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Water quality — Determination of cadmium by atomic absorption spectrometry

Qualité de l'eau — Dosage du cadmium par spectrométrie d'absorption atomique

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Foreword

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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 5961 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods*.

This second edition cancels and replaces the first edition (ISO 5961:1985), of which it constitutes a technical revision.

Annex A of this International Standard is for information only.

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Water quality — Determination of cadmium by atomic absorption spectrometry

Section 1: General

1.1 Scope

This International Standard specifies two methods for the determination of cadmium: flame atomic absorption spectrometry (AAS) (Section 2) and electrothermal atomization (AAS) (Section 3).

1.1.1 Determination of cadmium using AAS in an air-acetylene flame

The method is applicable to the analysis of water and waste water when the concentration of cadmium is between 0,05 mg/l and 1 mg/l. Higher concentrations can be determined after dilution of the sample. The range of application of the method can be extended to lower concentrations by carefully evaporating the water sample, previously acidified with nitric acid. Cadmium can be determined in sludges and sediments after an appropriate digestion procedure avoiding the formation of a precipitate.

1.1.2 Determination of cadmium by electrothermal atomization AAS

The method is suitable for the determination of cadmium in water when, with a dosing volume of 10 µl, the concentration range is 0,3 µg/l to 3 µg/l. The range of application of the method can be extended to higher concentrations by diluting the water sample or by the use of smaller dosing volumes. Cadmium can be determined in sludges and sediments after an appropriate digestion procedure.

1.2 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:—[1], *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

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

Section 2: Determination of cadmium using atomic absorption spectrometry in an air-acetylene flame

2.1 Interferences

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

Sulfate	10 000 mg/l
Chloride	10 000 mg/l
Phosphate	10 000 mg/l
Sodium	10 000 mg/l
Potassium	10 000 mg/l
Magnesium	10 000 mg/l
Calcium	3 000 mg/l
Iron	3 000 mg/l
Copper	10 000 mg/l
Nickel	3 000 mg/l
Cobalt	10 000 mg/l
Lead	10 000 mg/l
Silicon	1 000 mg/l
Titanium	3 000 mg/l

The total salt content of the measuring solution shall be less than 15 g/l and the electrical conductivity shall be lower than 20 000 mS/m. Samples of unpredictable matrix effects shall be examined appropriately. This influence shall be compensated for either by diluting the sample or by applying the method of standard additions (see 3.6.2.2).

2.2 Principle

Aspiration of the acidified sample into the air-acetylene flame of an atomic absorption spectrometer. Measurement of the cadmium concentration at a wavelength of 228,8 nm.

2.3 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity. The cadmium content of water used for blank determinations and for the preparation of standard solutions shall be negligibly low compared with the lowest mass concentration to be determined in the sample.

2.3.1 Nitric acid, $\rho = 1{,}40$ g/ml.

2.3.2 Hydrogen peroxide, $w(H_2O_2) = 30\ \%\ (m/m)$.

2.3.3 Cadmium stock solution I, $\rho(\mathrm{Cd}) = 1\ 000$ mg/l.

Dissolve 1,000 g ± 0,002 g of cadmium in 10 ml of nitric acid (2.3.1) and 10 ml of water (see 2.3) in a 1 000 ml one-mark volumetric flask. Dilute to volume with water.

Store the solution in polyethylene or borosilicate glass containers. The solution is stable for 1 year.

Alternatively, use any commercially available stock solution containing 1,000 g/l ± 0,002 g/l of cadmium.

2.3.4 Cadmium standard solution I, $\rho(\mathrm{Cd}) = 10$ mg/l.

Pipette 10 ml of the cadmium stock solution (2.3.3) into a 1 000 ml one-mark volumetric flask, add 10 ml of nitric acid (2.3.1) and dilute to volume with water.

Store the solution in polyethylene or borosilicate glass containers. The solution is stable for at least one month if stored at room temperature.

NOTE 1 The use of a microlitre pipette permits a standard solution of 100 ml to be prepared.

