INTERNATIONAL STANDARD

ISO 9965

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Water quality — Determination of selenium — Atomic absorption spectrometric method (hydride technique)

Qualité de l'eau — Dosage du sélénium — Méthode par spectrométrie d'absorption atomique (technique hydrure)

Reference number
ISO 9965:1993(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 9965 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 2, *Physical, chemical, biochemical methods*.

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Water quality — Determination of selenium — Atomic absorption spectrometric method (hydride technique)

1 Scope

This International Standard specifies a method for the determination of selenium and organically bonded selenium in drinking waters, ground waters and surface waters, in a concentration range of 1 µg/l and 10 µg/l.

Higher concentrations can be determined by a suitable dilution of the water sample.

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 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:—[1], *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

3 Principle

The method is based on the atomic absorption spectrometric measurement of selenium generated by the thermal decomposition of selenium hydride.

Under the conditions of this method, only Se(IV) is quantitatively converted to the hydride. To avoid errors in determination, other oxidation states need to be converted to Se(IV) prior to the determination. Se(IV) is reduced to gaseous selenium dihydride (SeH_2) by reaction with sodium tetrahydroborate in a hydrochloric acid medium.

The absorbance is measured at a wavelength of 196,0 nm.

4 Reagents

During the analysis, use only reagents of recognized analytical grade.

The selenium content of the water and the reagents shall be negligibly low, compared with the lowest concentration to be determined.

4.1 Sulfuric acid, ρ = 1,84 g/ml.

4.2 Hydrochloric acid, ρ = 1,16 g/ml.

4.3 Hydrogen peroxide, $w(H_2O_2)$ = 30 % (*m/m*).

4.4 Sodium hydroxide.

4.5 Sodium tetrahydroborate, solution.

Dissolve 1 g of sodium hydroxide (4.4) in about 20 ml of water. Add 3 g of sodium tetrahydroborate ($NaBH_4$). Dilute to 100 ml with water.

The solution shall be prepared daily.

4.6 Selenium, stock solution, corresponding to 1 000 mg of Se per litre.

Place 1,405 3 g of selenium dioxide in a volumetric flask of nominal capacity 1 000 ml. Add 2 g of sodium hydroxide (4.4) and dissolve in a small quantity of water. Dilute to volume with water.

1) To be published. (Revision of ISO 5667-3:1985)

NOTE 1 Selenium stock solutions are commercially available.

4.7 Selenium, standard solution 1, corresponding to 10 mg of Se per litre.

Pipette 10 ml of selenium stock solution (4.6) into a graduated flask of nominal capacity 1 000 ml. Add 20 ml of hydrochloric acid (4.2) and dilute to volume with water.

This solution is stable for at least 1 week.

4.8 Selenium, standard solution 2 corresponding to 0,1 mg of Se per litre.

Pipette 10 ml of selenium standard solution 1 (4.7) into a graduated flask of nominal capacity 1 000 ml. Add 20 ml of hydrochloric acid (4.2) and dilute to volume with water.

This solution is stable for at least 1 week.

5 Apparatus

Usual laboratory apparatus and

5.1 Atomic absorption spectrometer, fitted with a hydride system and a suitable radiation source for the determination of selenium, for example electrodeless discharge lamp or a hollow cathode lamp. A background correction facility may be appropriate.

5.2 Gas supply, with argon or nitrogen.

5.3 Glassware, to be cleaned immediately before use with warm, diluted nitric acid (e.g. 2 mol/l) and rinsed with water.

6 Sampling

Take samples according to ISO 5667-1 and ISO 5667-2.

Collect samples in polyethylene or borosilicate glass containers which have been previously cleaned with nitric acid (e.g. 2 mol/l) and then rinsed with water.

Add 20 ml of hydrochloric acid (4.2) to each 1 000 ml of the water sample.

If the pH is greater than 2, add more hydrochloric acid until the pH is 2 or less.

For sample conservation see ISO 5667-3.

7 Procedure

7.1 Blank solution

Pipette 2 ml of hydrochloric acid (4.2) into a graduated flask of nominal capacity 100 ml, and dilute to volume with water.

Treat the blank in exactly the same way as the sample.

