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Soil quality — Determination of arsenic, antimony and selenium in aqua regia soil extracts with electrothermal or hydride-generation atomic absorption spectrometry

Qualité du sol — Dosage de l'arsenic, de l'antimoine et du sélénium dans des extraits du sol à l'eau régale par spectrométrie d'absorption atomique avec atomisation électrothermique ou génération d'hydrures

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Foreword

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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 20280 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Soil quality — Determination of arsenic, antimony and selenium in aqua regia soil extracts with electrothermal or hydride-generation atomic absorption spectrometry

WARNING — Certain procedures, reagents and apparatus used in this International Standard pose hazards, especially in connection with concentrated acids, toxic solutions of arsenic (As), antimony (Sb) and selenium (Se), and high-pressure gases. Users should ensure that they are familiar with the safety procedures necessary in such situations, and with any legal requirements (including waste disposal). If in any doubt, seek advice from the competent authorities.

1 Scope

This International Standard specifies methods for the determination of arsenic, antimony and selenium, in an aqua regia extract of soil obtained in accordance with ISO 11466, by electrothermal or hydride-generation atomic absorption spectrometry.

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 11464:2006, *Soil quality — Pretreatment of samples for physico-chemical analysis*

ISO 11465:1993, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ISO 11466:1995, *Soil quality — Extraction of trace elements soluble in aqua regia*

3 Principle

Arsenic, antimony and selenium are extracted from soil samples with aqua regia according to ISO 11466. Arsenic, antimony and selenium are determined by electrothermal atomic absorption spectrometry (ETAAS), in which discrete volumes of sample solution are dispensed into a graphite tube. By increasing the temperature of this graphite tube stepwise, the processes of drying, thermal decomposition of the matrix and thermal dissociation into free atoms occur. The resulting absorption signal should (under optimum conditions) be a sharp symmetrical peak proportional to the element concentration in solution.

Alternatively, arsenic, antimony and selenium are determined by the hydride-generation technique (HGAAS). Arsenic and antimony are first pre-reduced in the aqua regia extract by a mixture of ascorbic acid and potassium iodide. Selenium is pre-reduced by hydrochloric acid at an elevated temperature. After that, the hydride formation occurs by reaction with a sodium borohydride solution. The hydrides are carried from the solution by an argon stream into a heated quartz cell and decomposed at 900 °C and then the atom concentration for arsenic and antimony is measured by atomic absorption spectrometry. There are several commercial systems available where the reaction of hydride formation occurs continuously (continuous flow or

flow injection systems) or stepwise (batch systems). All these techniques can be used, but adaptation of the working steps and reagent concentrations according to the advice of the manufacturer may be necessary. Refer to the manufacturer's recommendation for wavelengths and spectral band widths or see Table 1.

Table 1 — Measurement conditions for arsenic, antimony and selenium

Element	Wavelength nm	Spectral band width nm
Arsenic	193,7	0,7
Antimony	217,6	1,0
Selenium	196,0	1,0

4 Reagents

All reagents shall be of recognised analytical grade. Use demineralised water or water distilled from an all-glass apparatus conforming to Grade 2 of ISO 3696. The water used for blank determinations and for preparing reagents and standard solutions shall have element concentrations that are negligible compared with the lowest concentration to be determined in the sample solutions.

4.1 Hydrochloric acid, w(HCl) = 37 %, ρ(HCl) ≈ 1,2 g/ml.

The same batch of hydrochloric acid shall be used throughout the procedure.

4.2 Hydrochloric acid, diluted (1 + 9).

Pour 500 ml of water into a 1 000 ml volumetric flask. Add 100 ml of hydrochloric acid (4.1) with caution, mix and fill to the mark with water.

4.3 Nitric acid, $w(HNO_3)$ = 65 %, $\rho(HNO_3)$ ≈ 1,4 g/ml.

The same batch of nitric acid shall be used throughout the procedure.

4.4 Nitric acid, $c(HNO_3)$ = 0,5 mol/l.

Pour 500 ml of water into a 1 000 ml volumetric flask. Add 22 ml of nitric acid (4.3) with caution, mix and fill to the mark with water.

4.5 Aqua regia solution, diluted (1 + 9).

Pour 500 ml of water into a 1 000 ml volumetric flask. Add 75 ml of hydrochloric acid (4.1) and 25 ml of nitric acid (4.3) with caution, mix and fill to the mark with water.

4.6 Palladium/magnesium nitrate modifier solution.

Two sources of modifier solutions can be used:

— commercially available modifier solutions;

— modifier element solutions prepared in the laboratory from pure palladium (e.g. powder) or from stochiometrically defined and dried salts.

