TC 147

International Standard ISO 5961

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Water quality — Determination of cadmium — Flame atomic absorption spectrometric methods

Qualité de l'eau — Dosage du cadmium — Méthodes par spectrométrie d'absorption atomique dans la flamme

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Foreword

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Water quality — Determination of cadmium — Flame atomic absorption spectrometric methods

1 Scope and field of application

1.1 This International Standard specifies three methods for the determination of cadmium in water and waste water

- **method A**, by direct flame atomic absorption spectrometry, which is applicable for the determination of cadmium concentrations in the range from 0,05 to 5,0 mg/l

- **method B**, by flame atomic absorption spectrometry after chelation with ammonium pyrrolidin-1-yl dithiocarboxylate[1] (APDC) and extraction with methyl isobutyl ketone (MIBK), which is applicable for the determination of cadmium concentrations in the range from 0,001 to 0,010 mg/l

- **method C**, by flame atomic absorption spectrometry after chelation with hexamethyleneammonium hexamethylenedithiocarbamidate (HMA-HMDC) and extraction with di-isopropyl ketone (DIPK), which is applicable for the determination of cadmium concentrations in the range from 0,000 5 to 0,050 mg/l.

The upper limit of determination may be extended by dilution of the sample or by using a smaller volume of sample for the analysis.

1.2 Method A lacks sufficient sensitivity for the analysis of most natural waters and its application is, therefore, restricted to analysis of samples containing cadmium at concentrations greater than 0,05 mg/l. Samples containing cadmium at concentrations lower than this shall be analysed by one of the other methods. Method A is not suitable for the analysis of brines or waste waters with high calcium contents (for example above 1 000 mg/l). Extraction methods are always preferable if analysing samples containing high concentrations of dissolved solids.

1.3 Methods B and C may be used to determine cadmium in samples of most natural waters provided that significant amounts of organic materials are not present. Either method may also be used to determine cadmium in brines and brackish waters.

1.4 Methods B and C are essentially equivalent methods, and both may be expected to provide analytical data of acceptable reliability.

2 Sampling and samples

2.1 Only thoroughly clean bottles shall be used to collect samples to be analysed for cadmium. Both polyethylene and borosilicate glass bottles have been found suitable. The bottles shall be soaked overnight with dilute (1 + 1) nitric acid and then rinsed with water.

2.2 For the determination of total recoverable cadmium, the samples shall be preserved by adding, at the time of collection, concentrated nitric acid (ϱ = 1,41 g/ml) until the pH is 1,5 or less. In the case of fresh waters, 2 ml of concentrated nitric acid per litre of sample is usually sufficient.

2.3 For the determination of dissolved cadmium only, filter the sample at the time of collection through a membrane filter of pore size 0,45 µm, or its equivalent. Acidify the filtrate immediately with concentrated nitric acid (ϱ = 1,41 g/ml) until the pH is 1,5 or less.

NOTE — The membrane filters shall first be soaked in 1 % (*V*/*V*) nitric acid solution for 24 h, and then thoroughly rinsed with water.

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[1] The names ammonium 1-pyrrolidinecarbodithioate and ammonium pyrrolidine dithiocarbamate (ambiguous) are also used.

Section one : Method A — Direct flame atomic absorption spectrometric method

3 Applicability

See 1.1.

4 Principle

Direct aspiration of a prepared test portion into the flame of an atomic absorption spectrometer and comparison of the absorbance obtained with the absorbances of calibration solutions.

Dissolved cadmium may be determined by aspirating the acidified filtrate (3.3) directly with no pretreatment.

Total recoverable cadmium may be determined after hydrochloric acid-nitric acid mineralization and filtration (see 7.3.3 and 7.4.2).

5 Reagents

All reagents shall be of recognized analytical grade and shall be checked to ensure that they are of sufficient purity to permit their use without affecting the accuracy of the determination. Unless otherwise stated, the water used shall be deionized water or distilled and deionized water containing no detectable concentration of cadmium when analysed by a blank test.

