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Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace

Qualité de l'eau — Dosage des éléments traces par spectrométrie d'absorption atomique en four graphite

Reference number
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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15586 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard includes principles and procedures for the determination of trace levels of: Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, and Zn in surface water, ground water, drinking water, wastewater and sediments, using atomic absorption spectrometry with electrothermal atomization in a graphite furnace. The method is applicable to the determination of low concentrations of elements.

The detection limit of the method for each element depends on the sample matrix as well as of the instrument, the type of atomizer and the use of chemical modifiers. For water samples with a simple matrix (i.e. low concentration of dissolved solids and particles), the method detection limits will be close to instrument detection limits. The minimum acceptable detection limit values for a 20-µl sample volume are given in Table 1.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

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

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

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

ISO 5667-4, *Water quality — Sampling — Part 4: Guidance on sampling from lakes, natural and man-made*

ISO 5667-5, *Water quality — Sampling — Part 5: Guidance on sampling of drinking water and water used for food and beverage processing*

ISO 5667-6, *Water quality — Sampling — Part 6: Guidance on sampling of rivers and streams*

ISO 5667-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste waters*

ISO 5667-11, *Water quality — Sampling — Part 11: Guidance on sampling of groundwaters*

ISO 5667-15, *Water quality — Sampling — Part 15: Guidance on preservation and handling of sludge and sediment samples*

ISO 15587-1, *Water quality — Digestion for the determination of elements in water — Part 1: Aqua regia digestion*

ISO 15587-2, *Water quality — Digestion for the determination of elements in water — Part 2: Nitric acid digestion*

Table 1 — Approximate characteristic masses, instrument detection limits and optimum working ranges for water samples using a 20 µl sample volume

Element	Characteristic mass m_0[a] pg	Detection limit [b] µg/l	Optimum working range [c] µg/l
Ag	1,5	0,2	1 to 10
Al	10	1	6 to 60
As	15	1	10 to 100
Cd	0,7	0,1	0,4 to 4
Co	10	1	6 to 60
Cr	3	0,5	2 to 20
Cu	5 [d]	0,5	3 to 30
Fe	5	1	3 to 30
Mn	2,5	0,5	1,5 to 15
Mo	10	1	6 to 60
Ni	13	1	7 to 70
Pb	15	1	10 to 100
Sb	20	1	10 to 100
Se	25	2	15 to 150
Tl	10 [d]	1	6 to 60
V	35	2	20 to 200
Zn	0,8	0,5	0,5 to 5

[a] The characteristic mass (m_0) of an element is the mass in picograms, corresponding to a signal of 0,004 4 s, using the integrated absorbance (peak area) for evaluation.

[b] The detection limits are calculated as three times (3 ×) the standard deviation of repeated measurements of a blank solution.

[c] The optimum working range is defined as the concentration range that corresponds to integrated absorbance readings between 0,05 s and 0,5 s.

[d] If Zeeman effect background correction is used, the m_0-value will be higher.

3 Principle

Water samples are preserved by acid treatment, filtered and preserved by addition of acid, or digested. Sediment samples are digested. A small sub-sample of sample solution is injected into a graphite furnace of an atomic absorption spectrometer. The furnace is electrically heated. By increasing the temperature stepwise, the sample is dried, pyrolized and atomized. Atomic absorption spectrometry is based on the ability of free atoms to absorb light. A light source emits light specific for a certain element (or elements). When the light beam passes through the atom cloud in the heated graphite furnace, the light is selectively absorbed by atoms of the chosen element(s). The decrease in light intensity is measured with a detector at a specific wavelength. The concentration of an element in a sample is determined by comparing the absorbance of the sample with the absorbance of calibration solutions. If necessary, interferences may be overcome by adding a matrix modifier to the samples before analysis, or by performing the calibration with the standard addition technique.

The results are given as the mass of analyte (micrograms, µg, or milligrams, mg) per litre of water, or per kilogram of dried material in sediments.

4 Interferences

Some sample solutions, especially wastewaters and digestions of sediments, may contain large amounts of substances that may affect the results. High concentrations of chloride may cause low results, because the volatility of many elements is increased and analyte loss may occur during the pyrolysis step. Matrix effects may be overcome, partially or completely, by optimization of the temperature programme, the use of pyrolytically-coated tubes and platforms, the use of chemical modifiers, the standard addition technique and the use of background correction.

5 Reagents

For pre-treatment of samples and preparation of solutions, use only chemicals and solutions of highest possible purity unless stated otherwise.

5.1 **Water**, Grade 1 as specified in ISO 3696:1987 ($\leqslant$ 0,01 mS/m), or better.

Use this water to prepare all solutions. Check the quality of the water before use.