Dissolve 0,30 g of palladium nitrate [$Pd(NO_3)_2$] and 0,36 g of magnesium nitrate [$Mg(NO_3)_2 \cdot 6\,H_2O$] in a 100 ml volumetric flask, fill to the mark with 0,5 mol/l nitric acid (4.4) and mix.

Alternatively, prepare the palladium/magnesium nitrate modifier solution as follows: Dissolve, in a 250 ml beaker, 0,14 g of palladium powder in 3,5 ml of nitric acid (4.3) and add 10 µl of hydrochloric acid (4.1). Evaporate the solution to near dryness on a water bath or hot plate, then add 0,36 g of magnesium nitrate [$Mg(NO_3)_2 \cdot 6\ H_2O$]. Dissolve this solid residue in 50 ml of nitric acid (4.4), transfer the solution into a 100 ml volumetric flask, fill to the mark with nitric acid (4.4) and mix. 10 µl of this solution are equal to 14 µg of Pd and 36 µg of $Mg(NO_3)_2$.

NOTE The recommendations of instrument manufacturers may propose different modifier-solution concentrations. Also, recommendations of appropriate modifier-to-analyte ratios may be given depending on the furnace design.

4.7 Pre-reduction solutions, ascorbic acid and potassium iodide.

Dissolve 10 g of potassium iodide (KI) and 10 g of ascorbic acid ($C_6H_8O_6$) in 200 ml of water. This solution shall be prepared on the day of use.

4.8 Sodium borohydride solution.

The composition of this solution depends on the hydride-generation system used. Generally, the concentration of sodium borohydride ($NaBH_4$) varies from 0,2 g/l to 10 g/l, and the concentration of sodium hydroxide from 0,5 g/l to 5 g/l. Refer to the manufacturer's instruction for further information.

Dissolve an appropriate quantity of sodium hydroxide in water, add a quantity of sodium borohydride, wait until complete dissolution, filter the solution through a membrane filter of 0,45 µm porosity into a 1 000 ml volumetric flask, fill to the mark with water and mix. This solution should be prepared freshly on the day of use.

4.9 Preparation of stock and standard solutions of individual elements.

Two sources of stock solutions are available:

— commercially available stock solutions;

— stock solutions prepared in the laboratory from pure elements or stochiometrically defined dried salts or oxides.

NOTE Commercially available stock solutions have the advantage that they remove the need to handle toxic metals. However, special care needs to be taken that these solutions are supplied with a certified composition from a reputable source and are checked on a regular basis.

WARNING — Arsenic, antimony and selenium are highly toxic. Take appropriate measures to avoid ingestion. Care should be taken in disposal of such solutions.

4.10 Arsenic, stock solution corresponding to 1 000 mg/l of arsenic.

4.11 Arsenic, standard solution corresponding to 100 mg/l of arsenic.

Pipette 10,0 ml of the arsenic stock solution (4.10) into a 100 ml volumetric flask, add 1 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.12 Arsenic, standard solution corresponding to 1 mg/l of arsenic.

Pipette 1,00 ml of the 100 mg/l arsenic standard solution (4.11) into a 100 ml volumetric flask, add 2 ml of nitric acid (4.3), fill to the mark with water and mix well. Prepare this solution at least weekly.

4.13 Antimony, stock solution corresponding to 1 000 mg/l of antimony.

4.14 Antimony, standard solution corresponding to 100 mg/l of antimony.

Pipette 10,0 ml of the antimony stock solution (4.13) into a 100 ml volumetric flask, add 5 ml of nitric acid (4.3) and 10 ml of hydrochloric acid (4.1), fill to the mark with water and mix well.

4.15 Antimony, standard solution corresponding to 1 mg/l of antimony.

Pipette 1,00 ml of the 100 mg/l antimony standard solution (4.14) into a 100 ml volumetric flask, add 2 ml of nitric acid (4.3) and 2 ml hydrochloric acid (4.1), fill to the mark with water and mix well. Prepare this solution at least weekly.

4.16 Selenium, stock solution corresponding to 1 000 mg/l of selenium.

4.17 Selenium, standard solution corresponding to 100 mg/l of selenium.

Pipette 10,0 ml of the selenium stock solution (4.16) into a 100 ml volumetric flask, add 1 ml of nitric acid (4.3), fill to the mark with water and mix well.