2.3.5 Cadmium calibration solutions

Prepare a minimum of five calibration solutions in accordance with the expected cadmium concentrations.

As an example, proceed as follows for the range from 0,05 mg/l to 1,0 mg/l:

Pipette 0,5 ml; 2,0 ml; 4,0 ml; 6,0 ml; 8,0 ml and 10,0 ml respectively of the cadmium standard solution (2.3.4) into 100 ml one-mark volumetric flasks.

Add 1 ml of nitric acid (2.3.1) to each of these solutions. Dilute to volume with water and mix.

The calibration solutions contain 0,05 mg/l; 0,2 mg/l; 0,4 mg/l; 0,6 mg/l; 0,8 mg/l and 1,0 mg/l of cadmium respectively.

2.3.6 Blank test solution

Pipette 1 ml of nitric acid (2.3.1) into a 100 ml one-mark volumetric flask, and dilute to volume with water (2.3.4).

If the sample requires a pretreatment by digestion, the blank shall be given the same pretreatment (see 2.5.2).

2.3.7 Solution for zero-setting the instrument

Use water (2.3.4) as a zero-setting solution. The blank solution (2.3.6) may also serve for zero-setting provided its cadmium concentration is negligibly low.

2.4 Apparatus

Immediately before use, clean the glassware with warm, dilute nitric acid, approximately 2 mol/l (e.g. by soaking for 24 h), followed by a thorough rinsing with water (2.3). Verify that each lot of pipette tips and single-use plastics vessels is free from potential cadmium contamination by carrying out blank measurements (see 2.6.1).

Usual laboratory apparatus and

2.4.1 Atomic absorption spectrometer, equipped with background correction and a radiation source for the determination of cadmium, operated according to the manufacturer's instructions.

2.4.2 Gas supply for air and acetylene. It is essential that the manufacturer's safety instructions be observed. The residual gas pressure for acetylene cylinders shall be at least 5 × 10^5 Pa.

2.4.3 Air-acetylene burner.

2.4.4 One-mark volumetric flasks of capacity 10 ml, 100 ml and 1 000 ml.

2.4.5 One-mark pipettes, of nominal capacity 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 8 ml, 10 ml, 20 ml, 30 ml and 40 ml.

2.4.6 Microlitre pipettes or **diluters**.

2.4.7 Beakers, of capacity 250 ml.

2.4.8 Heating device, for example a hotplate.

2.4.9 Membrane filtration device with filters, of pore size 0,45 µm, washed thoroughly with dilute nitric acid and rinsed with water.

2.5 Sampling and sample pretreatment

See ISO 5667-3.

2.5.1 Sampling

Collect the samples in polyethylene or borosilicate glass containers which have previously been cleaned with nitric acid and water.

2.5.2 Pretreatment and preparation of the sample solutions

2.5.2.1 Pretreatment for the determination of the content of dissolved cadmium

Filter the water sample as soon as possible after sampling (2.5.1) through a membrane filter of pore size 0,45 µm.

To stabilize the filtrate, add, for example, 10 ml of nitric acid (2.3.1) per litre of water sample to achieve a pH of less than 2; add more acid, if necessary, to ensure a pH of less than 2.

2.5.2.2 Pretreatment for the determination of cadmium after mineralization

Acidify the water sample as soon as possible after sampling by adding 1 ml of nitric acid (2.3.1) per litre of sample; add more acid, if necessary, to ensure a pH of less than 2.

Completely mix the sample, for example by thorough shaking.

Place 100 ml of the homogenized sample in a 250 ml beaker. Add 1 ml of nitric acid (2.3.1) and 1 ml of hydrogen peroxide (2.3.2).

Heat the beaker on a hotplate until about 0,5 ml remains.

It is essential that the sample is not reduced to dryness.

If there is heavy organic contamination of the water sample, **consider a repeated addition of hydrogen peroxide (Caution)**.