5.2 **Nitric acid**, concentrated, $c(\mathrm{HNO_3})$ = 14,4 mol/l, $\rho \approx$ 1,4 kg/l (65 %).

If the concentrated nitric acid contains significant amounts of analyte elements, purify it by sub-boiling distillation in a quartz apparatus. The distillation should be performed under a fume cupboard.

Nitric acid is available both as ρ = 1,40 kg/l (65 %) and as ρ = 1,42 kg/l (69 %). Both are suitable for use in this method provided there is minimal content of analytes.

5.3 **Nitric acid**, $c(\mathrm{HNO_3}) \approx$ 7 mol/l.

Add one volume of concentrated nitric acid (5.2) to one volume of water (5.1) while stirring.

5.4 **Nitric acid**, $c(\mathrm{HNO_3}) \approx$ 1 mol/l.

To about 500 ml of water (5.1), add 70 ml of concentrated nitric acid (5.2) and dilute with water (5.1) to 1 000 ml.

5.5 **Nitric acid**, $c(\mathrm{HNO_3}) \approx$ 0,1 mol/l.

To about 500 ml of water (5.1), add 7 ml of concentrated nitric acid (5.2) and dilute with water (5.1) to 1 000 ml.

5.6 **Hydrochloric acid**, concentrated, $c(\mathrm{HCl})$ = 12,1 mol/l, $\rho \approx$ 1,19 kg/l (37 %).

If the concentrated hydrochloric acid contains significant amounts of analyte elements, purify e.g. by sub-boiling distillation in a quartz apparatus. The distillation should be performed under a fume cupboard.

5.7 **Hydrochloric acid**, $c(\mathrm{HCl}) \approx$ 6 mol/l.

Add one volume of concentrated hydrochloric acid (5.6) to one volume of water (5.1) while stirring.

5.8 **Hydrochloric acid**, $c(\mathrm{HCl}) \approx$ 1 mol/l.

To about 500 ml of water (5.1), add 83 ml of concentrated hydrochloric acid (5.6) and dilute with water (5.1) to 1 000 ml.

5.9 **Standard stock solutions**, ρ = 1 000 mg/l.

Stock solutions may be purchased from a commercial source.

Procedures for preparation of stock solutions from metals or metal salts are described in Annex A. Stock solutions are stable for about one year or in accordance with the manufacturer's recommendations.

5.10 Standard solution, ρ = 10 mg/l.

Using a pipette, transfer 1 000 µl of the stock solution (5.9) to a 100 ml volumetric flask, add 0,5 ml of concentrated nitric acid (5.2), and dilute to volume with water (5.1).

This solution may be stored for 6 months.

5.11 Standard solution, ρ = 1 mg/l.

Using a pipette, transfer 100 µl of the stock solution (5.9) to a 100 ml volumetric flask, add 0,5 ml of concentrated nitric acid (5.2), and dilute to volume with water (5.1).

This solution may be stored for six months.

5.12 Standard solution, ρ = 100 µg/l.

Using a pipette, transfer 1 000 µl of the standard solution 10 mg/l (5.10) to a 100 ml volumetric flask, add 0,5 ml of concentrated nitric acid (5.2), and dilute to volume with water (5.1).

This solution may be stored for one month.

5.13 Calibration solutions

Prepare calibration solutions from the standard solutions (5.10 to 5.12).

The following procedure can be used as an example:

To prepare a series of calibration solutions containing 2 µg/l; 4 µg/l; 6 µg/l; 8 µg/l and 10 µg/l of analyte, pipette, 200 µl, 400 µl, 600 µl, 800 µl and 1 000 µl respectively of the standard solution 1 mg/l (5.11) to 100 ml volumetric flasks. Add the same amount of acid to the calibration solutions as that of the samples. Cool if necessary and dilute to volume with water (5.1).

Calibration solutions below 1 mg/l should not be used for more than one month, and those below 100 µg/l should not be used for more than one day.

5.14 Blank calibration solution

Prepare a blank calibration solution in the same way as the calibration solutions, but add no standard solution. Use a 100 ml volumetric flask. Add the same amount of acid to the calibration solutions as that of the samples. Cool if necessary and dilute to volume with water (5.1).

5.15 Palladium nitrate/magnesium nitrate modifier

$Pd(NO_3)_2$ solution is commercially available (10 g/l). Dissolve 0,259 g of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 ml of water (5.1). Mix the palladium nitrate solution with twice as much magnesium nitrate solution. 10 µl of the mixed solution is equal to 15 µg Pd and 10 µg $Mg(NO_3)_2$. The mixture is also commercially available.

Prepare a fresh solution monthly.

