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Water quality — Determination of dissolved sulfide — Photometric method using methylene blue

Qualité de l'eau — Dosage des sulfures dissous — Méthode photométrique au bleu de méthylène

Reference number
ISO 10530:1992(E)

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 10530 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 2, *Physical, chemical, biochemical methods*.

Annex A forms an integral part of this International Standard.

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Water quality — Determination of dissolved sulfide — Photometric method using methylene blue

1 Scope

1.1 Application range

This International Standard specifies a photometric method for the determination of dissolved sulfide in water. The method is applicable to the determination of dissolved sulfide in a mass concentration range from 0,04 mg/l to 1,5 mg/l.

Higher concentrations may be determined by reducing and subsequently diluting the volume of the water sample used.

The method is applicable to waste water and natural waters requiring filtration.

1.2 Interferences

The following ions do not interfere with the method as long as the mass concentrations specified below are not reached or exceeded:

Cyanide	2 mg/l
Iodide	20 mg/l
Thiosulfate	900 mg/l
Thiocyanate	900 mg/l
Sulfite	700 mg/l

When applying this procedure, the determination of the sulfide portion from polysulfides will be incomplete.

Mass concentrations of carbon disulfide < 10 mg/l and/or ethyl mercaptan < 1 mg/l do not interfere with the method.

Waters which are not filterable according to clause 6 cannot be analysed by this method. In those cases sulfide which is easily liberated at pH 4 is determined. (An International Standard covering this is being prepared.)

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was 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 edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-3:1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*.

3 Principle

Filtration of the water sample in order to separate the suspended matter and sulfides of low solubility. Conservation of the sulfide in the filtrate by addition of ascorbate solution. Stripping of the sulfides from the filtrate using nitrogen and transfer into a receiving flask containing an aqueous zinc acetate solution.

Formation of leukomethylene blue in the receiving flask on the addition of acid dimethyl-*p*-phenylendiamine solution and oxidation to methylene blue by addition of iron(III) ions. Measurement of the absorbance of this complex at a wavelength of 665 nm.

4 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity which shall be freed from oxygen by appropriate measures, such as boiling out or gassing with nitrogen.

4.1 Sulfuric acid, $\rho(H_2SO_4) = 1{,}84$ g/ml.

4.2 Sodium hydroxide (NaOH), 32 % (m/m) solution, $c(\text{NaOH}) \approx 10$ mol/l.

4.3 Zinc acetate solution.

Dissolve 20 g of zinc acetate-dihydrate $[\text{Zn(CH}_3\text{COO)}_2.2\text{H}_2\text{O}]$ in water and make up to 1 l.

Some turbidity may occur, but this will not interfere with the determination.

4.4 Phthalate buffer solution, pH 4,0 ± 0,1.

Dissolve 80 g of potassium hydrogenphthalate ($C_8H_5KO_4$) in 920 ml of water. Check the pH of this solution and, if necessary, adjust to pH 4,0 by adding diluted sodium hydroxide solution [e.g. $c(\text{NaOH}) = 1$ mol/l] or hydrochloric acid solution [$c(\text{HCl}) = 1$ mol/l].

4.5 Ascorbate solution, pH 10 ± 0,1.

Dissolve 10 g of ascorbic acid ($C_6H_8O_6$) in 90 ml of water and adjust to pH 10 by adding sodium hydroxide solution (4.2). Stopper the bottle immediately.

Prepare this solution freshly before use.

4.6 Colour-forming reagent solution.

Suspend, in a 1 000 ml measuring flask, 2 g of N,N-dimethyl-1,4-phenyl diammonium chloride ($C_8H_{14}Cl_2N_2$) in 200 ml of water.

Cautiously add 200 ml of sulfuric acid (4.1), cool, and dilute to volume with water.

4.7 Ammonium iron(III) sulfate solution.

Place 50 g of ammonium iron(III) sulfate dodecahydrate $[\text{NH}_4\text{Fe(SO}_4)_2.12\text{H}_2\text{O}]$ in a 500 ml measuring flask. Add 10 ml of sulfuric acid (4.1) and then cautiously dilute to volume with water.

4.8 Sodium sulfide stock solution.

Place an adequate quantity of sodium sulfide hydrate $[\text{Na}_2\text{S}.x\,\text{H}_2\text{O}, (x = 7\text{-}9)]$ corresponding to approximately 0,5 g of sulfur as sulfide, with a thiosulfate content $< 0,5$ %, in a 1 000 ml measuring flask. Dissolve in water (clause 4) and dilute to volume.

