International Standard ISO 8288

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Water quality — Determination of cobalt, nickel, copper, zinc, cadmium and lead — Flame atomic absorption spectrometric methods

Qualité de l'eau — Dosage du cobalt, nickel, cuivre, zinc, cadmium et plomb — Méthodes par spectrométrie d'absorption atomique avec flamme

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Foreword

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Water quality — Determination of cobalt, nickel, copper, zinc, cadmium and lead — Flame atomic absorption spectrometric methods

1 Scope

This International Standard specifies three methods for the determination of cobalt, nickel, copper, zinc, cadmium and lead in water by flame atomic absorption spectrometry:

Section one: method A, for direct determination by flame atomic absorption spectrometry;

Section two: method B, for determination by flame atomic absorption spectrometry after chelation (APDC) and extraction (MIBK);

Section three: method C, for determination by flame atomic absorption spectrometry after chelation (HMA-HMDC) and extraction (DIPK-xylene).

2 Field of application

2.1 Method A is particularly applicable when concentrations of elements to be analysed are relatively high and when there are no interferences.

When the samples are of a complex or unknown nature or when they contain high concentrations of dissolved solids (brines or brackish waters) method A is not applicable and either method B or C should be selected.

The concentrations of elements which can be determined by method A may vary according to the characteristics of the atomic absorption spectrometric apparatus used but are generally in the ranges indicated in table 1.

Table 1

Element to be determined	Range of determination (mg/l)
Cobalt	0,1 to 10
Nickel	0,1 to 10
Copper	0,05 to 6
Zinc	0,05 to 2
Cadmium	0,02 to 2
Lead	0,2 to 10

If the concentrations are greater than the upper limits indicated in the table, the sample may be diluted before analysis.

2.2 Methods B and C are applicable when concentrations of elements to be analysed in the sample (or dilution of the sample) are greater than 0,5 µg/l.

2.2.1 Method B

The concentrations of the elements which can be determined by method B may vary according to the characteristics of the atomic absorption spectrometer used but are generally in the ranges indicated in table 2.

Table 2

Element to be determined	Range of determination (µg/l)
Cobalt	1 to 200
Nickel	1 to 200
Copper	1 to 200
Zinc	0,5 to 50
Cadmium	0,5 to 50
Lead	5 to 200

2.2.2 Method C

With a ratio of test portion to extraction solution of 20 to 1 by volume as indicated in 21.2, the concentrations of elements which can be determined by method C vary as indicated in table 3.

Table 3

Element to be determined	Range of determination (µg/l)
Cobalt	0,5 to 100
Nickel	0,5 to 100
Copper	0,5 to 100
Zinc	0,2 to 50
Cadmium	0,2 to 50
Lead	2 to 200

Lower concentrations may be determined by choosing a higher ratio of test portion to extraction solution. A ratio of 50 to 1 by volume is possible since the organic solvent mixture is only very slightly soluble in water.

With method C, separation of the aqueous and the organic phases is faster. The metal chelates, especially the Cd-chelate, are more stable in the organic solvent mixture.

NOTES

1 When determining total metals, it is necessary to pretreat the sample before analysis (see examples of procedures in annex A).

2 Methods B and C are not applicable when the chemical oxygen demand (COD) of the samples (or diluted samples) is greater than 500 mg/l.

Section one: Method A — Direct determination by flame atomic absorption spectrometry

3 Principle

Aspiration into the flame of an atomic absorption spectrometer of a test portion of the acidified filtrate of the sample (or diluted sample).

Direct determination of the concentration of each element, either from the specific absorbance of each element using a spectrometer fitted with a continuous background correction system, or, in the absence of such a system, after having carried out a correction for a non-specific absorbance.

4 Reagents

All reagents shall be of recognized analytical grade so that their use does not affect the accuracy of the determination. The water used shall be deionized water or distilled water containing no detectable concentration of the metals being determined when analysed by a blank test.