5.16 Magnesium nitrate modifier

Dissolve 0,865 g of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 ml of water (5.1). 10 µl of this solution is equal to 50 µg $Mg(NO_3)_2$.

5.17 Ammonium dihydrogen phosphate modifier

Dissolve 2,0 g of $NH_4H_2PO_4$ in 100 ml of water (5.1). 10 µl of this solution is equal to 200 µg $NH_4H_2PO_4$.

5.18 Ammonium dihydrogen phosphate/magnesium nitrate modifier

Dissolve 2,0 g of $NH_4H_2PO_4$ and 0,173 g of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 ml of water (5.1). 10 µl of this solution is equal to 200 µg $NH_4H_2PO_4$ and 10 µg $Mg(NO_3)_2$.

5.19 Nickel modifier

Dissolve 0,200 g of nickel powder in 1 ml concentrated nitric acid (5.2) and dilute to 100 ml with water (5.1). 10 µl of this solution is equal to 20 µg Ni. Solutions of $Ni(NO_3)_2$ are also commercially available.

5.20 Purge and protective gas, argon (Ar) ($\geqslant$ 99,99 %).

6 Apparatus

The following general cleaning procedure is the absolute minimum required for glass and plastics if nothing else is stated.

a) Prior to use, soak the equipment for at least one day in nitric acid, $c \approx 1$ mol/l (5.4), or hydrochloric acid, $c \approx 1$ mol/l (5.8).

b) Rinse with water (5.1) at least three times.

Remove parts of equipment made from polyamide (e.g. screws and nuts in sampling equipment) prior to soaking the equipment in acid.

Take the necessary precautions in such a way that equipment, once being used for samples with high concentration of metals, will not be used for trace element samples in the future.

6.1 Sample containers for water, consisting of bottles made of polypropylene, polyethylene or fluorinated ethylene propylene (FEP).

The material in bottles and caps should not contain or leach any analyte, and preferably be made of colourless material.

For determinations at ultra trace levels (< 0,1 µg/l) it is necessary to follow a very strict cleaning procedure, as described below.

a) Rinse new bottles with acetone to remove possible fatty remainders. Alternatively, a suitable detergent may be used.

b) Rinse with water (5.1).

c) Soak in hydrochloric acid, $c \approx 6$ mol/l (5.7), for one week, or at 45 °C to 50 °C for 24 h.

d) Rinse with water (5.1).

e) Soak in nitric acid, $c \approx 7$ mol/l (5.3), for one week, or at 45 °C to 50 °C for 24 h.

f) Rinse with water (5.1), and transfer to clean laboratory.

g) Soak in nitric acid $c \approx 0{,}1$ mol/l (5.5) for one week, to condition the bottles to the matrix in use.

h) Rinse with water (5.1) several times.

i) Dry under filtered air (clean bench), if drying is necessary.

j) Store the cleaned bottles in closed plastics bags.

If it is shown not necessary to use both steps c) and e), one of the acids may be excluded. In this case, hydrochloric acid is shown to be more effective for polyethylene and polypropylene, while nitric acid preferably should be used for FEP and glassware.

6.2 Sample containers for sediments, consisting of wide-necked containers of plastics or glass.

For cleaning of the containers, it may not be necessary to use acids. Washing with detergents and rinsing in deionized water (5.1) may be sufficient.

6.3 Filtering equipment, made of glass or plastics material without metal parts, cleaned as stated in the general cleaning procedure under Clause 6 heading.

6.4 Filters, either membrane filters or capillary filters, with a nominal pore width of 0,45 µm and 0,4 µm respectively.

The material should not release or absorb analytes. Clean filters in nitric acid, $c \approx$ 0,1 mol/l (5.5), and rinse several times with water (5.1).

6.5 Agate mortar, for crushing sediments into a fine powder.

6.6 Pipettes, of capacity varying from 100 µl to 1 000 µl.

Pipette tips preferably should be made of colourless plastics, which do not contain or leach any analyte to the solutions. It is important to check that the pipette tips do not contaminate samples. Always rinse the pipette tips with the solution to be used immediately before use.

Depending on the concentration levels to be determined, new and reused pipette tips may be cleaned with dilute acid. For example, clean with nitric acid, $c \approx$ 1 mol/l (5.4), and rinse with water (5.1).

6.7 Atomic absorption spectrometer equipped with graphite furnace, equipped with a background correction system and the necessary hollow cathode lamps.

Alternatively, electrode-less discharge lamps may be used.

It is necessary to place an exhaust venting system over the furnace to remove any smoke and vapours that might be harmful.

