area of the blank test, in scale divisions;
h_c	is the peak height or area of the calibration, in scale divisions;
F	is the ratio of volume of absorption liquid to the aliquots of solution transferred in 4.3.3;
m	is the mass of mercury, in micrograms, added from the calibration mixture (here 0,1 μg);
V	is the volume of gas, in cubic metres, calculated in 4.3.6.1.

5 Method B: Determination of mercury by sampling at atmospheric or higher pressure

5.1 Reagents and materials

All reagents shall be of recognized analytical grade and have a mercury content which is as low as possible. For all purposes where water is mentioned, water of a suitable purity shall be used; various types of water are described in ISO 3696.

5.1.1 Acetone (2-Propanone), if required.

5.1.2 Compressed air, free of oil and water. Apply a mercury filter (5.2.11) to the supply line to remove any mercury present.

5.1.3 Gold thread, diameter approximately 0,5 mm, minimum purity 99,99 % (m/m).

5.1.4 Iso-octane (2,2,4-Trimethylpentane), if required.

5.1.5 Mercury, purity 99,9 % (m/m).

5.1.6 Silver lint, approximately 0,05 mm \times 0,4 mm, minimum purity 99,99 % (m/m).

5.1.7 Aqua regia, cleaning solution.

Mix 3 volumes of concentrated hydrochloric acid ($\rho_{20} = 1,19 \text{ g/ml}$) with 1 volume of concentrated nitric acid ($\rho_{20} = 1,40 \text{ g/ml}$).

5.2 Apparatus

5.2.1 Atomic absorption spectrometer.

Any flameless atomic absorption spectrometer can be used if a suitable gas absorption cell can be

maintained, providing it can measure at 253,7 nm, in the range 0 to 100 $\mu\text{g}/\text{m}^3$ in the purging gas stream, and is equipped with a built-in sample suction pump.

5.2.2 Recorder or electronic integrator, suitable for the atomic absorption spectrometer (5.2.1).

5.2.3 Combustion furnace, with temperature controller, capable of maintaining a temperature of $850 \text{ }^\circ\text{C} \pm 25 \text{ }^\circ\text{C}$, inside diameter 20 mm and length 120 mm.

5.2.4 Two silica tubes, outside diameter 12 mm and length 300 mm, provided with two spherical joints S13/5 (balls) (see ISO 641) with O-rings and two sets of three indentations, as shown in figure 3.

5.2.5 High-pressure vessel (as shown schematically in figure 6), stainless steel, working pressure 8 MPa (80 bar), provided with a by-pass having a stainless steel needle-valve, and a pressure gauge (for example Bourdon-type), range from 0 MPa to 10 MPa (0 bar to 100 bar), with divisions at 0,1 MPa (1 bar) or less. The inlet tube shall be provided with a coupling to connect a silica tube (5.2.4). A safety device bleeding off at a pressure of 8 MPa (80 bar) at the inlet side of the vessel shall be used.

NOTE 9 It is also possible to use higher working pressures. In this case, all equipment shall be suited for this higher pressure.

5.2.6 Two heated valve assemblies, stainless steel (see figure 6).

5.2.7 Two flowmeters, e.g. of the rotameter type, capable of measuring air flow rates up to 75 l/h and 8 m^3/h , respectively.

5.2.8 Gas meter, dry type, capable of measuring an air flow rate of 8 m^3/h , including a thermometer.

5.2.9 Two serum bottles, of capacity 50 ml, provided with metal screw caps fitted with holes and rubber septums.

5.2.10 Syringe, of capacity 1 ml, for the injection of gases.

5.2.11 Mercury filter, e.g. a glass tube filled with silver lint (5.1.6), with suitable connections for assembly in the air supply line (see figures 2 and 7).

5.2.12 T-piece, glass, provided with couplings and an injection port with a silicone-rubber septum (see figure 5).

5.2.13 Tubes, stainless steel, inside diameter 1,4 mm, outside diameter 2,0 mm, or **syringe needles**, for use in the calibration assembly (see figure 4).

5.3 Sampling and analysis

Any connection of sampling equipment to the sampling point shall be as short as possible and preferably be heated to pipeline temperature.

Whenever the distance from the sampling point to sampling equipment is too long, special care shall be taken (e.g. the use of a by-pass fast loop).

Clean all glassware to be used with aqua regia (5.1.7). Check the glassware, air, nitrogen and reagents for mercury contamination by making frequent blank tests.