Dissolve the residue in 1 ml of nitric acid (2.3.1) and some water, transfer quantitatively to a 100 ml one-mark volumetric flask and dilute to volume with water.

If sample volumes other than those specified are used, the apparatus and reagents shall be adjusted to the respective ratio of volumes.

It is not necessary to carry out a digestion in cases where cadmium is quantitatively determinable without this treatment. In such circumstances, only acidify the water sample.

2.6 Procedure

Prior to measurement, adjust the instrumental parameters of the spectrometer (2.4.1) in accordance with the manufacturer's operating instructions.

Optimize flame conditions.

Zero the spectrometer by aspirating the zero-setting solution (2.3.7) into the flame.

2.6.1 Blank test

Carry out a blank test with the blank solution (2.3.6) at the same time as the determination, using the same procedure and the same quantities of all the reagents as in the sampling and determination, but replacing the test portion with water (2.3).

2.6.2 Calibration

To establish the calibration curve, spray in the calibration solutions (2.3.5) successively, in ascending order of concentration, and record the absorbance.

Check the zero with the zero-setting solution (2.3.7) after the measurement of each calibration solution.

2.6.3 Test portion measurement

Continue by measuring the blank solution (2.6.1) and the measuring solutions (2.5.2) and record the absorbances.

After each measuring series, but at least after 10 to 20 measurements, re-analyse the blank solution and a mid-range calibration solution to check whether the calibration curve is still valid.

If the cadmium content of the measuring solution exceeds the range of validity of the calibration curve, dilute the measuring solution accordingly with blank solution.

2.7 Evaluation

2.7.1 Calculation

Establish the calibration function by linear regression using the data obtained from the measurement of the calibration solutions.

Calculate the mass concentration $\rho(\mathrm{Cd})$ of cadmium, expressed in milligrams per litre, in the water sample using the equation

$$\rho(\mathrm{Cd}) = \frac{(A_1 - A_0) \times V_1}{b \times V_2}$$

where

A_0 is the absorbance of the blank solution;

A_1 is the absorbance of the measuring solution;

b is the slope of the calibration curve, in litres per milligram, according to 2.6.2;

V_1 is the volume, in millilitres, of the measuring solution;

V_2 is the volume, in millilitres, of the water sample applied to prepare the measuring solution.

Dilution steps which differ from those specified above shall be taken into account during the calculation.

2.7.2 Expression of results

The values shall be rounded to the nearest 0,01 mg/l.

EXAMPLES

Cadmium (Cd): 0,07 mg/l

Cadmium (Cd): 0,41 mg/l

2.8 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) complete identification of the water sample;

c) expression of the results, according to 2.7.2;

d) details of sample pretreatment, if applicable;

e) any deviations from this procedure and all the circumstances which may have affected the results.

2.9 Precision

See table 1.

Table 1 — Precision data

Sample No.	l	n	n_a %	x mg/l	$\bar{x}$ mg/l	σ_r mg/l	VC$_r$ %	σ_R mg/l	VC$_R$ %	WFR %	**Suitable for**
A1) 2)	23	63	0	0,113	0,118	0,009 7	8,2	0,005 8	5,0	104,1	
B1) 2)	23	60	5	0,563	0,587	0,030 9	5,3	0,009 2	1,6	104,3	
C1) 3)	23	63	0	0,968	1,008	0,073 3	7,3	0,012 1	1,2	104,1	
			%	µg/l	µg/l	µg/l	%	µg/l	%	%	
D4) 2)	52	133	2	0,91	1,292	0,319 6	24,7	0,083 0	6,4	141,9	all methods5)
	22	55	2	0,91	1,148	0,270 4	23,5	0,048 3	4,2	126,2	method 3.6.2.1
	17	45	0	0,91	1,363	0,356 8	26,2	0,115 9	8,5	149,8	addition: manual
	13	31	11	0,91	1,39	0,171 8	12,4	0,064 3	4,6	152,7	addition: automatic
E4) 2)	52	136	0	2,70	2,96	0,639 9	21,6	0,266 3	9,0	109,6	all methods5)
	22	56	0	2,70	2,78	0,631 8	22,8	0,199 4	7,2	102,9	method 3.6.2.1
	17	40	11	2,70	2,99	0,344 5	11,5	0,195 1	6,5	110,7	addition: manual
	13	35	0	2,70	3,22	0,559 2	17,4	0,158 3	4,9	119,2	addition: automatic
F4) 6)	53	135	7	16,2	18,34	3,348 7	18,3	1,420 8	7,7	113,2	all methods5)
	23	56	11	16,2	17,14	2,232 8	13,0	0,756 7	4,4	105,8	method 3.6.2.1
	17	43	7	16,2	18,33	3,969 7	21,7	1,497 6	8,2	113,1	addition: manual
	13	33	8	16,2	20,17	3,107 7	15,4	1,309 6	6,5	124,5	addition: automatic