4.18 Selenium, standard solution corresponding to 1 mg/l of selenium.

Pipette 1,00 ml of the 100 mg/l selenium standard solution (4.17) into a 100 ml volumetric flask, add 2 ml of nitric acid (4.3), fill to the mark with water and mix well. Prepare this solution at least weekly.

4.19 1,10 Phenanthrolin-monohydrate solution.

Dissolve 10 g of 1,10 phenanthrolin-monohydrate ($C_{12}H_8N_2 \cdot H_20$) in 100 ml of water. The solution shall be prepared on the day of use.

5 Apparatus

5.1 General

Usual laboratory apparatus should be used.

Quartz vessels should be the preferred material for the whole procedure (especially if lower calibration ranges (0,1 µg/l to 1 µg/l) are to be used for measurement).

NOTE Cleaning of glassware: All glassware used must be cleaned carefully before use, e.g. by immersion in $\varphi(HNO_3) \approx 50$ ml/l aqueous nitric acid solution for a minimum of 6 h, followed by rinsing with water before use. It can be helpful to keep a separate set of glassware exclusively for these determinations.

5.2 Water bath.

5.3 Atomic absorption spectrometer, equipped with a hollow cathode of the element or, preferably, a high-energy discharge lamp (which gives a greater and more stable light intensity) operated at a current recommended by the lamp and instrument manufacturer, an automatic background-correction device, preferably Zeeman correction for ETAAS-measurement, and a computerised readout.

5.4 Electrothermal atomiser, equipped with an automated sample introduction system (sample dispenser), which should be adaptable to the atomic absorption spectrometer (5.3).

5.5 Hydride-generation system, commercially available, where the reaction occurs continuously (continuous flow or flow injection systems) or stepwise (batch systems). It should be adaptable to the atomic absorption spectrometer (5.3). Heat the quartz cell at least to 900 °C for complete dissociation of metal hydrides.

WARNING — It is essential that the manufacturer's safety recommendations are strictly observed. Metal hydrides are highly toxic. Care must be taken not to inhale these gases.

NOTE When using an automated hydride-generation system, where the reaction occurs continuously (continuous flow or flow injection systems), the concentration of sodium borohydride solution, reaction time and the gas-liquid separator configuration must be optimised due to the slow reaction kinetics of this reducing system. Severe matrix interferences are possible.

6 Procedure

6.1 Test portion

Grind a representative portion of air-dried sample (prepared in accordance with ISO 11464) until it passes entirely through the 150 µm aperture sieve to give a sub-sample of approximately 20 g. Use a separate portion of that sub-sample to determine the dry matter in accordance with ISO 11465.

6.2 Aqua regia extraction for arsenic, antimony and selenium

6.2.1 Test portion solution

Extract the soil with aqua regia in accordance with ISO 11466. If the element mass fractions of soil samples are low, carry out another dilution to match the calibration range. For the ETAAS technique, a dilution (1 + 9) is described as an example.

6.2.2 Test portion solution diluted (1 + 9)

Dilute 10,00 ml of test portion solution (6.2.1) in a 100 ml volumetric flask with water, fill to the mark and mix.

6.3 Blank test

6.3.1 Blank test solution

Carry out a blank test at the same time as the determination and following the same extraction procedure with aqua regia according to ISO 11466, using the same quantities of all the reagents for the determination but omitting the test portion.

6.3.2 Blank test solution diluted (1 + 9)

Dilute 10,00 ml of blank test solution (6.3.1) in a 100 ml volumetric flask with water, fill to the mark and mix.

7 Method A — Electrothermal atomic absorption spectrometry: Preparation of calibration solutions and measurement

7.1 General

The standard solutions shall be prepared before each batch of determinations.

7.2 Calibration solutions for arsenic

Pipette 0 ml, 2,00 ml, 4,00 ml and 6,00 ml of the arsenic standard solution of 1 mg/l (4.12) into a series of 100 ml volumetric flasks, dilute to the mark with aqua regia solution (1 + 9) (4.5) and mix well. These solutions correspond to arsenic concentrations of 0 µg/l, 20 µg/l, 40 µg/l and 60 µg/l, respectively.

7.3 Calibration solutions for antimony

Pipette 0 ml, 5,00 ml, 10,00 ml and 15,00 ml of the antimony 1 mg/l standard solution (4.15) into a series of 100 ml volumetric flasks, dilute to the mark with aqua regia solution (1 + 9) (4.5) and mix well. These solutions correspond to antimony concentrations of 0 µg/l, 50 µg/l, 100 µg/l and 150 µg/l, respectively.