5.1 Cadmium, standard solution corresponding to 1,000 g of Cd per litre.

WARNING — Cadmium is highly toxic. Avoid ingestion.

Dissolve 1,000 g cadmium in 5 ml nitric acid (5.4), heat to complete dissolution, cool and dilute to 1 000 ml with water.

It is also possible to use metallic salts, provided that their cadmium content has been accurately verified in an independent procedure.

1 ml of this standard solution contains 1 mg Cd.

NOTE — The standard solution is commercially available.

5.2 Cadmium, standard solution corresponding to 0,1 g of Cd per litre.

Dilute 100 ml of the standard cadmium solution (5.1) to 1 000 ml with nitric acid solution (5.5).

1 ml of this standard solution contains 0,1 mg of cadmium.

Prepare this solution on the day of use.

5.3 Hydrochloric acid, concentrated (ϱ = 1,19 g/ml).

5.4 Nitric acid, concentrated (ϱ = 1,41 g/ml).

5.5 Nitric acid, dilute (1 + 499).

Add 1 ml of the concentrated nitric acid (5.4) to 400 ml of water and dilute to 500 ml.

6 Apparatus

Usual laboratory apparatus and

Atomic absorption spectrometer, suitable for making measurements at 228,8 nm with automatic background correction and equipped with a cadmium hollow cathode lamp or cadmium electrodeless discharge lamp (high frequency excitation) and an air-acetylene flame.

Follow the manufacturer's instructions for safety and for adjusting all instrument parameters.

NOTE ON CLEANING OF GLASSWARE

Clean all glassware with warm, dilute (1 + 1) nitric acid solution and rinse with water.

7 Procedure

7.1 Test portion

Take, by means of a pipette, a volume of the well-mixed, acidified laboratory sample (see clause 2) such that the cadmium content is less than 0,5 mg (not more than 100 ml of laboratory sample). Transfer to a 100 ml measuring flask and make up to volume with water, if necessary, using a pipette.

7.2 Blank test

Carry out a blank test simultaneously with the determination, using the same reagents in the same quantities and following the same procedure, but replacing the test portion by 100 ml of water.

7.3 Preparation of the calibration graph

7.3.1 Preparation of the set of calibration solutions

Prepare 100 ml of at least four calibration solutions by diluting the cadmium standard solution (5.2) with nitric acid (5.5), such that the cadmium contents are equally dispersed over the range corresponding to the expected cadmium content of the sample. Use, as the zero member, 100 ml of nitric acid solution (5.5).

Prepare the solutions on the day of use.

7.3.2 Dissolved cadmium

For the determination of dissolved cadmium only, proceed directly with the spectrometric measurements (7.3.4).

7.3.3 Total recoverable cadmium

If the total recoverable cadmium is to be determined, treat each calibration solution and the zero member as follows.

Add 0,5 ml of the concentrated nitric acid (5.4) and 5 ml of concentrated hydrochloric acid (5.3). Heat on a steam-bath until the volume of each solution has been reduced to 15 to 20 ml; do not allow the solutions to boil.

Cool and filter the solutions through filter papers[1] into 100 ml volumetric flasks. The filter papers shall have been previously washed. Wash the filter papers three times with water, collecting the washings in the volumetric flasks, then dilute the contents of the flasks to the mark with water.

7.3.4 Spectrometric measurements

Aspirate each of the solutions into the flame of the atomic absorption spectrometer and measure their absorbances. Aspirate nitric acid solution (5.5) into the flame after each measurement.

NOTE — Any non-specific or continuous absorption in the wavelength region below 300 nm will cause erroneous results. The existence or absence of this continuous absorption should be verified for each sample by measuring the absorption in the immediate proximity of the resonance wavelength at which the cadmium absorption is determined. The absorbance of the continuum should then be subtracted from the observed absorbance at the cadmium resonance wavelength to determine the true cadmium absorbance. Instruments of modern design permit this in a single operation which automatically corrects for the difference between the resonance wavelength and the continuous radiation.