l is the number of participating laboratories

n is the number of values

n_a is the percentage of outliers

x is the true value

$\bar{x}$ 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

1) AAS method in an air-acetylene flame.

2) Industrial waste water with a low level of pollution.

3) C: spiked drinking water.

4) Electrothermal atomization AAS method.

5) "All methods" means that both the manual and the automated addition have been included in the calculation.

6) F: spiked distilled water.

Section 3: Determination of cadmium by electrothermal atomization atomic absorption spectrometry

3.1 Interferences

The following ions will not, if present individually, interfere with the method as long as their mass concentrations do not exceed 100 mg/l: iron, copper, nickel, cobalt and lead.

No interferences could be observed up to mass concentrations of 1 000 mg/l for sodium, potassium, calcium, magnesium, sulfate and chloride.

Combinations of the above-mentioned ions, even if present in much lower concentrations, can lead to depression or enhancement of the measured signals. Some other ions, if present in low concentrations, can cause interferences. The method of standard additions should therefore be given preference to the normal calibration. Samples of unpredictable matrix behaviour need to be analysed using the method of standard additions. Interferences caused by background absorption can be eliminated to a large extent by the application of a background compensating system.

3.2 Principle

Injection of the acidified sample into an electrically heated graphite tube of an electrothermal atomization atomic absorption spectrometer. Measurement of the absorbance at a wavelength of 228,8 nm. If necessary, application of the standard additions technique.

3.3 Reagents

The requirements for the purity of the reagents are given in 2.3.

3.3.1 Nitric acid, $\rho = 1{,}40$ g/ml.

3.3.2 Hydrogen peroxide, $w(H_2O_2) = 30\ \%\ (m/m)$.

3.3.3 Cadmium stock solution I, $\rho(\text{Cd}) = 1\ 000$ mg/l.

See 2.3.3.

3.3.4 Cadmium stock solution II, $\rho(\text{Cd}) = 10$ mg/l.

See 2.3.4.

3.3.5 Cadmium standard solution II, $\rho(\text{Cd}) = 100$ µg/l.

Pipette 10,0 ml of the cadmium stock solution II (3.3.4) into a 1 000 ml one-mark volumetric flask, add 10 ml of nitric acid (3.3.1) and dilute to volume with water.

Store the solution in a polyethylene or borosilicate glass container. Prepare the solution immediately before use.

3.3.6 Cadmium standard solution III, $\rho(\text{Cd}) = 5$ µg/l.

Pipette 50 ml of the cadmium standard solution II (3.3.5) into a 1 000 ml one-mark volumetric flask, add 10 ml of nitric acid (3.3.1) and dilute to volume with water (2.3).

Store the solution in a polyethylene or borosilicate container. Prepare the solution immediately before use.

3.3.7 Cadmium calibration solutions

Prepare at least five calibration solutions using the cadmium standard solution II (3.3.5) and matching the expected cadmium concentrations.

As an example, proceed as follows for the range from 0,3 µg/l to 3 µg/l.