4.1 Nitric acid, $\varrho = 1{,}4$ g/ml.

4.2 Nitric acid, $c(HNO_3) \approx 1{,}5$ mol/l.

Add 100 ml of nitric acid (4.1) to 600 ml of water and dilute to 1 000 ml.

4.3 Nitric acid, $c(HNO_3) \approx 0{,}03$ mol/l.

Add 1 ml of nitric acid (4.1) to 400 ml of water and dilute to 500 ml with water.

4.4 Metals, standard solutions corresponding to 1,000 g of metal per litre.[1]

For each element to be determined, weigh 1,000 g of pure metal and dissolve it in nitric acid (4.1), heating to effect complete dissolution. Allow to cool and transfer each solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

For preparing standard solutions, it is also permissible to use metal salts of accurately known composition.

Store each of the standard solutions in either polyethylene or borosilicate glass containers.

1 ml of each of these standard solutions contains 1,00 mg of the respective metal.

5 Apparatus

Usual laboratory equipment, and

Atomic absorption spectrometer, fitted with hollow cathode lamps for the appropriate metals or electrodeless discharge lamps, and with a suitable device for allowing for the correction of the non-specific absorbance and with a nebulizer-burner with an acetylene-air flame.

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

NOTE ON CLEANING OF GLASSWARE

All the glassware shall be carefully soaked in nitric acid (4.2) then rinsed with water.

6 Sampling and samples

6.1 Polyethylene or borosilicate glass containers which have been previously cleaned with nitric acid (4.2) then rinsed with water, shall be used for sampling.

6.2 If total metals are to be determined, samples shall be treated by the addition of nitric acid (4.1) immediately after collection in order to obtain a pH between 1 and 2 (usually 2 ml of acid per litre of sample is sufficient). Note the amount of acid added and use the same volume in the preparation of the blank (7.2).

If only dissolved metals are to be determined, filter the sample as soon as possible after collection through a membrane filter of nominal pore diameter 0,45 µm and acidify the filtrate immediately with nitric acid (4.1) in order to obtain a pH between 1 and 2.

Before use, filters shall be thoroughly washed with nitric acid (4.2) and rinsed with water.

7 Procedure

7.1 Test portion

Into a 100 ml one-mark volumetric flask, place a test portion of the acidified sample (6.2) such that it contains 0,2 to 1 mg of metal (see table 1 for the upper limits corresponding to each element). Make up to the mark with water.

7.2 Blank test

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

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[1] Standard solutions are commercially available.

7.3 Preparation of the sets of calibration solutions

Before each batch of determinations, prepare from each of the standard solutions (4.4) at least four calibration solutions covering, for each element, the range of the concentrations to be determined.

Prepare these calibration solutions by diluting standard solutions (4.4) with nitric acid (4.3).

7.4 Calibration and determination

Proceed as follows for each metal being determined. Before carrying out the spectrometric measurements, set up the spectrometer according to the manufacturer's instructions by aspirating a calibration solution (7.3) of the particular metal being determined and using the information in table 4. Optimize the aspiration and flame conditions (aspiration rate, nature of the flame, position of the optical beam in the flame). Adjust the response of the instrument to zero absorbance with water.

Table 4

Element to be determined	Wavelength (nm)	Flame
Cobalt	240,7	Acetylene-air
Nickel	232,0	Oxidizing acetylene-air
Copper	324,7	Oxidizing acetylene-air
Zinc	213,8	Acetylene-air
Cadmium	228,8	Acetylene-air
Lead	283,3 217,0	Acetylene-air

For each metal being determined, aspirate the set of calibration solutions (7.3) and, as zero member, the blank solution (7.2). Plot a graph having the metal contents, in milligrams per litre, of the calibration solutions as abscissae and the corresponding values of absorbance as ordinates. It is advisable that the calibration graph be checked, for example by measuring the absorbance of a calibration solution every 5 samples.

Aspirate the test portion (7.1) into the flame of the burner.

Measure the absorbance of the metal being determined and after each measurement aspirate the nitric acid (4.3) in order to rinse the nebulizer system.