6.8 Autosampler, may be used to improve the precision of the determination.

Depending on the concentration levels to be determined, new autosampler cups may be cleaned with dilute acid. Reused caps should always be washed with acid. For example, clean the vessels with nitric acid, $c \approx$ 1 mol/l (5.4), and rinse with water (5.1). If they will be used for ultra trace determination (< 0,1 µg/l), an extra cleaning step before use may be necessary by filling them with acid of the same kind and concentration as in the samples that are to be analysed. Allow to stand for at least 2 h. Rinse several times with water (5.1).

6.9 Graphite tubes, pyrolytically-coated with platforms, preferably for highly and medium volatile elements, whereas elements of low volatility should be atomized from the wall.

Provided satisfactory results are achieved, manufacturer's recommendations regarding the use of graphite tubes and platforms should be followed.

7 Sampling and pre-treatment

7.1 Sampling

Sampling shall be carried out in accordance with ISO 5667-1, ISO 5667-2, ISO 5667-3, ISO 5667-4, ISO 5667-5, ISO 5667-6, ISO 5667-10, ISO 5667-11 and ISO 5667-15.

The sampling equipment for water samples should be constructed in such a way that the sample does not come in contact with parts made of metal. It should be made of plastics not releasing analytes into the sample, and be suitable for cleaning in dilute hydrochloric acid.

7.2 Pre-treatment of water samples

7.2.1 General

Pre-treatment and analysis of samples with especially low element concentrations should be carried out under "clean laboratory" conditions. The "clean laboratory" technique requires that the laboratory be supplied with filtered air, and that the samples be continuously protected from contamination originating from various sources. In some cases, "clean benches" with filtered laminar airflow under a weak over-pressure, may be used as a suitable alternative.

Trace elements in water samples are analysed in one or more of the following fractions.

a) Preserved by addition of acid (non-filtered). Preserve the sample by addition of nitric acid. Particles should be allowed to sediment before analysis.

b) Filtered (dissolved). Filter the sample through a membrane or capillary filter and preserve the filtrate by addition of nitric acid.

c) Digested in acid. Digest the preserved sample with nitric acid or aqua regia.

Store preserved water samples in cool conditions in accordance with ISO 5667-3 until analysis (1 °C to 5 °C).

7.2.2 Filtration

Filtration of samples is necessary if the dissolved forms of trace elements are analysed. Filter the sample immediately after sampling and before preservation. Avoid equipment where the sample may come in contact with metal parts. To reduce the risk of contamination, pressure filtration is preferable to vacuum filtration.

Prepare at least one blank test solution by filtration (and preservation) of water (5.1) in the same way as the test samples.

7.2.3 Preservation

Preserve water samples in accordance with ISO 5667-3. To obtain a $\text{pH} < 2$ in the samples, add 0,5 ml of concentrated nitric acid (5.2) per 100 ml of sample. For the preservation of water samples with high alkalinity, it may be necessary to add more acid. It is important that sufficient acid is added to the sample to avoid loss of elements through adsorption effects. Report the amount of acid added.

Preferably preserve the samples in the laboratory in a clean atmosphere to avoid contamination risks. For the reagent blank solution, preserve water (5.1) in the same way as the test samples.

7.2.4 Digestion of water samples

Methods for digestion of water with aqua regia and nitric acid are specified in ISO 15587-1 and ISO 15587-2, respectively. Since chloride may cause severe interference in the graphite furnace technique, digestion with nitric acid is recommended. For some elements (e.g. Sb in this International Standard) nitric acid is not suitable and aqua regia should be used.

Prepare at least one blank test solution by digesting water (5.1) in the same way as the test samples.

Before analysis of the digests, make up to volume with water (5.1).

7.3 Pre-treatment of sediment samples

7.3.1 Storage of sediment samples

After sampling, store sediment samples in their original containers (6.2) in a refrigerator, or frozen until further treatment (ISO 5667-15).

If the determination is to be performed on a dry sample, preferably freeze-dry the sample , or alternatively dry it at 105 °C for 24 h. Crush the dried sample in an agate mortar (6.5), homogenize and sieve it if necessary.

Dried sediments are hygroscopic and will absorb moisture if stored. Freeze-dried samples contain a few percent water. It is necessary to control the water content by drying a sub-sample at 105 °C, before digestion and analysis.

7.3.2 Digestion of sediment samples

See Annex B.

8 Chemical modification

Chemical modifiers are used to overcome spectral and/or non-spectral interferences in a sample (matrix effects).

By measuring a sample with and without addition of an analyte and by comparing the recovery of the analyte with a calibration standard, it is often possible to recognize the existence of a non-spectral interference. In order to ascertain that the modification works, the same procedure is repeated with the addition of a chosen chemical modifier.