This solution is stable for 2 d to 3 d.

Prior to use, the exact concentration is determined iodometrically (see annex A).

4.9 Sodium sulfide standard solution.

Pipette 10 ml of sodium sulfide stock solution (4.8) into a 1 000 ml measuring flask. Dilute to volume with water.

1 ml of this Standard solution contains approximately 5 µg of sulfide. The exact concentration is determined iodometrically (see annex A).

Prepare this solution freshly before use.

5 Apparatus

5.1 Filtration device, e.g. three-ring piston syringe, of capacity 50 ml, with one-way filtering attachment (pore size 0,45 µ/m) (see figure 1).

Alternatively, for waters which are difficult to filter, a pressure filtration device with membrane filter (pore size 0,45 µm) can be used. (See figure 2.)

5.2 Stripping apparatus for the separation of sulfide, for example as shown in figure 3. It consists of a reaction flask, of capacity 250 ml, with a lateral ground-glass joint attachment for the drop funnel, of capacity 100 ml, provided with a gas inlet tube ending at the bottom of the flask, vertically mounted condenser or riser tube, and an absorption vessel.

Dimensions: see figure 3.

5.3 Measuring cylinder, of capacity 25 ml.

5.4 Measuring flasks, of capacity 50 ml, 100 ml, 500 ml and 1 000 ml.

5.5 Measuring pipettes, of capacity 1 ml and 10 ml.

5.6 One-mark pipette, of capacity 1 ml, 2 ml, 5 ml, 10 ml, 20 ml, 50 ml and 100 ml.

5.7 Dispensers.

5.8 Microlitre syringes.

5.9 Gas supply with nitrogen, of high purity [99,996 % (m/m) pure].

5.10 Gas flow measuring device, suitable for a volume flow of 40 l/h.

5.11 pH-meter, equipped with an appropriate electrode.