NOTE ON CORRECTION FOR NON-SPECIFIC ABSORPTION

If the spectrometer used is not fitted with a background correction system which supplies automatically a signal corresponding to the specific absorbance A of the metal to be determined, it is necessary to measure the non-specific absorbance A_0. To do this, proceed as follows.

Choose a spectral line in the proximity of that of the metal to be determined in order to ensure that the difference between the wavelengths of the two spectral lines does not exceed 1 nm.

Use a spectral line of the gas contained in a hollow cathode lamp (argon or neon), or a spectral line emitted by a zirconium or deuterium hollow cathode lamp (see table 5).

Measure the absorbance A_0 corresponding to this spectral line by re-aspirating the test portion.

Calculate the specific absorbance

$$A = A_1 - A_0$$

where A_1 is the total absorbance at the wavelength of analysis.

The flame conditions and the energy assigned to the lamps shall remain unchanged throughout the measurements of the absorbances A_1 and A_0.

Table 5

Element	A_1 measurement wavelength (nm)	A_0 measurement wavelength (nm)
Cobalt	240,72	241 (D)
Nickel	232,00	232 (D)
Copper	324,75	325 (Zr)
Zinc	213,86	214 (D)
Cadmium	228,80	229 (D)
Lead	283,30	283,7 (Zr)

7.5 Check test

Carry out check tests in order to reveal any matrix effect. To do this, use the method of standard additions.

If a matrix effect is found to be present, the method is not applicable: recommence the determination using either method B or method C or use the results obtained by the method of standard additions.

8 Expression of results

By reference to the calibration graph, determine, for each metal, the concentrations corresponding to the absorbances of the test portion (7.4) and of the blank (7.2).

For each metal being determined, the concentration, expressed in milligrams per litre, of the sample is given by the formula:

$$(\varrho_t - \varrho_b) \times \frac{100}{V}$$

where

ϱ_t is the metal concentration, in milligrams per litre, corresponding to the absorbance of the test portion;

ϱ_b is the metal concentration, in milligrams per litre, corresponding to the absorbance of the blank;

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

9 Test report

The test report shall contain the following information:

- a reference to this International Standard;
- a reference to the method used;
- complete identification of the sample;
- the results of the determinations;
- any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.

Section two : Method B — Determination by flame atomic absorption spectrometry after chelation (APDC) and extraction (MIBK)

10 Principle

Formation of a complex between the metals being determined and ammonium 1-pyrrolidinedithiocarbamate (APDC) and extraction at pH 2,5 with methyl-isobutylketone (MIBK).

Determination of the metals in this organic phase by flame atomic absorption spectrometry.

11 Reagents

See clause 4.

11.1 **Nitric acid,** ϱ = 1,4 g/ml.

11.2 **Sodium hydroxide,** $c(\text{NaOH})$ = 2,5 mol/l.

With care, dissolve 100 g of sodium hydroxide in water and dilute to 1 litre.

11.3 **Hydrochloric acid,** $c(\text{HCl})$ = 0,3 mol/l.

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

11.4 **Methyl-isobutylketone** (MIBK).[1]

11.5 **Ammonium 1-pyrrolidinedithiocarbamate** (APDC)[2], 20 g/l solution.

Dissolve 2,0 g of APDC in water. Make up the volume to 100 ml with water and mix. Filter the solution if a precipitate is present. If the solution is coloured, purify it by repeated extraction with MIBK (11.4) until the solution is colourless.

Prepare this solution freshly for each batch of samples.

11.6 **Bromophenol blue,** indicator solution, 1 g of bromophenol blue per litre of 50 % (*V*/*V*) ethanol solution.

11.7 **Metals,** standard solutions, corresponding to 1,000 g of metal per litre. See 4.4.

12 Apparatus

See clause 5.

13 Sampling and samples

See clause 6.