In general, the aim of chemical modification is to allow a pyrolysis temperature that is high enough to remove the bulk of concomitants before the atomization step. The combination of Pd and $Mg(NO_3)_2$ is regarded as a “universal” modifier that is used for a number of elements. The combination of Pd with a reducing agent, e.g. ascorbic acid, is sometimes used instead of $Pd/Mg(NO_3)_2$. The background absorption tends to be high with $Mg(NO_3)_2$. Other modifiers are also used. Some of them (e.g. Ni compounds) may be disadvantageous, because they contain elements that are frequently determined with the same equipment and can cause contamination of the furnace. In Table 2 some recommendations of chemical modifiers are given for the elements in this International Standard. Other chemical modifiers may be used if they show consistent results.

If chemical modifiers are used, add them both to test samples, reagent blank solutions, blank test solutions, calibration solutions, and blank calibration solutions. To achieve the recommended amounts in Table 2, 10 µl of modifier solution shall be added. Preferably inject the modifier solution with the autosampler directly into the atomizer after the sample is delivered.

Table 2 — Recommended chemical modifiers

Element	Chemical modifiers (5.15 to 5.19)	Amounts µg [a]
Ag	Pd + $Mg(NO_3)_2$ or $NH_4H_2PO_4$	15 + 10 200
Al	Pd + $Mg(NO_3)_2$ or $Mg(NO_3)_2$	15 + 10 50
As	Pd + $Mg(NO_3)_2$ or Ni (as nitrate)	15 + 10 20
Cd	Pd + $Mg(NO_3)_2$ or $NH_4H_2PO_4$ + $Mg(NO_3)_2$	15 + 10 200 + 10
Co	$Mg(NO_3)_2$	50
Cr	$Mg(NO_3)_2$	50
Cu	Pd + $Mg(NO_3)_2$	15 + 10
Fe	$Mg(NO_3)_2$	50
Mn	Pd + $Mg(NO_3)_2$ or $Mg(NO_3)_2$	15 + 10 50
Mo	No modifier required	—
Ni	$Mg(NO_3)_2$	50
Pb	Pd + $Mg(NO_3)_2$ or $NH_4H_2PO_4$ + $Mg(NO_3)_2$	15 + 10 200 + 10
Sb	Pd + $Mg(NO_3)_2$ or Ni (as nitrate)	15 + 10 20
Se	Pd + $Mg(NO_3)_2$ or Ni (as nitrate)	15 + 10 20
Tl	Pd + $Mg(NO_3)_2$	15 + 10
V	No modifier required	—
Zn	Pd + $Mg(NO_3)_2$ or $Mg(NO_3)_2$	15 + 10 6

[a] These amounts are only recommendations. Significantly lower amounts may be required in some atomizers. See also recommendations from instrument manufacturers.

9 Determination

Examples of how to program the graphite furnace are given in Annex C.

A temperature programme for the graphite furnace usually includes four steps:

a) drying,

b) pyrolysis,

c) atomization,

d) cleaning.

Preferably, as a start, use the temperatures and times recommended by the manufacturer. Interrupt the argon flow during the atomization step.

Always use background correction.

Alternative wavelengths (with different sensitivities) may be used. For example, for lead, the wavelength 217,0 nm may be used, where the sensitivity is about twice of that at 283,3 nm. However, the noise is higher and the risk for interferences is greater. In the case of high concentrations a wavelength with lower sensitivity may be used, i.e. 307,6 nm for Zn and 271,9 nm or 305,9 nm for Fe.

For evaluation the integrated absorbance (peak area) is recommended.

10 Calibration

10.1 Standard calibration technique

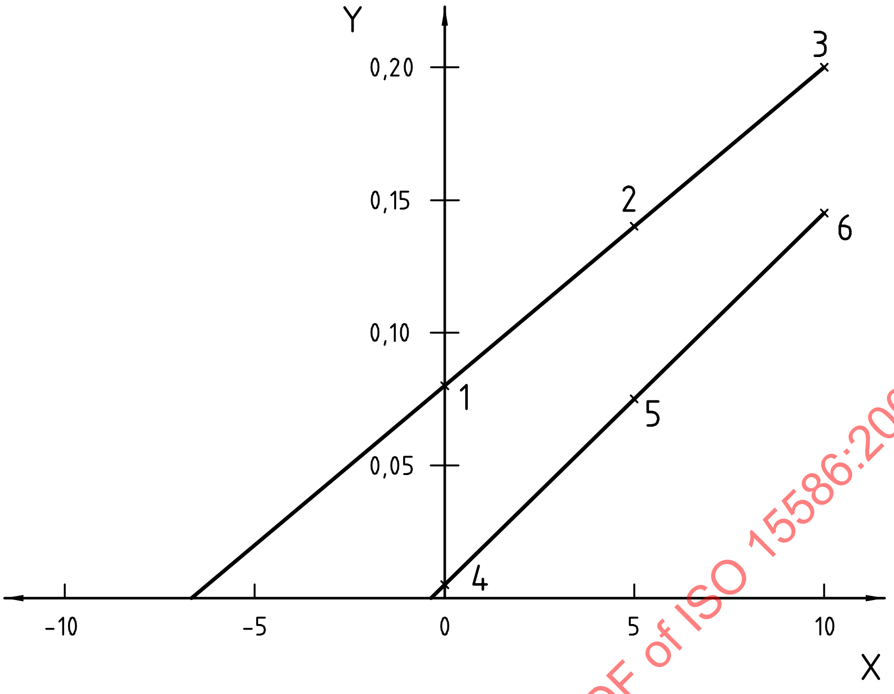
Perform the calibration with a blank calibration solution (5.14) and 3 to 5 equidistant calibration solutions (5.13) for an appropriate concentration range. It should be stressed that the linearity of the calibration curve is often limited.