Pipette 0,3 ml; 1,0 ml; 1,7 ml; 2,4 ml; and 3,0 ml respectively of the cadmium standard solution II (3.3.5) into five 100 ml graduated flasks.

Add 1 ml of nitric acid (3.3.1) to each of these solutions. Dilute to volume with water and mix.

The calibration solutions contain 0,3 µg/l; 1,0 µg/l; 1,7 µg/l; 2,4 µg/l; and 3,0 µg/l of cadmium, respectively.

Prepare the calibration solutions immediately before use.

3.3.8 Blank test solution

Pipette 1 ml of nitric acid (3.3.1) into a 100 ml one-mark volumetric flask and dilute to volume with water.

If the sample requires a pretreatment by digestion, the blank shall be given the same pretreatment (see 2.5.2).

3.3.9 Zero-setting solution

Use water (2.3) as a zero-setting solution. The blank solution (3.3.8) may also serve for zero-setting, provided its cadmium concentration is negligibly low.

3.3.10 Matrix-matching solutions (see [2] in annex A)

Dissolve 1,0 g of palladium powder in 3 ml of nitric acid (2.3.1) and 20 ml of hydrochloric acid (ρ = 1,19 g/ml) whilst gently warming, and dilute to 100 ml with water.

Dissolve 10 g of ammonium nitrate (NH_4NO_3) in water and dilute to 100 ml with water.

3.3.10.1 Solution for waters of high salinity

Mix equal volumes of the palladium solution and the ammonium nitrate solution (see 3.3.10).

10 µl of this solution contain 50 µg of Pd and 500 µg of NH_4NO_3.

3.3.10.2 Solution for water with a low level of pollution

Mix 15 ml of the palladium solution and 15 ml of the ammonium nitrate solution in a 100 ml measuring flask, and dilute to volume with water.

10 µl of this solution contain 15 µg of Pd and 150 µg of NH_4NO_3.

3.4 Apparatus

For cleaning of glassware see 2.4.

Usual laboratory apparatus and

3.4.1 Atomic absorption spectrometer, equipped with background correction and a radiation source for the determination of cadmium.

3.4.2 Graphite furnace, equipped with a control unit.

3.4.3 Pyrolytically coated graphite tube with a platform.

NOTE 2 If no interference is expected, normal tubes may be used.

3.4.4 Gas supply for argon.

3.4.5 Other apparatus (see 2.4).

NOTE 3 For optimum precision an automatic sample injector is recommended.

3.5 Sampling and sample pretreatment

Proceed as specified in 2.5.

3.6 Procedure

Prior to measurement, adjust the instrumental parameters of the spectrometer (3.4.1) in accordance with the manufacturer's operating instructions.

Zero the spectrometer using the zero-setting solution (3.3.9).

3.6.1 Blank test

Carry out a blank test at the same time as the determination, using the same procedure and the same quantities of all the reagents as in the sampling and determination, but replacing the test portion with water.

3.6.2 Calibration and determination

Before each batch of determinations, prepare from the cadmium standard solution II (3.3.5) at least five calibration solutions covering the range of concentrations to be determined.

3.6.2.1 Direct measurement

Direct measurement shall only be used if the matrix influences dealt with in 3.1 can be ignored. Otherwise, apply the procedure of standard additions as described in 3.6.2.2.

Measure the absorbances or the integrated absorbances (peak areas) of the calibration solutions (3.3.7), the blank solutions (3.3.8) and the sample solutions (see 2.5.2) in accordance with the instructions given by the manufacturer of the instrument.

Prior to the measurement and in addition to the volume applied, inject 10 µl of matrix-matching solution (3.3.10.1 or 3.3.10.2 depending on the type of water) into the graphite furnace (3.4.2).

Measure each solution at least twice in order to detect any unusual results.

3.6.2.2 Procedure using the method of standard additions

Proceed as described in 3.6.2.2.1 or 3.6.2.2.2.

NOTE 4 This procedure minimizes matrix interferences in many cases, as long as additive errors can be eliminated and the cadmium contents, even in the spiked sample solutions, are in the linear working range.