5.12 Spectrometer or **filter photometer**, suitable for absorbance measurements at 665 nm.

5.13 Cuvettes, of path length 1 cm.

Dimensions in millimetres

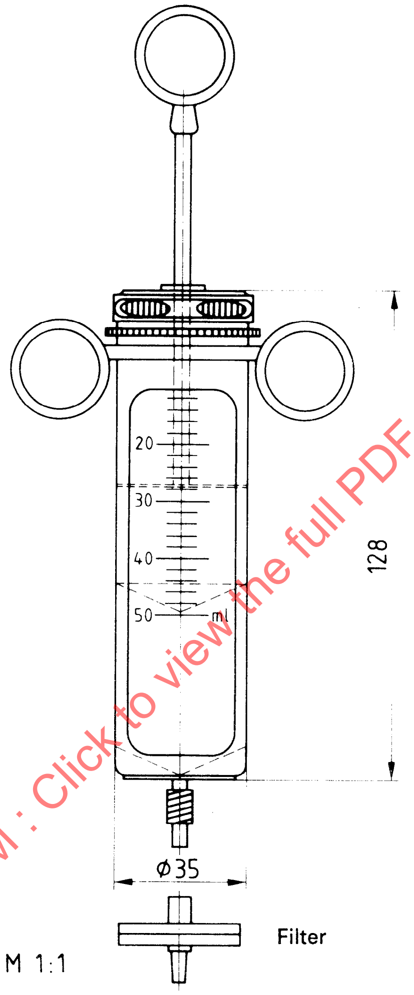

Figure 1 — Three-ring piston syringe

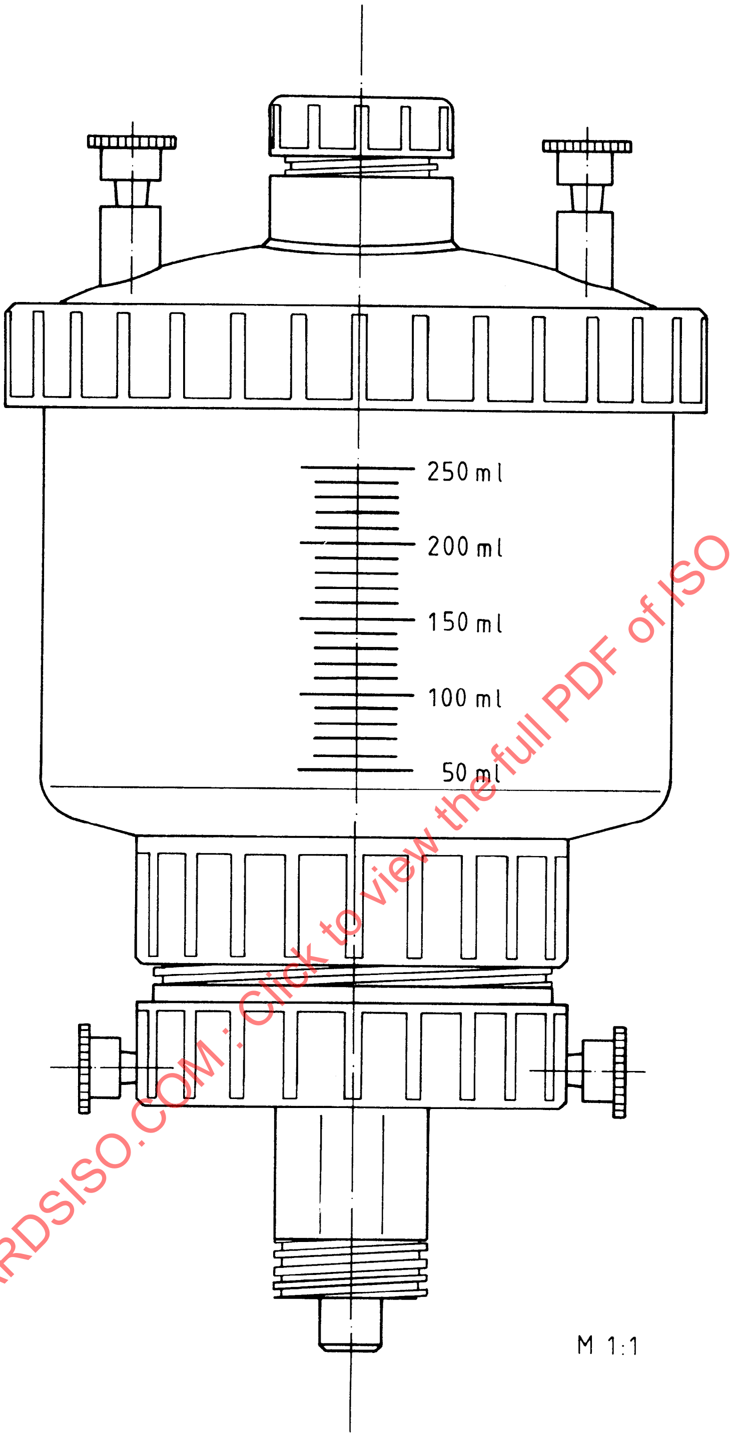

Figure 2 — Membrane filtration device

Dimensions in millimetres

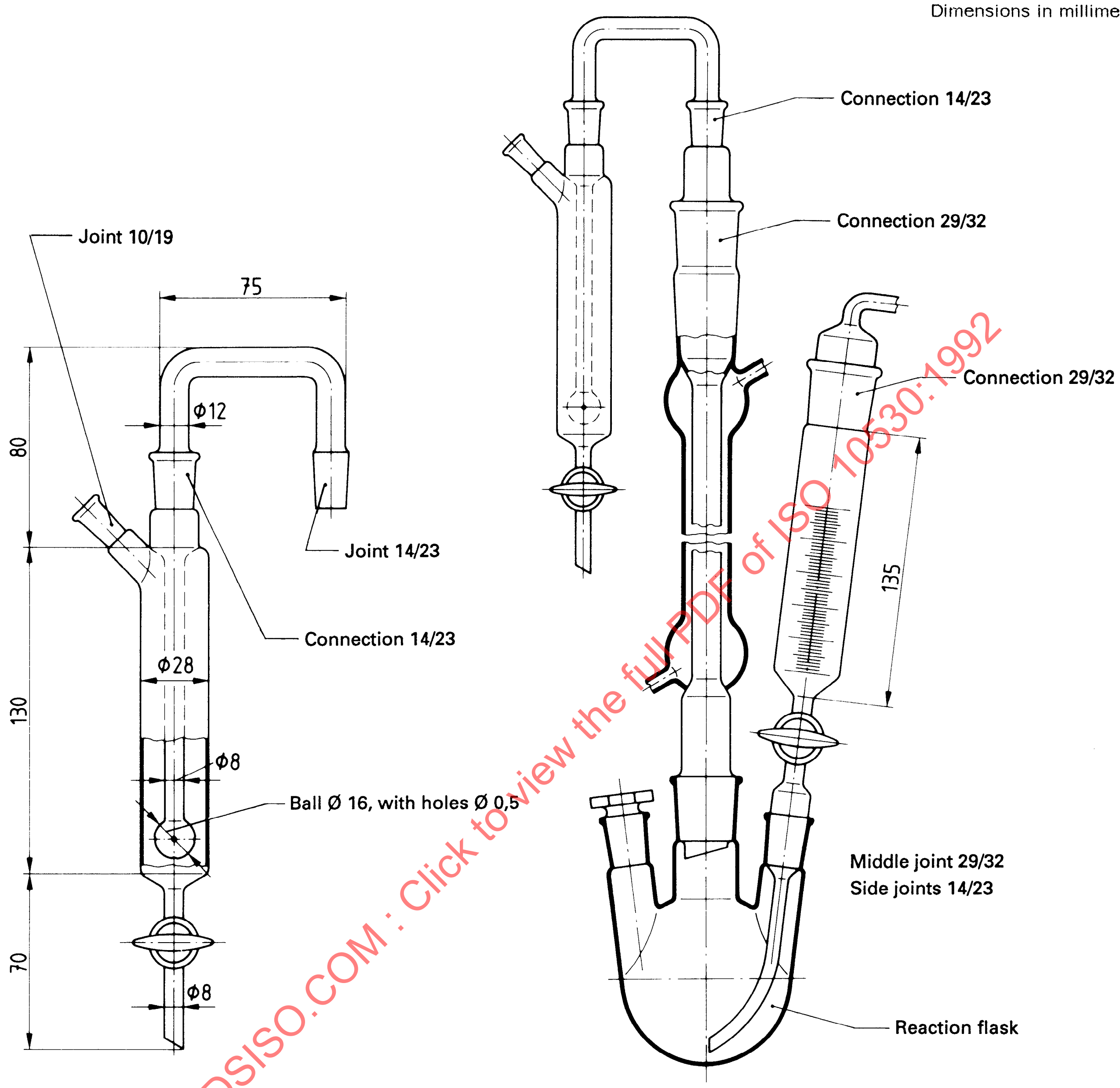

Figure 3 — Stripping apparatus for the determination of dissolved sulfide

6 Sampling and sample pretreatment at the sampling location

If it is not predictable whether or not the sulfide concentration will be within the range of application of the method, several sample portions should be filtered and preserved in accordance with 6.1 and 6.2, respectively, in order to allow for the determination of smaller quantities.

The preserved filtrates obtained according to 6.1 or 6.2, shall be analysed as soon as possible, but at the latest 24 h after sampling.

6.1 Sampling of easily filterable waters

Pipette 5 ml of ascorbate solution (4.5) into a 50 ml measuring flask.

Draw the water sample into the three-ring piston syringe, of capacity 50 ml.

Attach a one-way filtering adapter (see 5.1) and filter water into the measuring flask until its measuring mark is reached.

6.2 Sampling of waters which are more difficult to filter

Pipette 5 ml of ascorbate solution (4.5) into a 50 ml measuring flask.

