INTERNATIONAL STANDARD

ISO 13358

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1997-10-15

Water quality — Determination of easily released sulfide

Qualité de l'eau — Dosage des sulfures aisément libérables

Reference number
ISO 13358:1997(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 13358 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annex A of this International Standard is for information only.

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Water quality — Determination of easily released sulfide

1 Scope

This International Standard specifies a method for the determination of easily released sulfide in water and waste water in mass concentrations ranging from 0,04 mg/l to 1,5 mg/l. Reduction of the volume of the water sample applied allows the determination of higher mass concentrations.

Soluble sulfides will be completely determined and undissolved sulfides will be either completely or partially determined, depending on their solubility and ageing properties. Examples are sulfides of zinc, iron, manganese.

The sulfide portion of polysulfides is incompletely determined by this method.

Some sulfides cannot be determined, such as mercury sulfide.

2 Interferences

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

cyanide	2 mg/l
iodide	20 mg/l
thiosulfate	900 mg/l
thiocyanate	900 mg/l
sulfite	700 mg/l

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

3 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 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

ISO 10530:1992, *Water quality — Determination of dissolved sulfide — Photometric method using methylene blue.*

4 Principle

The soluble sulfide contained in the water sample is stabilized by the addition of zinc acetate.

The sulfide is stripped with nitrogen at pH 4 (this is, by definition, easily released sulfide) and transferred to an aqueous zinc acetate solution. An acidic dimethyl-*p*-phenylenediamine solution is added, which forms leucomethylene blue which is oxidized, after the addition of iron(III) ions, to methylene blue. Its absorbance is measured at a wavelength of 665 nm.

5 Reagents

If not stated otherwise, use only reagents of recognized analytical grade, and only double-distilled water or water of equivalent quality, with its oxygen previously removed by boiling or degassing with nitrogen.

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

5.2 Sodium hydroxide solution, c(NaOH) approximately 2 mol/l.

5.3 Zinc acetate solution

Dissolve 20 g of zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] in water and make up to 1 l with water.

Turbidity may occur which, however, will not interfere with the determination.

5.4 Phenolphthalein solution, w = 0,1 %, in ethanol.

5.5 EDTA solution

Dissolve 100 g of ethylenedinitrilotetraacetic acid, disodium salt dihydrate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) in 940 ml of warm water.

5.6 Phthalate buffer solution, pH = 4,0 ± 0,1.

Dissolve 80 g of potassium hydrogen phthalate ($C_8H_5KO_4$) in 920 ml of water.

Measure the pH of the solution, and, if necessary, adjust to pH 4,0 by adding either sodium hydroxide solution [e.g. c(NaOH) = 1 mol/l] or hydrochloric acid [e.g. c(HCl) = 1 mol/l].

5.7 Colour-forming reagent solution

In a 1 000 ml graduated flask, suspend 2 g of N,N-dimethyl-1,4-phenylenediamine dihydrochloride ($C_8H_{14}Cl_2N_2$) in 200 ml of water.

Cautiously add 200 ml of sulfuric acid (5.1), cool, and make up to volume with water.

5.8 Ammonium iron (III) sulfate solution

Place 50 g of ammonium iron(III) sulfate dodecahydrate, [$NH_4Fe(SO_4)_2 \cdot 12H_2O$], in a 500 ml graduated flask, add 10 ml of sulfuric acid (5.1), and cautiously make up to volume with water.

5.9 Sulfide stock solution

In a 1 000 ml graduated flask, dissolve an adequate quantity of sodium sulfide hydrate, $Na_2S \cdot xH_2O$ (x = 7 to 9), thiosulfate mass portion w < 0,5 %, corresponding to approximately 0,5 g of sulfide-sulfur, in water, and make up to volume with water.

Determine the exact concentration iodometrically (see ISO 10530:1992, annex A) using titrants of appropriate concentration (such as 0,01 mol/l).

Store the solution in a dark brown bottle.

The solution is stable for 2 to 3 days.

5.10 Sulfide standard solution

Pipette 10 ml of the sulfide stock solution (5.9) into a 1 000 ml graduated flask and make up to volume with water, carefully avoiding intake of oxygen.