Correct the absorbance values of the calibration solutions by subtracting the absorbance value of the blank calibration solution. For plotting of a calibration curve or for calculation of the calibration function, use the resulting values together with the analyte concentrations of the calibration solutions.

10.2 Standard addition technique

To reduce the effect of non-spectral interferences, where chemical modification is not used or does not eliminate matrix effects, the standard addition technique may be applied provided the calibration curve is linear in the absorbance range used. The standard addition technique cannot be used to correct for spectral interferences, such as unspecific background absorption, and shall not be used if interferences change the signal by a factor of more than three.

Transfer equal volumes of the test sample to three vessels (e.g. autosampler cups). Add a small amount of standard solution to two of the vessels so as to obtain corresponding absorption values that are 100 % and 200 % higher than that which would be expected from the original sample. Add an equal amount of water (5.1) to the third vessel. Mix the solutions well. Measure the integrated absorbance of each solution, and then plot the concentration added along the abscissa against the measured absorbance along the ordinate, as illustrated in Figure 1. Determine the analyte concentration in the reagent blank solution or blank test solution in the same way. In Figure 1 the analyte concentration of the test sample solution is 6,67 µg/l, and the blank test solution is 0,36 µg/l.



Key

X addition (ug/l)

Y integrated absorbance

1	test sample solution	4	blank test solution
2	test sample solution + 5 µg/l	5	blank test solution + 5 µg/l
3	test sample solution + 10 µg/l	6	blank test solution + 10 µg/l

Figure 1 — Example of a standard addition calibration function

11 Calculation

11.1 Results for water

Read the values of the analyte concentrations of the test sample solutions, the reagent blank solution and the blank test solution from the calibration graph or calculate them from the calibration function. Correct the analyte concentrations of the test sample solutions by subtracting the analyte concentrations of the reagent blank solution or the blank test solution.

Correct for dilution steps, if appropriate.

Report results for water in micrograms per litre (µg/l). For test samples for which no detectable signal can be obtained, report results as less than “the detection limit”.

11.2 Results for sediments

Read off the analyte concentrations of the test sample solutions and the blank test solution from the calibration graph or calculate them from the calibration function. Correct the analyte concentrations of the test sample solutions by subtracting the analyte concentration of the test blank solution.

Calculate the analyte content of the test samples, when the determination is performed on a dried material, from the following equation:

$$w_{\mathrm{s,dm}} = \rho_{\mathrm{digs}} \left(\frac{V_{\mathrm{digs}}}{m_{\mathrm{drs}}} \right)$$

or when the determination is performed on wet sample

$$w_{\mathrm{s,dm}} = \rho_{\mathrm{digs}} \left(\frac{V_{\mathrm{digs}}}{m_{\mathrm{ws}} w_{\mathrm{dm,ws}}} \right) \times 100$$

where

$w_{\mathrm{s,dm}}$	is the analyte content of the sample, expressed as in milligrams per kilogram (mg/kg) of dried material;
ρ_{digs}	is the analyte concentration, expressed in micrograms per litre (µg/l), of the digested sample corrected for the blank test solution;
V_{digs}	is the volume, expressed in millilitres, of the digested sample after dilution;
m_{drs}	is the mass, expressed in milligrams, of dried sample;
m_{ws}	is the mass, expressed in milligrams, of wet sample;
$w_{\mathrm{dm,ws}}$	is the content, expressed as a percentage, of dried material in the wet sample.

Report results for sediments in milligrams per kilogram (mg/kg). For test samples for which no detectable signal can be obtained, report results as less than “the detection limit”.