7.3.5 Plotting the graph

Plot a graph having, for example, the cadmium contents, in milligrams per litre, of the calibration solutions including the zero member as abscissae and the corresponding values of absorbance as ordinates.

7.4 Determination

7.4.1 Dissolved cadmium

For the determination of dissolved cadmium only, proceed directly with the spectrometric measurements (7.4.3) on the test portion (7.1) and blank test solution (7.2).

7.4.2 Total recoverable cadmium

If the total recoverable cadmium is to be determined, treat the test portion (7.1) and the blank test solution (7.2) by the procedures described in 7.3.3, from the second paragraph onwards, ["Add 0,5 ml of the concentrated nitric acid (5.4) ..."].

7.4.3 Spectrometric measurements

Aspirate the test portion (7.1) and the blank test solution (7.2), treated as described in 7.4.2 in the case of determination of total recoverable cadmium, into the flame of the spectrometer and measure their absorbances. Aspirate nitric acid solution (5.5) into the flame after each measurement.

See the note to 7.3.4.

8 Expression of results

By reference to the calibration graph (7.3.5), determine the cadmium contents corresponding to the absorbances of the test solution (7.1) and of the blank test solution (7.2).

8.1 Dissolved cadmium

The dissolved cadmium content, expressed in milligrams per litre, of the sample (see 7.4.1) is given by the formula

$$(\varrho_{\mathrm{Cd1}} - \varrho_{\mathrm{Cd2}}) \times \frac{100}{V}$$

where

ϱ_{Cd1} is the cadmium content, in milligrams per litre, corresponding to the absorbance of the test portion;

ϱ_{Cd2} is the cadmium content, in milligrams per litre, corresponding to the absorbance of the blank test solution;

V is the volume, in millilitres, of laboratory sample taken for the analysis (see 7.1).

8.2 Total recoverable cadmium

The total recoverable cadmium content, expressed in milligrams per litre, of the sample (see 7.4.2) is given by the formula

$$(\varrho_{\mathrm{Cd3}} - \varrho_{\mathrm{Cd4}}) \times \frac{100}{V}$$

where

ϱ_{Cd3} is the cadmium content, in milligrams per litre, corresponding to the absorbance of the test portion;

ϱ_{Cd4} is the cadmium content, in milligrams per litre, corresponding to the absorbance of the blank test solution;

V is the volume, in millilitres, of laboratory sample taken for the analysis (see 7.1).

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[1] A suitable filter paper, available commercially, is Whatman No. 41. This information is given for the convenience of the user of this International Standard and does not constitute an endorsement of this product by ISO.

9 Precision

Analysis of test samples with a mean of 0,05 mg/l gave a reproducibility coefficient of variation of 8,2 %.[1]

10 Notes on procedure

10.1 Calibration check

It is essential that no change occurs in the calibration graph as a result of variation in instrument conditions. It is advisable that this be checked by measuring the absorbance of the calibration solutions every five samples.

10.2 Interferences

10.2.1 Calcium ions, at concentrations greater than 1 000 mg/l, suppress cadmium absorption. At a concentration of 2 000 mg/l, the suppression may be about 20 %.

NOTE — This interference may be compensated for by using the standard addition method.

10.2.2 The following ions do not interfere significantly at concentrations up to the values indicated :

a) sodium, potassium, sulfate and chloride, up to 9 000 mg/l each;

b) magnesium, up to 4 500 mg/l;

c) iron, up to 4 000 mg/l;

d) nickel, copper, lead, cobalt, chromium, up to 10 mg/l each.

11 Test report

The test report shall include the following information :

a) a reference to this International Standard;

b) the reference of the method used;

c) an identification of the sample;

d) the results and the method of expression used;

e) any unusual features noted during the determination;

f) any operations not specified in this International Standard or regarded as optional.