7.2 Calibration solutions

Using selenium standard solution 2 (4.8), prepare at least five calibration solutions covering the expected working range.

For example, for the range 1 µg/l to 10 µg/l, pipette 1 ml, 3 ml, 5 ml, 8 ml and 10 ml of selenium standard solution 2 (4.8) into a series of 100 ml one-mark volumetric flasks. To each of these flasks, add 2 ml of hydrochloric acid (4.2) and dilute to volume with water. These solutions correspond to selenium concentrations of 1 µg/l, 3 µg/l, 5 µg/l, 8 µg/l and 10 µg/l respectively.

The calibration solutions shall be prepared daily.

7.3 Treatment

For the determination of the total selenium content, the samples shall be digested in order to decompose organic selenium compounds. If experience has shown that the selenium will be recovered quantitatively without decomposition, the digestion process (7.3.1) may be omitted.

Place 50 ml of the sample in a round-bottomed flask.

7.3.1 Method of digestion

Add 5 ml of sulfuric acid (4.1) and 5 ml of hydrogen peroxide (4.3) to the round-bottomed flask (see 7.3).

Add some boiling beads and connect the flask to an apparatus as shown, for example, in figure 1. Close the cock. Heat the contents of the flask to boiling and collect the condensate in the condensate reservoir.

Continue heating until turbid fumes of sulfuric acid appear. Check the appearance of the sample. If it is turbid and almost colorless, cool and add another 5 ml of hydrogen peroxide (4.3) and continue boiling as described in the previous paragraph.

After cooling, return the condensate to the round-bottomed flask.

NOTE 2 Care should be taken to ensure that the sample is never evaporated to complete dryness.