1 ml of this solution contains approximately 5 µg of sulfide.

The exact concentration is derived from the iodometrically determined sulfide concentration of the stock solution. Prepare the solution freshly before use.

6 Apparatus

6.1 Bottles with conical shoulder and ground glass stopper, 500 ml.

6.2 Stripping apparatus (see figure 1), for the separation of sulfide, consisting of: Reaction flask, 250 ml, with side-attached ground glass assembly for a dropping funnel (100 ml), and a gas inlet tube ending at the bottom of the flask, a vertically mounted condenser or glass tube, and an absorption vessel.

6.3 Measuring flasks, 25 ml and 500 ml.

6.4 Graduated flasks, 50 ml, 100 ml, 500 ml and 1 000 ml.

6.5 Measuring pipettes, 1 ml and 10 ml.

6.6 One-mark pipettes, nominal capacity 1 ml, 2 ml, 5 ml, 10 ml, 20 ml, 50 ml and 100 ml.

6.7 Dispenser.

6.8 Microlitre syringes.

6.9 Nitrogen gas supply, purity 99,996 % (*V*/*V*).

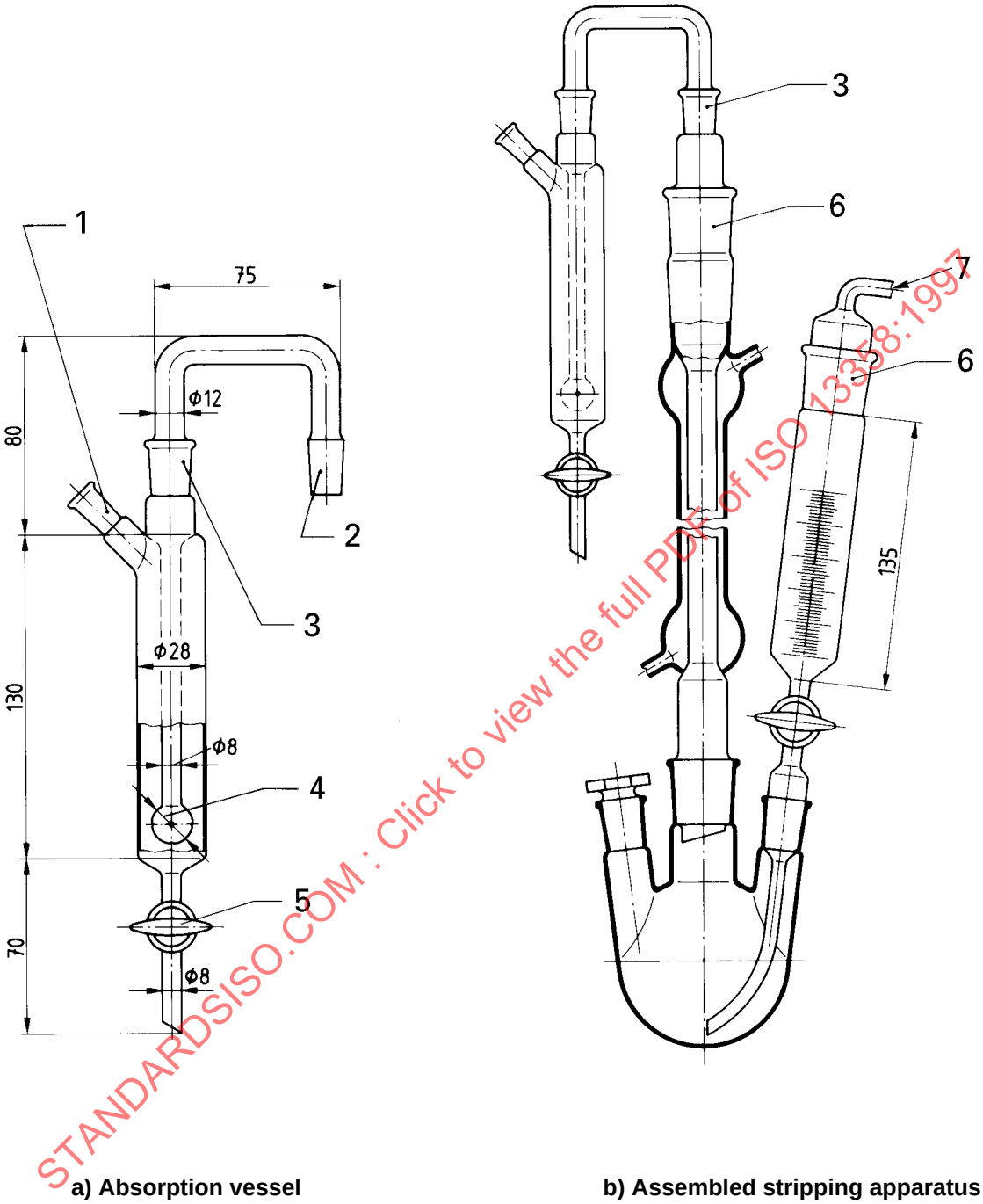
6.10 Gas flow measuring device, suitable for a volume flowrate of 40 l/h.