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[1] AMERICAN PUBLIC HEALTH ASSOCIATION, AMERICAN WATERWORKS ASSOCIATION, WATER POLLUTION CONTROL FEDERATION, JOINT EDITORIAL BOARD. *Standard Methods for the Examination of Water and Wastewater*, 15th ed., Denver, Colorado, USA, 1980.

Section two : Method B — Flame atomic absorption spectrometric method after chelation with APDC and extraction with MIBK

12 Applicability

12.1 This method may be used to analyse samples containing cadmium in the concentration range 0,001 to 0,01 mg/l. Samples containing more than 0,01 mg/l shall be diluted prior to chelation and extraction. If the cadmium concentration exceeds 0,05 mg/l, use method A.

12.2 If the concentration of iron in the sample exceeds 25 mg/l, and if the cadmium concentration is greater than 0,05 mg/l, use method A. If the cadmium concentration is less than 0,05 mg/l, use method C after separation of the interfering iron.

12.3 If cadmium is suspected to be present as a complex compound that is not extracted by APDC/MIBK, oxidize the sample completely prior to extraction, for example by evaporation after addition of sulfuric acid/hydrogen peroxide.

12.4 A mineralization procedure (see 7.3.3 and 7.4.2) may be used in order to determine total recoverable cadmium in an unfiltered, acidified sample.

12.5 It is recommended that samples containing a high concentration of dissolved solids (brines) should be analysed by method C or, if method B is to be used, the effect of the dissolved solids content on the solubility of MIBK in water shall be taken into account in preparing the calibration graph.

13 Principle

Chelation with ammonium pyrrolidin-1-yl dithiocarboxylate[1] (APDC), extraction with methyl isobutyl ketone (MIBK), and determination by flame atomic absorption spectrometry.

Because the APDC/MIBK extract is not stable, the analysis shall not be interrupted for more than 1 h.

14 Reagents (see clause 5)

14.1 Ammonium pyrrolidin-1-yl dithiocarboxylate,[1] (APDC), 25 g/l solution.

Dissolve 2,5 g of APDC in 100 ml of water. Filter before use. Extract the solution with MIBK at least once before use until the MIBK remains colourless.

Prepare this solution on the day of use.

14.2 Bromophenol blue, 1 g/l indicator solution.

Dissolve 0,1 g of bromophenol blue in 100 ml of 50 % (*V*/*V*) ethanol or 2-propanol.

14.3 Cadmium, standard solutions.

See 5.1 and 5.2.

NOTE — For low cadmium concentrations, prepare a further standard solution by diluting 10 ml of standard solution (5.2) to 1 000 ml with nitric acid solution (5.5).

1 ml of this standard solution contains 0,001 mg of Cd.

Prepare this solution on the day of use.

14.4 Hydrochloric acid, approximately 0,3 mol/l.

Mix 25 ml of concentrated hydrochloric acid (ϱ = 1,19 g/ml) with water and dilute to 1 litre.

14.5 Methyl isobutyl ketone (MIBK).

Some batches contain zinc and possibly cadmium; such grades shall be distilled before use.

14.6 Sodium hydroxide, approximately 2,5 mol/l solution.

Dissolve 10 g of sodium hydroxide in water and dilute to 100 ml.

15 Apparatus

See clause 6.

16 Procedure

16.1 Test portion

16.1.1 Dissolved cadmium

Take, by means of a pipette, a volume of the well-mixed, acidified, filtered laboratory sample (see clause 2) such that the cadmium content is less than 0,001 mg (not more than 80 ml of laboratory sample). Transfer to a 100 ml volumetric flask and make up, if necessary, using a pipette, to 80 ml.

16.1.2 Total recoverable cadmium

Transfer a suitable volume of the acidified, unfiltered laboratory sample to a beaker or conical flask and carry out the acid mineralization described in 7.3.3, from the second paragraph onwards ["Add 0,5 ml of the concentrated nitric acid (5.4) ..."].

Take, by means of a pipette, a volume of the filtrate thus obtained, such that the cadmium content is less than 0,01 mg/l. Transfer to a 100 ml volumetric flask and dilute, if necessary, using a pipette, to 80 ml.