3.6.2.2.1 Manual addition

Transfer 0,10 ml each of nitric acid (3.3.1) and 5,0 ml of the sample solution (2.5.2) to four 10 ml one-mark volumetric flasks.

Make the first volumetric flask up to the mark with water; pipette 0,05 ml of the cadmium standard solution (3.3.5) into the second flask, 0,1 ml into the third flask and 0,15 ml into the fourth flask and dilute them to volume with water.

This procedure provides three spiked sample solutions.

If the cadmium content is greater than 3 µg/l in the spiked sample solutions, use an accordingly smaller sample volume. This shall be taken into account in calculating the results.

Treat aliquots of the blank solution (3.3.8) in the same way by adding the same three volumes of cadmium standard solutions as above.

This procedure provides three spiked blank solutions.

NOTE 5 The addition of 0,05 ml corresponds to 1 µg/l, that of 0,1 ml corresponds to 2 µg/l, and that of 0,15 ml corresponds to 3 µg/l, related to the volume of 5 ml of sample and blank solutions used. The dilution obtained by filling up the flasks is not taken into account in the calculation.

Measure the absorbances of the spiked sample solutions and the spiked blank solutions as described in 3.6.2.1.

Measure each solution at least twice.

3.6.2.2.2 Automated addition

Place the measuring solution (pretreated sample 2.5.2), the cadmium standard solution III (3.3.6), the blank solution (3.3.8), the zero-setting solution (3.3.9) and the matrix-matching solution (3.3.10) on the autosampler.

Set up the programme according to the manufacturer's instructions, in order to allow the injection of the following solutions into the graphite furnace (3.4.2):

- 10 µl of measuring solution, 10 µl of zero-setting solution, 10 µl of matrix-matching solution;
- 10 µl of measuring solution, 2 µl of cadmium standard solution III, 8 µl of zero-setting solution and 10 µl of matrix-matching solution;
- 10 µl of measuring solution, 4 µl of cadmium standard solution III, 6 µl of zero-setting solution, 10 µl of matrix-matching solution;
- 10 µl of measuring solution, 6 µl of cadmium standard solution III, 4 µl of zero-setting solution, 10 µl of matrix-matching solution.

Treat the blank solution in the same way as the measuring solution.

The additions correspond to 1 µg/l, 2 µg/l and 3 µg/l of cadmium, referring to the measuring solutions and the blank solutions respectively.

The mass concentrations of the measuring solution and the blank solutions can be read directly from the instrument.

3.7 Determination

3.7.1 Direct determination

See 2.7, except that the mass concentrations are expressed in micrograms per litre.

3.7.2 Determination according to the method of standard additions

Construct a graph with the absorbance values obtained for the sample solutions and the spiked sample solutions plotted on the ordinate and the cadmium mass concentrations plotted on the abscissa.

The regression line passing through these points will intercept the abscissa on its negative side. The intercept represents the mass concentration of cadmium in the sample solution. From this value, subtract the mass concentration of cadmium in the blank solution, determined in the same manner.

The resulting difference is the mass concentration of cadmium in the water sample.

NOTE 6 Evaluation using linear regression is also possible.

3.8 Expression of results

The values shall be rounded to the nearest 0,1 µg/l, but by not more than two significant figures.

EXAMPLES

Cadmium (Cd): 0,7 µg/l

Cadmium (Cd): 1,3 µg/l

3.9 Test report

See 2.8.

3.10 Precision

See table 1.

Annex A
(informative)

Bibliography

[1] WELZ, B. Atomic Absorption Spectrometry, Verlag Chemie, Weinheim (1983).

[2] YIN, X., SCHLEMMER, G. and WELZ, B. Cadmium Determination in Biological Material Using Graphite Furnace Atomic Absorption Spectrometry with Palladium Nitrate-Ammonium Nitrate Modifier, *J. Amer. Chem. Soc.*, **59** (1987), pp. 1462-1466.