14 Procedure

14.1 Test portion

Place in a 100 ml one-mark volumetric flask a test portion of the acidified sample (see clause 6) containing 5 to 20 µg of the metal being determined (see table 2 for the upper limits corresponding to each element). Make up to the mark with water.

14.2 Chelation and extraction

Place the test portion (14.1) and 100 ml of each of the calibration solutions (14.4) into a series of 250 ml separating funnels fitted with polytetrafluoroethylene (PTFE) taps.

Add to each funnel 2 to 3 drops of bromophenol blue indicator (11.6) and sodium hydroxide (11.2) until a blue colour persists.

While stirring, add dropwise hydrochloric acid (11.3) until the blue colour just disappears. Then add 2 ml of hydrochloric acid (11.3) in excess. The pH value shall then be 2,3 to 2,5. (See note 1.)

Add 5 ml of APDC (11.5), mix then add 10,0 ml of MIBK (11.4). Shake vigorously for 2 min. The pH shall be approximately 2,8.

Allow the mixture to settle for at least 1 h away from light or heat in the stoppered funnel. The settling time shall be strictly the same for all the solutions. Collect the organic layer taking care to avoid any trace of the aqueous phase (centrifuge if necessary). (See note 2.)

NOTES

1 A pH meter may be used in place of the indicator.

2 The settling period may be prolonged without disadvantage if it takes place in the dark at a temperature of about 5 °C. In this case it may not be necessary to centrifuge the organic phase.

14.3 Blank test

Carry out a blank test in parallel with the determination, by the same procedure (14.2), using the same quantities of all the reagents as in the sampling and chelation and extraction, but replacing the test portion by water.

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[1] 4-Methyl-2-pentanone.

[2] Ammonium-pyrrolidinocarbodithioate.

14.4 Preparation of the sets of calibration solutions

Dilute with water[1] immediately before use, each of the standard solutions (4.4) corresponding to the elements to be determined, in order to obtain diluted solutions containing 10 mg of element per litre.

In a 500 ml one-mark volumetric flask, place

- 5 ml of each of the zinc and cadmium solutions that contain 10 mg/l of the respective metal;
- 20 ml of each of the copper, cobalt, nickel and lead solutions that contain 10 mg/l of the respective metal;
- 0,5 ml of nitric acid (11.1).

Make up to the mark with water. This is solution S. Prepare at least four calibration solutions by diluting solution S with water so as to cover the following ranges of concentrations:

Zn, Cd = 0 to 50 µg/l

Cu, Co, Ni, Pb = 0 to 200 µg/l

Acidify each calibration solution by adding the same nitric acid (11.1) which has been added to preserve the samples (see 6.2). The volume added shall be such that the concentrations of nitric acid are the same in the sample and in the calibration solutions.

14.5 Calibration and determination

Proceed as follows for each metal being determined. Before carrying out the spectrometric measurements, set up the spectrometer according to the manufacturer's instructions by aspirating the organic extract (14.2) of a calibration solution of the metal being determined and using information in table 4. Optimize the aspiration and flame conditions as before (7.4). Adjust the response of the instrument to zero absorbance with MIBK (11.4).

For each metal being determined, aspirate the set of organic extracts of the calibration solutions. Plot a graph having the metal contents, in micrograms per litre, of the calibration solutions as abscissae and the corresponding values of absorbance as ordinates. It is advisable that the calibration graph be checked, for example by measuring the absorbance of a calibration solution every 5 samples.

Aspirate the organic extract of the test portion.

Measure the absorbance of the metal being determined and after each measurement aspirate MIBK in order to rinse the nebulizer system.

For correction of non-specific absorption see the note to 7.4.

NOTE — It is very important to protect the organic solutions from heat and light because the complexes of cobalt, copper, zinc and especially cadmium are unstable in MIBK. Cadmium must be measured immediately. The other metals can be stored for a few hours.

15 Expression of results

15.1 Calculation

By reference to the calibration graph, determine, for each metal, the concentrations corresponding to the absorbances of the test portion and of the blank.