12 Precision

An interlaboratory trial was performed in 2002 that included synthetic water samples, natural water, wastewater, sediment digest, and dried homogenized lake sediment. All samples were sent out and analysed in duplicate. Results for Fe, Mn and Al were not reported for the sediment samples because the concentration levels were far beyond the optimum working range for the method and very few laboratories reported results. Iron in wastewater, antimony in wastewater and sediment samples and thallium in the synthetic sample at the lower concentration, wastewater and sediment digest were determined by fewer than three laboratories. Therefore, a complete statistical evaluation is not possible (see Table 3).

Table 3 — Performance characteristics of the method, based on an international interlaboratory comparison, March 2002

Element analysed	Sample	n	o	x_{true} µg/l	X µg/l	Recovery %	Repeatability CV %	Reproducibility CV %
Ag	SL	9		0,8	1,00	126	8,2	53,1
	SH	9		7,2	8,13	113	3,6	22,9
	FWL	5	1		0,774		8,2	56,9
	FWH	9			5,92		5,0	33,0
	WW	7	1		3,43		8,8	32,0
	Dig	9			1,00		14,0	69,0
	Sed	4	1		0,172[a]		6,5	27,1
Al	SL	6	2	5	5,85	117	14,2	44,3
	SH	10	2	45	38,6	86	2,4	16,4
	FWL	11			170		6,6	46,2
	FWH	11			193		5,4	44,0
	WW	4	2		147		3,9	40,3
As	SL	17	2	9	9,00	100	2,8	14,1
	SH	19	2	81	77,5	96	2,7	10,5
	FWL	19			8,74		7,4	25,2
	FWH	21			68,6		3,6	17,8
	WW	14	1		11,6		4,0	35,9
	Dig	18	1		74,4		4,2	26,9
	Sed	17	1		16,3 [a]		3,8	26,2
Cd	SL	33	1	0,3	0,303	101	3,5	17,0
	SH	34	2	2,7	2,81	104	1,9	10,7
	FWL	31	2		0,572		2,9	14,9
	FWH	31	3		3,07		2,1	10,4
	WW	27	2		1,00		3,1	27,5
	Dig	29	2		48,7		2,2	14,8
	Sed	27	3		9,53 [a]		3,5	17,0
Co	SL	13		5,5	5,71	104	3,1	8,5
	SH	12	2	49,5	50,6	102	1,0	7,9
	FWL	13			4,23		9,0	14,8
	FWH	13	1		40,5		2,6	10,6
	WW	10			11,6		7,0	32,9
	Dig	11			337		1,6	12,2
	Sed	10			68,0 [a]		1,8	15,4

Table 3 (*continued*)

Element analysed	Sample	n	o	x_{true} µg/l	X µg/l	Recovery %	Repeatability CV %	Reproducibility CV %
Cr	SL	21	3	1,9	1,91	101	7,5	12,4
	SH	24	1	17,1	17,5	102	2,0	7,9
	FWL	23	1		1,95		7,7	24,7
	FWH	23	2		14,0		2,0	7,3
	WW	17	4		3,91		4,2	40,5
	Dig	19			246		3,7	8,7
	Sed	18	3		51,3 [a]		1,3	21,7
Cu	SL	18	1	2,5	2,60	104	8,1	13,2
	SH	19	1	22,5	23,0	102	3,8	5,6
	FWL	19			2,37		6,4	15,4
	FWH	20	1		29,8		2,3	7,2
	WW	11	1		5,08		10,0	30,3
	Dig	10	2		216		2,1	9,0
	Sed	12	1		43,9 [a]		4,0	18,1
Fe	SL	5	1	3	4,43	148	9,0	33,0
	SH	7		27	27,0	100	3,4	13,8
	FWL	7			98,3		2,4	9,9
	FWH	6			116		1,6	11,2
Mn	SL	8		1,5	1,71	114	4,4	30,0
	SH	10		13,5	14,5	108	2,0	15,3
	FWL	8	1		5,47		2,7	22,5
	FWH	10			17,7		3,2	14,6
	WW	5			100		4,3	13,8
Mo	SL	6		4,5	5,69	126	4,6	23,8
	SH	7		40,5	44,3	109	2,8	14,0
	FWL	4			5,76		11,5	13,7
	FWH	6			29,4		3,9	12,7
	WW	5			10,8		5,6	60,2
	Dig	6			12,0		9,5	88,4
	Sed	4			2,84 [a]		2,6	73,7

Table 3 (*continued*)