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[1] The names ammonium 1-pyrrolidinecarbodithioate and ammonium pyrrolidine dithiocarbamate (ambiguous) are also used.

16.2 Blank test

See 7.2, but replacing the test portion by 80 ml of water.

16.3 Preparation of the calibration graph

16.3.1 Preparation of the set of calibration solutions

Prepare a zero member, and prepare at least three calibration solutions by dilution of the cadmium standard solution (14.3) to 100 ml such that the cadmium contents cover the range from 0 to 0,01 mg/l.

16.3.2 Chelation and extraction

Add two drops of the bromophenol blue indicator solution (14.2) to 80 ml of each calibration solution in a volumetric flask.

Adjust the pH by adding, drop by drop, the sodium hydroxide solution (14.6) until a blue colour persists. Then add the hydrochloric acid (14.4), drop by drop, until the blue colour just disappears and add a further 2,0 ml in excess. The pH of the solution should be about 2,4.

NOTES

1 Alternatively use a pH meter.

2 Adjustment of the pH is not critical, a range from 1 to 5 being sufficient if cadmium only is to be determined. The pH should be 2 to 4 if lead and cadmium are to be determined.

Add 1 ml of the APDC solution (14.1) and mix. The pH should be approximately 2,8. Add 10,0 ml of the MIBK (14.5) and shake vigorously, for 1 min by hand or for 10 min if using a mechanical device.

Allow the phases to separate. Add water until the organic phase is completely in the neck of the volumetric flask.

16.3.3 Spectrometric measurements

Adjust the absorbance of the spectrometer to zero using the extraction solvent (14.5).

Aspirate each of the organic phases twice into the flame of the atomic absorption spectrometer and record the average absorbances (see the note to 7.3.4). Aspirate MIBK into the flame after each measurement.

NOTE — Precautions should be taken when aspirating organic solvents.

16.3.4 Plotting the graph

Plot a graph having, for example, the cadmium contents, in milligrams per litre, of the calibration solutions as abscissae and the corresponding values of absorbance as ordinates.

Calculate the best straight line but only on the linear portion of the graph.

16.4 Determination

16.4.1 Chelation and extraction

Proceed as described in 16.3.2 on the test portion (16.1.1 or 16.1.2).

16.4.2 Spectrometric measurements

Aspirate the organic phase twice into the flame of the atomic absorption spectrometer and record the average absorbance. Aspirate MIBK into the flame after each measurement.

17 Expression of results

By reference to the calibration graph (16.3), determine the cadmium content corresponding to the absorbances of the test portion (16.4) and of the blank test solution (16.2). The cadmium concentration, expressed in milligrams per litre, of the sample is given by the formula

$$(\varrho_{\mathrm{Cd5}} - \varrho_{\mathrm{Cd6}}) \times \frac{80}{V}$$

where

ϱ_{Cd5} is the cadmium concentration, expressed in milligrams per litre, corresponding to the absorbance of the test portion;

ϱ_{Cd6} is the cadmium concentration, expressed in milligrams per litre, corresponding to the absorbance of the blank test solution;

V is the volume, in millilitres, of the laboratory sample taken for analysis (see 16.1.1).

18 Precision

Analysis of two test samples by 11 and 13 laboratories resulted in means of 0,004 and 0,30 mg/l, with reproducibility coefficients of variation of 7,5 and 4,3 % respectively.

19 Interferences

19.1 Iron interferes if present in concentrations greater than 25 mg/l, by combining with the APDC to produce a compound which renders extraction of the cadmium non-quantitative. (See 12.2).

19.2 Other possible sources of interference are eliminated by the extraction with MIBK which isolates the cadmium.

20 Test report

The test report shall include the following information :

a) a reference to this International Standard;

b) the reference of the method used;

c) an identification of the sample;

d) the results and the method of expression used;

e) any unusual features noted during the determination;

f) any operations not specified in this International Standard or regarded as optional.