Flush the measuring flask and the pressure filtration apparatus with nitrogen for approximately 10 min.

Completely fill the storage vessel with the water sample to be examined and filter with a nitrogen pressure of up to 2 bar into the measuring flask until its mark is reached.

The connection between the pressure filtration apparatus and the measuring flask shall be designed in such a way that access of air is reduced to a minimum.

The filtration time shall not exceed 5 min (see 1.2).

7 Procedure

7.1 Determination

Pour 25 ml of phthalate buffer solution (4.4) into the reaction flask (see figure 3).

Pour 20 ml of zinc acetate solution (4.3) into the absorption vessel.

Assemble the apparatus and pass a stream of nitrogen of 40 l/h through the solution for 2 min.

Transfer the filtrate, obtained according to clause 6, via the drop funnel into the reaction vessel.

Rinse with a small amount of water (clause 4) and pass a stream of nitrogen of 40 l/h through the solution for 30 min.

Remove the absorption vessel and add, through the lateral ground glass joint attachment, 10 ml of the colour-forming reagent solution (4.6), followed by 1 ml of ammonium iron(III) sulfate solution (4.7).

Completely fill the absorption vessel with water (clause 4), close it, shake and wait for 10 min.

Run the solution into a 100 ml measuring flask, thoroughly rinse the absorption vessel with a small amount of water (clause 4) and add the washings to the solution in the measuring flask.