Element analysed	Sample	n	o	x_{true} µg/l	X µg/l	Recovery %	Repeatability CV %	Reproducibility CV %
Ni	SL	20		6	5,92	99	3,5	15,0
	SH	20		54	53,6	99	2,0	8,8
	FWL	17	1		3,11		11,7	24,0
	FWH	19			33,2		2,5	9,1
	WW	15	1		11,4		4,1	27,5
	Dig	14	2		294		2,4	6,8
	Sed	12	3		58,9 [a]		1,6	7,6
Pb	SL	30	2	5	5,07	101	3,1	12,8
	SH	34	3	45	46,5	103	1,8	8,8
	FWL	32			7,76		8,5	17,2
	FWH	33	1		68,2		2,8	15,0
	WW	25	2		14,6		5,5	36,9
	Dig	29			541		3,1	14,7
	Sed	29	1		104 [a]		3,4	14,5
Sb	SL	5		8	7,39	92	3,3	17,9
	SH	7		72	66,9	93	3,4	13,8
	FWL	5			5,78		4,9	21,2
	FWH	7			52,7		3,1	6,6
Se	SL	10		12	11,9	99	5,7	23,0
	SH	11		108	109	101	3,7	21,9
	FWL	10	1		10,2		5,9	13,4
	FWH	11			85,2		2,9	20,8
	WW	8			16,0		9,8	25,6
	Dig	4	1		4,94		7,7	39,5
	Sed	3	1		0,887 [a]		0,7	21,7
Tl	SH	5	—	36	37,0	103	6,6	19,9
	FWL	3			4,20		3,4	40,6
	FWH	5			27,7		3,0	40,7
	Sed	3			0,928 [a]		6,3	34,2

Table 3 (*continued*)

Element analysed	Sample	n	o	x_{true} µg/l	X µg/l	Recovery %	Repeatability CV %	Reproducibility CV %
V	SL	5		15	15,1	101	1,2	15,9
	SH	5		135	138	102	1,4	12,4
	FWL	3			12,3		8,4	11,1
	FWH	5			83,8		2,3	13,1
	WW	3			50,0		1,1	56,4
	Dig	5			330		1,6	17,3
	Sed	4			63,0 [a]		6,0	19,2
Zn	SL	5	1	0,5	0,579	116	10,8	47,6
	SH	5	1	4,5	3,71	82	2,1	35,9
	FWL	6	1		1,17		8,8	40,3
	FWH	7			5,99		6,5	30,4
	WW	4			120		2,0	7,0
	Dig	3			1373		3,0	25,0
	Sed	4			233 [a]		1,6	23,4

n	is the number of outlier-free individual analytical values;
o	is the number of the outliers;
x_{true}	is the "true" value by convention;
X	is the total mean;
CV	coefficient of variation;
SL	is the synthetic solution at the lower concentration;
SH	is the synthetic solution at the higher concentration;
FWL	is the fresh water at lower concentration;
FWH	is the fresh water at higher concentration;
WW	is the wastewater, digested by the participants;
Dig	is the sediment digested in HNO_3;
Sed	is the sediment sample digested by the participants.

[a] Results for the dried sediment sample in µg/g.

13 Test report

The test report shall give the following information:

a) reference to this International Standard (ISO 15586:2003);

b) complete identification of the sample;

c) information about sample pre-treatment [e.g. preserved by addition of acid (non-filtered), filtered (dissolved) or digested in acid];

d) amount of preservation acid added, if more than 0,5 ml per 100 ml sample;

e) information about digestion method applied;

f) results from water and sediment samples;

g) date of sampling and determination;

h) information about other factors that may have affected the results.

Annex A
(informative)

Preparation of stock solutions, 1 000 mg/l

A.1 General

The following procedures for preparation of stock solutions have been taken from references [1] and [2] in the Bibliography.

All salts should be dried for 1 h at 105 °C, unless otherwise specified.

Amount of metals and metal salts used for preparation of stock solutions are presented in Table A.1.

Table A.1 — Amount of metals and metal salts for preparation of stock solutions

Element	Compound	Formula	Amount g
Ag	Metal	Ag	1,000
Al	Metal	Al	1,000
As	Arsenic trioxide	As_2O_3	1,320
Cd	Metal [a]	Cd	1,000
Co	Metal [a]	Co	1,000
Cr	Chromium trioxide	CrO_3	1,923
Cu	Metal [b]	Cu	1,000
Fe	Metal [b]	Fe	1,000
Mn	Metal	Mn	1,000
Mo	Molybdenum trioxide	MoO_3	1,500
Ni	Metal	Ni	1,000
Pb	Lead nitrate	$Pb(NO_3)_2$	1,599
Sb	Metal powder	Sb	1,000
Se	Selenium dioxide	SeO_2	1,405
Tl	Thallium nitrate	$TlNO_3$	1,303
V	Metal [a]	V	1,000
Zn	Metal [a]	Zn	1,000

[a] Acid cleaned with (1+9) HNO_3.

[b] Acid cleaned with (1+1) HCl.