Section three : Method C — Flame atomic absorption spectrometric method after chelation with HMA-HMDC and extraction with DIPK/xylene

21 Applicability

21.1 If the ratio of the volume of the sample to the volume of the extraction solution (23.7) is 20 to 1, cadmium concentrations in the range from 0,000 5 to 0,05 mg/l may be determined.

Lower concentrations may be determined by choosing a higher ratio of volume of sample to volume of extraction solution. Volume ratios of 50 to 1 are possible, since the organic solvent mixture is only very slightly soluble in water.

21.2 A mineralization procedure (see 7.3.3 and 7.4.2) may be used in order to determine total recoverable cadmium in an unfiltered, acidified sample.

22 Principle

Chelation with hexamethyleneammonium hexamethylenedithiocarbamate (HMA-HMDC), extraction with a mixture of di-isopropyl ketone and xylene, and determination by flame atomic absorption spectrometry.

23 Reagents (see clause 5)

23.1 Cadmium, standard solutions.

See 5.1 and 5.2.

23.2 Cadmium, standard solution corresponding to 50 mg of cadmium per litre in organic solvent.

Pipette 5 ml of the cadmium standard solution (5.1) into a dry, 100 ml volumetric flask. Add 50 ml of formic acid (ϱ = 1,22 g/ml) and make-up to the mark with di-isopropyl ketone having a boiling point of 124,5 °C.

1 ml of this standard solution contains 0,05 mg of cadmium.

NOTE — Keep all organic solutions away from direct sunlight. If stored in a refrigerator at 5 °C, these solutions are stable for several days.

23.3 Buffer solution, pH = 4,0.

Dissolve 368 g of formic acid and 14 g of citric acid monohydrate in 350 ml of water. Add slowly, with constant cooling and stirring, 243 g of sodium hydroxide, 50 mg of *m*-cresolsulfonephthalein (metacresol purple), and dilute with water to 1 000 ml.

Extract this solution twice with 50 ml of the extraction solution (23.5) to remove traces of extractable cadmium.

23.4 Hexamethyleneammonium hexamethylenedithiocarbamate (HMA-HMDC).[1]

CAUTION — Carbon disulfide and diethyl ether are highly flammable.

Add 224 ml of distilled hexamethyleneimine (boiling point 136 to 138 °C) to 300 ml of xylene, cool in an ice-bath, and add, within 30 min and with constant stirring and cooling, 60 ml of distilled carbon disulfide (boiling point 46,2 °C). Collect the crystalline white precipitate on a funnel, wash three times with diethyl ether and dry between filter papers.

NOTE — The reagent is commercially available.

23.5 Extraction solution.

Dissolve, in a dry 250 ml volumetric flask, 1,7 g of the HMA-HMDC (23.4) in 75 ml of xylene, heating gently if necessary, and dilute to the mark with di-isopropyl ketone.

Prepare this solution on the day of use.

23.6 HMA-HMDC, 0,2 mol/l solution in methanol.

Dissolve, in a dry 100 ml volumetric flask, 5,5 g of the HMA-HMDC (23.4) in methanol, heating gently if necessary. Cool to room temperature and make-up to the mark with methanol.

23.7 Mixed solvent.

Transfer 30 ml of xylene to a 100 ml volumetric flask and make up to the mark with di-isopropyl ketone.

24 Apparatus

The apparatus specified in clause 6, and

Microlitre pipettes.

Clean the plastic tips of the microlitre pipettes by treating with dilute nitric acid solution (5.5) for several hours. Avoid temperatures above 40 °C. Rinse with water before use.

NOTE — Plastic tips are frequently contaminated, especially with cadmium and zinc. The use of colourless plastic tips is recommended.

25 Procedure

25.1 Test portion

Transfer, by means of a measuring cylinder, 400 ml of the sample (see clause 2) to a 500 ml volumetric flask.

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[1] IUPAC nomenclature : hexahydroazepinium hexahydroazepin-1-yl dithiocarboxylate.