For each metal being determined, the concentration, expressed in micrograms per litre, of the sample is given by the formula:

$$(\varrho_t - \varrho_b) \times \frac{100}{V}$$

where

ϱ_t is the metal concentration, in micrograms per litre, corresponding to the absorbance of the test portion;

ϱ_b is the metal concentration, in micrograms per litre, corresponding to the absorbance of the blank;

V is the volume, in millilitres, of the acidified sample taken for the analysis (see 14.1).

15.2 Precision

An international interlaboratory trial was organized in 1981 in order to compare the repeatability and reproducibility of the two methods with extraction (methods B and C).

The composition of the two samples analysed was as given in table 6.

Table 6

Sample L (low level) (µg/l)		**Sample H** (high level) (µg/l)
Lead	20	100
Cadmium	4	30
Copper	6	40
Cobalt	5	120
Nickel	10	100

The statistical analysis of results according to ISO 5725 is given in table 7.

15.3 Interferences

Other substances when present at concentrations of less than 5 mg/l do not normally interfere.

16 Test report

See clause 9.

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[1] When determining metals in sea water or other waters containing a high concentration of sodium chloride, prepare the calibration solution and the blank solution with a water of the same content of NaCl as the water being analysed.

Table 7

Metal	**Lead**		**Cadmium**		**Copper**		**Cobalt**		**Nickel**	
Level	L	H	L	H	L	H	L	H	L	H
Number of participating laboratories	14	14	14	14	14	14	14	14	14	14
Number of retained laboratories after statistical elimination	14	12	11	13	12	14	13	14	14	14
Mean (µg/l)	19,7	96	4	30,2	5,7	40,6	5,1	121,3	10,7	103,2
Repeatability										
Standard deviation, σ_r	1,5	2,6	0,1	0,7	0,2	1,7	0,4	1,9	0,4	2,3
Coefficient of variation of repeatability	7,6 %	2,7 %	2,5 %	2,3 %	3,5 %	4,2 %	7,8 %	1,6 %	3,7 %	2,2 %
Repeatability, r ($= 2,83\ \sigma_r$)	4,24	7,36	0,28	1,98	0,57	4,8	1,13	5,38	1,13	6,51
Reproducibility										
Standard deviation, σ_R	3,2	5,3	0,3	1,3	0,7	5,9	1,4	7,6	1,4	16,2
Coefficient of variation of reproducibility	16,2 %	5,5 %	7,5 %	4,3 %	12,3 %	14,5 %	27,5 %	6,3 %	13,1 %	15,7 %
Reproducibility, R ($= 2,83\sigma_R$)	9,05	15	0,85	3,68	1,98	16,7	3,96	21,51	3,96	45,85

Section three : Method C — Determination by flame atomic absorption spectrometry after chelation (HMA-HMDC) and extraction (DIPK-xylene)

17 Principle

Formation of a complex between metals and hexamethylene-ammonium-hexamethylenedithiocarbamate (HMA-HMDC) and extraction with diisopropylketone-xylene in a buffered medium of pH value 2 to 4.

Determination of the metals in this organic phase by flame atomic absorption spectrometry.

18 Reagents

See clause 4.

18.1 Nitric acid, ϱ = 1,4 g/ml.

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

To a solution of 224 ml of distilled hexamethylene imine (bp 136 to 139 °C) in 300 ml of xylene, which is cooled by an ice-bath, add within 30 min and with constant stirring and cooling, 60 ml of distilled carbon disulfide (bp 46,2 °C).

Continue cooling and stirring for 1 h. Filter the solution and collect the flocculent white precipitate; wash it three times with diethylether and dry between two filter papers.

18.3 HMA-HMDC, 6,8 g/l extraction solution.

Dissolve, in a dry 250 ml one-mark volumetric flask, 1,7 g of HMA-HMDC (18.2) in 75 ml of xylene, heating gently. Make up to the mark with diisopropylketone[2] (DIPK) (bp 124,5 °C).

This solution is stable for a week if stored at 5 °C away from light.