Dilute to volume with water (clause 4) and measure the absorbance at 665 nm against water.

If the mass concentration exceeds 1,5 mg/l of sulfide, the determination shall be repeated using a smaller portion of the preserved filtrate.

7.2 Blank determination

In the same way, run a blank replacing, however, the sample by the same volume of water (clause 4).

The response obtained for the blank shall not deviate significantly from the calculated value A_{so} (see clause 8).

8 Establishment of the calibration curve

The calibration curve, obtained from measurements with a 1 cm cuvette, is not strictly linear over the whole concentration range. For the evaluation, only a linear part of the calibration curve shall be used.

Dilute the sodium sulfide standard solution (4.9) to give calibration solutions that cover the sulfide concentration expected in the water sample being analysed.

The mass concentrations of sulfide in these calibration solutions should be spaced equally over the expected measuring range.

As an example, for the concentration range of 0,2 mg/l to 0,7 mg/l (corresponding to 0,01 mg to 0,03 mg of sulfide), proceed as follows.

Introduce 20 ml of zinc acetate solution (4.3) into each of seven 100 ml measuring flasks.

Pipette 4 ml, 6 ml, 8 ml, 10 ml, 12 ml and 14 ml of the sodium sulfide standard solution (4.9) into each of six measuring flasks. Use the seventh flask for the blank.

Add 10 ml of the colour-forming reagent solution (4.6) and 1 ml of ammonium iron(III) sulfate solution (4.7) to the solution of each flask, then dilute with water to approximately 40 ml.

Stopper the flasks, shake and dilute to volume with water (clause 4).

After 10 min to 20 min, measure the absorbance at 665 nm against water in the reference cell.

The mass concentrations, as sulfide, of the calibration solutions are approximately:

> 0 (blank), 0,2 mg/l, 0,3 mg/l, 0,4 mg/l, 0,5 mg/l, 0,6 mg/l and 0,7 mg/l.

Determine the exact concentration of the sulfide calibration solutions iodometrically (see annex A).

Plot, on the abscissa in a coordinate system, the mass concentrations as sulfide of the calibration solutions.

Plot the respective absorbance values on the ordinate.

Fit a regression line through the measuring series thus obtained.

A calibration function may also be established by means of a statistical regression analysis using the mass concentrations of the calibration solutions and their respective absorbance values.

The slope of the line is a measure of the sensitivity b in litres per milligram. The ordinate intercept is the absorbance A_{so} of the sample without the addition of sulfide standard solution. The ordinate intercept as well as the slope of the analytical function shall be checked at regular intervals for significant deviations. This is especially relevant when a new batch of any of the reagents is used.

Each spectrometer and each path length of a cuvette requires its own, separate calibration curve or function, respectively.

9 Calculation

The mass concentration of dissolved sulfide in the water sample, in milligrams per litre, is calculated using the formula

$$\frac{(A_l - A_{l,0}) \cdot f}{b \cdot V}$$

where

A_l is the absorbance of the water sample (see 7.1);

$A_{l,0}$ is the calculated absorbance of the blank (see 7.2);

l is the subscript indicating the path length of the cuvette;

f is the conversion factor, here $f = 100$ ml;

b is a measure of the sensitivity, in litres per milligram, obtained according to clause 8;

V is the volume of the filtrate used for the analysis, here $V = 45$ ml.

When calculating the results, any dilution steps shall be taken into account.

10 Expression of results

The mass concentration of dissolved sulfide in a water sample shall be rounded to the nearest 0,01 mg, but not more than two significant digits shall be reported.

Example:

Dissolved sulfide: 0,55 mg/l

11 Performance characteristics

As the filtration of the non-stabilized sample is part of this International Standard, and the common practice of shipping samples was not feasible due to the instability of the dissolved sulfide, a comparative study was carried out in place of an interlaboratory trial. This comparative study was performed by analysts from various institutes in one laboratory.

A sulfide solution containing 1 mg/l of sulfide was used for the determination.

The following calibration function was established by the host laboratory prior to the meeting:

$$y = 0{,}010\,79x + 0{,}022\,8$$

The performance characteristics are given in table 1.

NOTE 1 For all participants reporting more than four blank values, the first four values were included in the evaluation.

12 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) identity of the water sample;

c) expression of results, in accordance with clause 10;

d) sample pretreatment;

e) any deviation from this method and any other circumstances which may have influenced the results.