6.11 pH-meter, provided with an appropriate electrode.

6.12 Spectrometer or filter photometer, suitable for measurements at 665 nm.

6.13 Cuvettes, optical pathlength 10 mm.

Dimensions in millimetres



a) Absorption vessel **b) Assembled stripping apparatus**

Centre connection: Ground joint 29/32
Side connection: Ground joint 14/23
1 Ground joint male 10/19
2 Ground joint male 14/23
3 Connection 14/23
4 Ball, ∅ 16, with holes (∅ 0,5)
5 One-way cock
6 Connection 29/32
7 Gas inlet

Figure 1 — Stripping apparatus for the determination of easily released sulfide

7 Sampling and onsite sample preparation

Take samples in accordance with the respective ISO standards; handle in accordance with ISO 5667-3.

Pipette 10 ml of zinc acetate solution (5.3) into a bottle with conical shoulder (6.1).

Add 490 ml of the sample to be analyzed, and mix thoroughly.

Add a few drops of phenolphthalein solution (5.4), followed by the addition of sodium hydroxide solution (5.2) until the solution turns a slight pink colour.

For alkaline or strongly coloured water samples, use electrometric indication and adjust to a pH between 8,5 and 9.

Close the bottle with the ground stopper.

Analyze the sample, preserved as specified above, as soon as possible but within 72 h at the latest.

Keep the sample in the refrigerator (at 4 °C) until analyzed.

8 Procedure

Place 25 ml of phthalate buffer solution (5.6) and 5 ml of EDTA solution (5.5) into the reaction vessel of the stripping apparatus (figure 1).

Add 20 ml of zinc acetate solution (5.3) to the absorption vessel.

Assemble the stripping apparatus, and pass a stream of nitrogen at a rate of 40 l/h for 10 min through the solution.

Stir the sample, preserved in accordance with clause 7, vigorously for 5 min by means of a magnetic stirrer. With the stirrer running, take an aliquot (max. 50 ml) and add it to the reaction vessel via the dropping funnel.

Rinse the dropping funnel with a small quantity of water and pass a stream of nitrogen through the reaction solution at a rate of 40 l/h for 60 min.

Remove the absorption vessel from the stripping apparatus and add to it, through the side ground-joint attachment, 10 ml of colour-forming reagent solution (5.7) and 1 ml of ammonium iron(III) sulfate solution (5.8).

Fill the absorption vessel with water, close, mix and let it stand for 10 min.

Run the solution into a 100 ml graduated flask, thoroughly rinse the absorption vessel with water, and add the rinsings to the solution in the graduated flask.

Make up to volume with water, and in the spectrometer (6.12) measure the absorbance of the solution against water at a wavelength of 665 nm.

Analyze a blank, strictly following the same procedure, with the sample being replaced by the same volume of water.

The blank absorbance value thus measured shall not deviate significantly from the calculated value A_{s0} (see clause 9).

For mass concentrations $> 1{,}5$ mg/l sulfide, the determination shall be repeated with a smaller aliquot of the preserved sample solution. Be sure that this subsample is representative.