18.4 HMA-HMDC, 55 g/l solution in methanol.

In a dry 100 ml one-mark volumetric flask, dissolve 5,5 g of HMA-HMDC (18.2) in methanol, heating gently. Cool to room temperature and make up to the mark with methanol.

18.5 Formate, buffer solution.

Dissolve 368 g of formic acid [98 to 100 % (*m*/*m*)] and 14 g of citric acid monohydrate in 350 ml of water. Slowly add, with constant stirring and cooling, 243 g of sodium hydroxide. Add 50 mg of *m*-cresolsulfonephthalein (metacresol purple). Purify this solution by two consecutive extractions with extraction solution (18.3), with constant stirring.

18.6 Metals, standard solutions, corresponding to 1,000 g of metal per litre.

Dissolve jointly 1,000 g of each metal to be determined in nitric acid (18.1) by heating until complete dissolution. Cool and make up to 1 000 ml with water. The acid concentration of this solution shall be approximately 0,1 to 0,5 mol/l.

When preparing the standard solutions, it is also permissible to use metal salts of accurately known composition.

18.7 Metals, organic standard solution, corresponding to 50 mg of metal per litre.

In a dry 100 ml one-mark volumetric flask, place 5 ml of aqueous standard solution (18.6). Add 50 ml of formic acid [98 to 100 % (*m*/*m*)] and 0,2 to 0,5 g of citric acid monohydrate. Make up to the mark with diisopropylketone.

19 Apparatus

The apparatus specified in clause 5, and

Microlitre pipettes.

Clean the plastic tips of microlitre pipettes by soaking in nitric acid (4.2) for several hours. Avoid temperatures above 40 °C. Rinse with water before use.

20 Sampling and samples

See clause 6.

21 Procedure

21.1 Test portion

The test portion of the acidified sample (see clause 6) is generally 400 ml.

Other volumes which give a ratio of aqueous phase to organic phase of up to 50 to 1 by volume may be used when it is desired to obtain greater or smaller enrichment factors.

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[1] This reagent is commercially available.

[2] 2,4-Dimethyl-3-pentanone.

21.2 Chelation and extraction

Place the test portion (21.1) in a 500 ml one-mark volumetric flask. Add 20 ml of formate buffer solution (18.5). The colour of the indicator shall be a pure yellow. If a red colour appears, add an additional 20 ml of formate buffer solution.

Add 2,0 ml of HMA-HMDC solution in methanol (18.4), shake and allow to stand for 3 to 5 min.

Add 20,0 ml of extraction solution (18.3) and shake the flask vigorously for at least 3 min.

Allow the mixture to settle for 10 to 15 min in order to obtain a good separation of the layers. Then carefully add water until the organic layer is completely in the neck of the flask.

Aspiration of the organic layer for the determination (21.5) may be done directly from the neck of the flask.

If the organic layer has to be kept for a longer time, pipette it off, taking care to avoid any trace of the aqueous phase, and store in a cool dark place.

21.3 Blank test

Carry out a blank test in parallel with the determination, by the same procedure (21.2), using the same quantities of all the reagents as in the sampling and chelation and extraction, but replacing the test portion by nitric acid (4.3).

21.4 Preparation of the sets of calibration solutions

21.4.1 Aqueous solutions

Before each batch of determinations, prepare at least four aqueous calibration solutions covering the range of the concentrations to be determined. Prepare these calibration solutions by diluting the aqueous standard solution (18.6) with nitric acid (4.3).

NOTE — These sets of aqueous solutions are used for verification of completeness of extraction. Laboratories which are not familiar with extraction are advised to check complete extraction following the procedure described in annex B.

21.4.2 Organic solutions

Immediately prior to use, prepare at least four organic calibration solutions covering the range of the concentrations to be determined.

Prepare these calibration solutions by diluting the organic standard solution (18.7) with extraction solution (18.3) using dry 25 ml one-mark volumetric flasks and microlitre pipettes (clause 19).