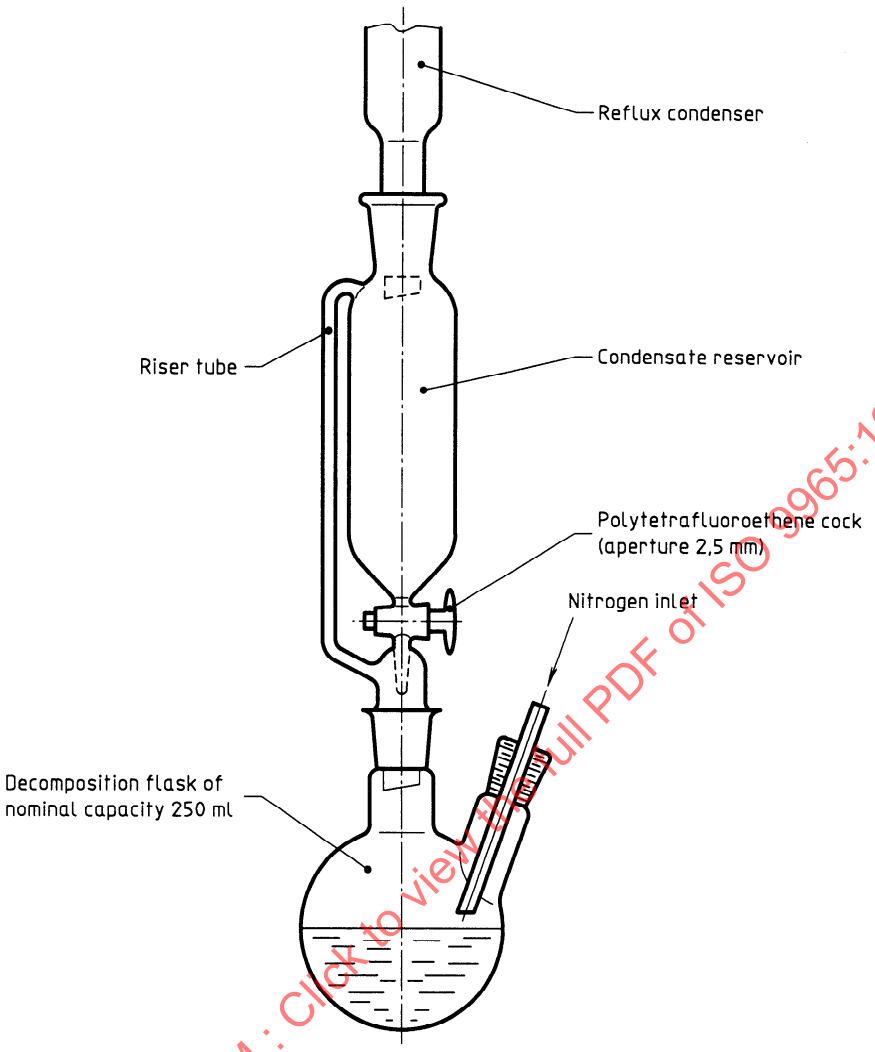

Figure 1 — Example of a decomposition apparatus

7.3.2 Reduction from Se(VI) to Se(IV)

Add 20 ml of hydrochloric acid (4.2) to the round-bottomed flask.

Gently boil the mixture under reflux for 15 min with the cock open. If there is no prior digestion and if the sample contains free chlorine, aerate the solution with nitrogen (about 1 l/min) for the same period of time.

Cool the sample solution and transfer it quantitatively into a graduated flask of nominal capacity 100 ml. Dilute to volume with water.

Treat the blank solution (7.1) and the calibration solutions (7.2) in the same way.

7.4 Calibration and determination

Depending on the hybride system used, volumes that are greater or smaller than those described in this subclause may be used. However, the quantity ratios defined shall be maintained.

Set all the instrumental parameters of the atomic absorption spectrometer in accordance with the manufacturer's operating manual (wavelength: 196,0 nm) and optimize the position of the absorption cell in order to obtain a maximum transmission.

Measure the solutions in the following order:

— blank solution;

— calibration solutions;

— samples.

Pass a stream of argon or nitrogen through the system and zero the instrument. Introduce for example, 20 ml of the reduced solution (see 7.3) into the reaction vessel.

Connect the reaction vessel to the hydride system.

Pass argon or nitrogen through the solution until the absorption signal returns to zero.

Add about 5 ml of sodium tetrahydroborate solution (4.5) to the solution and record the signal.

Establish the calibration curve using values obtained with the blank and calibration solutions.

Repeat the procedure using separate portions of each solution.

NOTES

3 It is good practice to check the blank and calibration points from time to time.

4 With unknown samples, it is good practice to check the validity of the method by adding a known volume of selenium, in one sample at least. If recovery tests are not satisfactory, the procedure of standard additions should be used.

8 Evaluation of the results using the standard calibration method

Obtain the mass concentration of selenium, in micrograms per litre, in the measuring solution on the basis of the absorbance and the calibration function.

All dilution steps shall be taken into account.

9 Expression of results

Express the results to two significant figures and one decimal place.

EXAMPLE

Selenium (Se): 8 µg/l

Selenium (Se): 32 µg/l

10 Precision

An interlaboratory trial, carried out in 1992 with an almost identical method, yielded the results given in table 1.

11 Interferences

Table 2 gives details of potential interfering substances which have been present during part of the analytical procedure. The solutions for interference testing were prepared from either solid reagents or concentrated solutions of the reagents, in such a way that 500 ml of the solution contains the stated mass of the other substance and the stated mass of selenium. The solutions were then run through the measurement stage of the method and the results expressed as the effect on the stated mass of selenium.

Assuming that samples containing 250 mg of dried solids are ashed, extracted and diluted to the equivalent of 500 ml, then 100 mg and 250 mg of the other substance used would correspond to the solid samples containing 40 % and 100 % of the other substance, respectively; and 3,75 µg of Se would correspond to the solid samples containing 15 mg/kg of Se.

Table 1 — Precision data

Sample No.	l	n	n_a %	x µg/l	$\bar{\bar{x}}$ µg/l	σ_r µg/l	VC_r %	σ_R µg/l	VC_R %	WFR %
A	19	50	0	3,0	2,92	0,525	18,0	0,191	6,5	97,4
B	19	42	11	9,0	7,76	0,869	11,2	0,439	5,7	86,2

l is the number of laboratories;
n is the number of values;
n_a is the percentage of outliers;
x is the true value;
$\bar{\bar{x}}$ is the total mean;
σ_r is the repeatability standard deviation;
VC_r is the repeatability variation coefficient;
σ_R is the reproducibility standard deviation;
VC_R is the reproducibility variation coefficient;
WFR is the recovery rate.

A: Drinking water
B: Waste water