9 Establishment of a calibration curve

The calibration curve, established from spectrometric measurements using a 1 cm cuvette, is not strictly linear over the entire range. For the purpose of sample evaluation, a linear part of the calibration curve shall be used.

In accordance with the sample's expected sulfide concentration from the sulfide standard solution (5.10), prepare sulfide calibration solutions whose concentrations should span the expected measuring range at equal intervals. As an example, for the range of 0,2 mg/l to 0,7 mg/l, proceed as follows:

Into seven 100-ml graduated flasks, pipette 20 ml each of zinc acetate solution (5.3).

Into six of the graduated flasks, pipette 4 ml, 6 ml, 8 ml, 10 ml, 12 ml and 14 ml of sulfide standard solution (5.10); use the seventh flask for the blank.

To the contents of each flask, add 10 ml of colour-forming reagent solution (5.7), followed by 1 ml of ammonium iron(III) sulfate solution (5.8), and predilute with water to approximately 40 ml.

Close the flasks, mix and make up to volume with water.

After 10 min to 20 min, measure the absorbance of the solution against water at a wavelength of 665 nm.

The calibration solutions contain the following approximate concentrations of sulfide:

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.

The exact concentrations are obtained from the sulfide concentration of the sulfide stock solution, iodometrically determined according to 5.9.

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

Plot the respective absorbance values on the ordinate.

Fit a regression line through the pairs of measured values thus obtained.

Apart from the graphic approach described above, a calibration function can be estimated by means of statistical regression analysis, using the mass concentrations of the calibration solutions and their respective absorbance values.

The slope of the line b is a measure of the sensitivity with the unit l/mg. The ordinate intercept is the absorbance A_{s0} of the blank solution with no sulfide standard solution added. 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 whenever a new batch of reagents is used.

Each spectrometer requires its own calibration curve or function.

10 Evaluation

The mass concentration, ρ, in milligrams per litre, of easily released sulfide in the water sample, is calculated using the following equation:

$$\rho = \frac{(A_s - A_{s0}) \times f \times V_2}{b \times V_1 \times V_3}$$

where

A_s absorbance of the water sample;

A_{s0} calculated absorbance of the blank;

f conversion factor correcting for the final volume, in millilitres, of the measuring solution; here f = 100 ml;

V_2 volume, in millilitres, of the stabilized water sample; here V_2 = 500 ml;

b slope of the calibration curve, as a measure of sensitivity, determined in accordance with clause 9, in litres per milligram;

V_1 volume, in millilitres, of the original water sample; here V_1 = 490 ml;

V_3 volume, in millilitres, of the test portion used for stripping.

Dilution steps other than those given here shall be taken into account in the calculation.

11 Expression of results

The mass concentration of easily released sulfide is rounded to the nearest 0,01 mg, but not more than two significant figures shall be reported.

EXAMPLE:

Easily released sulfide 0,55 mg/l.

12 Test report

The test report shall contain the following information:

a) a reference to this International Standard, i.e. ISO 13358;

b) identity of the water sample;

c) expression of results in accordance with clause 11;

d) sample pretreatment;

e) any deviation from this procedure and all circumstances that may have affected the results.

13 Precision characteristics of the method

All measurement results are affected by an inevitable uncertainty; this relative uncertainty is in most cases larger in the lower part of the range of application.

For this International Standard, the uncertainty of the measurement result (expressed as cœfficient of variation CV) was estimated for a concentration range of 0,97 mg/l to1,22 mg/l. As can be seen from the values listed in table A.1, the uncertainty of the measurement result ranges between 4,9 % and 5,3 %.

For each individual case, the uncertainty of the measurement result may be estimated from the documentation of the quality assurance data of a laboratory (e.g. range control charts based on replicate determinations). Another possibility of estimation is the external quality assurance by means of interlaboratory trials, where the uncertainty of the measurement results is estimated by comparison of the results from several laboratories.

Matrix influences may considerably affect the uncertainty of the measurement result.

The precision characteristics of the method are given in annex A.