Check the breakthrough of mercury through the silica tube with silver lint regularly, especially in the case of gases which have been processed. Do this by connecting two silica tubes containing silver in series and checking the mercury content of the second tube.

WARNING — Ascertain that the sampling procedure complies with local safety regulations.

5.3.1 Filling of silica tube with silver lint

Connect end A of the silica tube (5.2.4) (see figure 3) to a vacuum source and feed the silver lint (5.1.6) into the other end (C) of the tube so as to fill section B. Do not pack the tube tightly.

NOTE 10 As a rough guide, a quantity of 3 g of material per tube filling is sufficient.

5.3.2 Filling of silica tube with gold thread

From the gold thread (5.1.3) make curls of 5 mm length and 2 mm diameter and feed them into end C of a silica tube (5.2.4) (see figure 3). Fill section B of the tube approximately half full.

5.3.3 Cleaning of filled silica tubes

Set the temperature of the combustion furnace (5.2.3) at 850 °C and insert one of the filled silica tubes (5.3.1 or 5.3.2). Apply an air stream of 60 l/h for several minutes. Allow the tube to cool and repeat this procedure at least three times. Connect the tube to the mercury vapour determination apparatus as shown schematically in figure 8 and check that the mercury signal is zero.

Repeat the above procedure with the other filled silica tube.

5.3.4 Calibration

NOTE 11 To improve the accuracy of the method it is recommended that the amount of mercury in the test solution be as close as possible to the amount of mercury in the mercury standard solution (4.1.8).

Introduce a few droplets of mercury (5.1.5) into two 50 ml serum bottles (5.2.9), close them with screw cap and septum and connect them with stainless steel tubing (or alternatively with polyvinyl chloride tubing with syringe needles at both ends) (5.2.13) and make an assembly as shown in figure 4.

Connect a T-piece with injection port (5.2.12) to an air supply as shown in figure 5 and attach the silica tube containing gold thread. Adjust the air flow to 60 l/h. Flush the syringe at least three times. Take out 1 ml of head space calibration sample from the serum bottle and inject it into the system. Measure the temperature to the nearest 1 °C and record the concentration of the mercury, in nanograms per millilitre, with the help of table 1. Keep the serum bottles and syringe at the same constant temperature. Proceed as specified in 5.3.7. Repeat at least three times.

Table 1 — Saturated concentration of mercury in air at different temperatures

Temperature °C	Saturated concentration of mercury in air ng/ml
16	9,4
18	11,2
20	13,2
22	15,6
24	18,3
26	21,5
28	25,2
30	29,5
32	34,4
34	40,1
36	46,6
38	54,0
40	62,5

5.3.5 Adsorption of mercury

5.3.5.1 Place the silica tube filled with silver lint in the high-pressure vessel (5.2.5) and assemble the apparatus as shown in figure 6. Place the valve assemblies (B and D) in suitable containers filled with hot water (> 80 °C) and connect valve (A) to the sampling point.

NOTES

12 Alternatively, the valve assemblies can be heated by other means (trace heating, etc.).

13 If the pressure of the gas is less than 8 MPa (80 bar), the heated valve assembly (B) may be omitted.

5.3.5.2 Open by-pass valve (C) and supply valve (A) and admit the gas through valve (B) into the high-pressure vessel until the pressure has built up to the pressure of the sampling point. Carefully adjust valves (B) and (D) in order to obtain a sample flow rate expressed in cubic metres per hour at atmospheric pressure, which is numerically equal to the absolute pressure in the high-pressure vessel in megapascals (or 0,1 of the absolute pressure in bars). Take care to ensure that the maximum working pressure of the equipment is not exceeded.

5.3.5.3 Close by-pass valve (C) and simultaneously read the gas meters (5.2.8). Measure the temperature of the gas near the gas meter to the nearest 1 °C. Pass between 0,1 m³ and 6 m³ of gas through the system in order to collect 2 ng to 100 ng of mercury.

5.3.5.4 Open by-pass valve (C) and simultaneously read the gas meter. Close valve (A). As soon as atmospheric pressure is again reached read the gas meter, disconnect the high-pressure vessel and remove the silica tube. Seal both ends with rubber plugs. Calculate the volume passed through the gas meter and read the temperature at the gas meter.

NOTE 14 If gas at atmospheric pressure is available, the sampling procedure can be simplified as shown in figure 9. The maximum flow rate through the silica tube is 0,1 m³/h.