21.5 Calibration and determination

Proceed as follows for each metal. Before carrying out the spectrometric measurements, set up the spectrometer according to the manufacturer's instructions by aspirating one of the organic calibration solutions (21.4.2) and using the information in table 4. Optimize the aspiration and flame conditions as before (7.4). Adjust the response of the instrument to zero absorbance with extraction solution (18.3).

For each metal being determined, aspirate the set of organic calibration solutions (21.4.2). Plot a graph having the metal contents, in micrograms per litre, of the organic calibration solutions as abscissae and the corresponding values of absorbance as ordinates.

Aspirate the organic extract of the test portion (21.2).

Measure the absorbance of the metal to be determined. After each measurement rinse the nebulizer system by aspirating with methanol to avoid clogging.

If necessary, correct for non-specific absorption (see the note to 7.4).

22 Expression of results

22.1 Calculation

By reference to the calibration graph, determine, for each metal, the concentrations corresponding to the absorbances of the test portion and of the blank.

For each metal being determined, the concentration, expressed in micrograms per litre, of the sample is given by the formula:

$$(\varrho_t - \varrho_b) \times \frac{20}{V}$$

where

ϱ_t is the metal concentration, in micrograms per litre, corresponding to the absorbance of the test portion;

ϱ_b is the metal concentration, in micrograms per litre, corresponding to the absorbance of the blank;

V is the volume, in millilitres, of the acidified sample taken for the analysis (see 21.1).

22.2 Repeatability and reproducibility

An international interlaboratory trial was organized in 1981 in order to compare the repeatability and reproducibility of the two methods with extractions (methods B and C).

The compositions of the two samples analysed were as given in table 6.

The statistical analysis of results according to ISO 5725 is given in table 8.

22.3 Interferences

A total concentration of heavy metals, iron included, up to 20 mg/l is tolerable. If the total concentration of heavy metals exceeds 20 mg/l, a ratio of test portion to extraction solution smaller than 20 to 1 by volume shall be taken.

Table 8

Metal	Lead		Cadmium		Copper		Cobalt		Nickel	
Level	L	H	L	H	L	H	L	H	L	H
Number of participating laboratories	16	16	16	16	16	16	15	16	15	16
Number of retained laboratories after statistical elimination	14	14	13	13	15	16	14	14	11	14
Mean (µg/l)	20,3	97,7	4	29,8	6,4	41	5,8	115,8	10,9	100,2
Repeatability										
Standard deviation, σ_r	1,06	3,8	0,3	0,8	0,5	3,3	0,6	3,6	1,8	4,7
Coefficient of variation of repeatability	5,2 %	3,9 %	7,5 %	2,7 %	7,8 %	8,0 %	10,3 %	3,1 %	16,5 %	4,7 %
Repeatability, r (= 2,83 σ_r)	3,0	10,7	0,85	2,26	1,41	9,34	1,7	10,2	5,1	13,3
Reproducibility										
Standard deviation, σ_R	2,8	3,4	0,4	2,7	1,1	4,8	1,2	8,2	4	13,7
Coefficient of variation of reproducibility	13,8 %	3,5 %	10 %	9,1 %	17,2 %	11,7 %	20,7 %	7,1 %	36,7 %	13,7 %
Reproducibility, R (= 2,83 σ_R)	7,9	9,62	1,13	7,64	3,11	13,6	3,4	23,21	11,3	38,8

The tolerable concentration of nitriloacetic acid is 250 mg/l. Ethylenediaminetetraacetic acid (EDTA) interferes in the extraction of nickel; concentration of 25 mg/l of ethylenediaminetetraacetic acid disodium salt dihydrate ($C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$) is tolerable in the extraction of the five other metals.

Humic acid contained in neutral water samples precipitates upon acidification. This precipitate should be removed by filtration; it does not retain heavy metals. Extraction of the heavy metals from the filtrate as hexamethylene dithiocarbamates with diisopropylketone-xylene can be performed with complete recovery.

23 Test report

See clause 9.