5.3.6 Desorption of mercury

5.3.6.1 Remove the plugs of the charged tube containing silver lint, connect it to the silica tube containing gold thread and construct the assembly for the stripping step as shown in figure 7; however, do not yet insert the part of the tube containing the silver lint into the furnace. The charged tube should be connected in such a way that the air stream flows in the opposite direction to the flow during charging.

IMPORTANT — In the case of a condensate-rich natural gas, it is recommended to flush the tube with iso-octane (5.1.4) and acetone (5.1.1) in order to remove most of the hydrocarbons prior to analysis. Dry the tube in an air stream.

5.3.6.2 Bring the furnace temperature to 850 °C and adjust the air stream to 60 l/h. Heat the charged tube by sliding it slowly into the hot furnace. Maintain the tube at this temperature for 10 min.

5.3.7 Spectrometric measurement

Disconnect the charged silica tube filled with gold thread and connect it to the mercury vapour determination apparatus by means of PVC tubing (see figure 8). Switch the apparatus to standby position (pump switched off) and place the tube in the furnace at 850 °C. After 30 s, switch the apparatus to

the selected range (the pump is now automatically switched on) and the mercury signal will be presented on the recorder (5.2.2). Measure the peak height area.

NOTES

15 For measuring the peak area, an analog or a digital integrator is suitable. If the peak area is measured by hand, either geometrically or by planimeter, use a high chart speed on the recorder in order to obtain a wide peak.

16 As an alternative to a suction pump, a stream of nitrogen or argon may be used to transport the mercury from the heated silica tube to the spectrometer.

5.3.8 Expression of results

5.3.8.1 Calculate the volume V of gas passed through the high-pressure vessel, in cubic metres at 0 °C and 101,325 kPa (1 013,25 mbar), by means of the following equation:

$$V = V_1 \times \frac{273,15}{273,15 + t} \times \frac{p}{101,325}$$

where

V_1 is the gas volume, in cubic metres, as calculated in 5.3.5.4;

t is the temperature, in degrees Celsius, of the gas in the gas meter;

p is the barometric pressure, in kilopascals.

5.3.8.2 Calculate the mercury content of ρ_{Hg} of the gas, in micrograms per cubic metre of gas at 0 °C and 101,325 kPa (1 013,25 mbar), by means of the following equation:

$$\rho_{\text{Hg}} = \frac{A_s \cdot m}{A_c \cdot V}$$

where

A_s is the height or area of the sample peak, in arbitrary units;

A_c is the height or area of the average peak of the calibration peaks, in arbitrary units;

m is the mass, in micrograms, of mercury added during the calibration;

V is the volume, in cubic metres, of gas as calculated in 5.3.8.1.

6 Precision

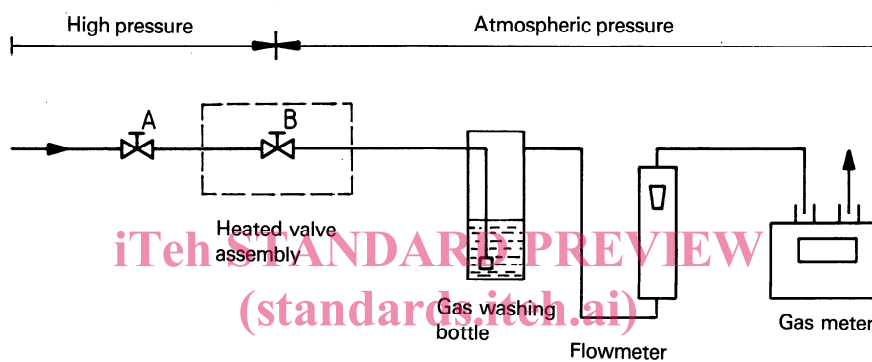
No statistically justified criteria are available. From a limited number of data considered it has appeared

that duplicate results by the same operator do not normally differ from each other by more than 6 % of their mean at a level of 10 ng of mercury, using method B.

7 Test report

The test report shall include the following particulars:

- a) the date and time of sampling;
- b) the place at which the sample was taken;
- c) the conditions of the gas at the sampling point such as temperature, pressure and throughput;
- d) reference to the sampling method used (including the cylinder size);
- e) reference to the method used for analysing the sample;
- f) the concentrations determined;
- g) if possible, the precision of the determination, including the number of determinations;
- h) any unusual features noted during the determination;
- i) reference to this International Standard.



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Figure 1 Method A: Assembly of sampling equipment