7.4 Calibration solutions for selenium

Pipette 0 ml, 2,00 ml, 4,00 ml and 6,00 ml of the selenium 1 mg/l standard solution (4.18) into a series of 100 ml volumetric flasks, dilute to the mark with aqua regia solution (1 + 9) (4.5) and mix well. These solutions correspond to selenium concentrations of 0 µg/l, 20 µg/l, 40 µg/l and 60 µg/l, respectively.

7.5 Calibration and determination with ETAAS measurement

7.5.1 General

Set up the instrument and align the electrothermal atomiser according to the manufacturer's instructions. Use of background correction is essential.

Determine the optimum electrothermal atomiser parameters for the particular type of atomiser and sample size as recommended by the instrument manufacturer or normal laboratory practice (Table 2). The temperatures given are only approximate values. The temperature programme should be optimised with the instrument used. Refer to the manufacturer's recommendation or see Table 2.

Table 2 — Recommended ETAAS conditions

	As	Sb	Se
Wavelength in nm	193,7	217,6	196,0
Graphite furnace	Pyrolitic coated tube with platform		
Background correction	Zeeman	Zeeman	Zeeman
Matrix modifier	Palladium/magnesium nitrate (4.6)		
Drying temperature in °C	90/130	90/130	90/130
Pretreatment temperature in °C	1 150	1 050	1 200
Atomising temperature in °C	2 2 00	1 900	2 400
Clean-up temperature in °C	2 500	2 500	2 500

NOTE For ETAAS, the application of deuterium background correction systems is limited. The presence of a structured spectral background can occur. The application of a Zeeman background correction is preferred to correct this interference. To increase the analyte-to-background signal ratio, the use of a graphite tube with a pyrolitic platform, together with palladium and magnesium nitrate as matrix modifiers, is recommended.

7.5.2 Measurement of calibration and test solutions, ETAAS

Ensure that the blank test solutions (6.3.2), the calibration solutions (7.2, 7.3 or 7.4) and the test portion solutions (6.2.2) have approximately the same temperature by storing them for a sufficient time in the same room. Zero the instrument and set the baseline. Check the zero stability and lack of spectral interferences within the atomisation system by running the pre-set heating programme for blank firing of the graphite atomiser. Repeat to ensure baseline stability.

Using an auto sampler (see 5.4), inject a fixed volume of modifier solution (4.6) and measurement solution and atomise the calibration blank (7.2, 7.3 or 7.4), calibration solution (7.2, 7.3 or 7.4), blank test solution (6.3.2) and test portion solutions (6.2.2) in order of increasing instrument response. If the peak height or peak area of the test portion exceeds the value of the highest calibration solution, a diluted solution of the test portion solution shall be used.

Atomise each solution at least twice and, if the repeatability is acceptable, average the readings. Check the instrument for memory effects, especially at high analyte levels, by running a blank firing programme between determinations. Reset the baseline to zero if necessary.

For each type of soil, it is mandatory to determine the corresponding extract solution, at least once, by means of the standard addition method. If the analytical results according to the standard addition method and the calibration curve method are equal, the calibration curve method can be applied. If the analytical results are different, matrix interferences are likely and the standard addition method shall be used for each corresponding soil extract solution.

Alternatively, it is possible to use the matrix check or quality control spike option.

The calibration shall be established from standard solutions for arsenic, antimony and selenium which give peak absorbances lower than the maximum absorbance specified for that wavelength and element.

8 Method B — Hydride-generation atomic absorption spectrometry: Preparation of calibration solutions and measurement

8.1 Pre-reduction and calibration for the determination of arsenic

Pipette 0 ml, 2,00 ml, 5,00 ml, 7,50 ml, 12,5 ml and 20,0 ml of arsenic standard solution of 1 mg/l (4.12) into a series of 50 ml volumetric flasks and fill up to the mark with hydrochloric acid (4.2). Add 1 ml of these solutions, 2,5 ml of pre-reduction solution (4.7) and 2,5 ml of hydrochloric acid (4.1) to a series of 25 ml volumetric flasks and mix well. Allow to stand at room temperature for 2 h (pre-reduction does not occur immediately) and fill up with water prior to analysis. These solutions correspond to concentrations of 0 µg/l, 1,6 µg/l, 4,0 µg/l, 6,0 µg/l, 10 µg/l and 16 µg/l of arsenic.

Pipette 1,00 ml of blank test solution (6.3.1) and test portion solution (6.2.1) into a series of 25 ml volumetric flasks and add 2,5 ml of hydrochloric acid (4.1) and 2,5 ml of pre-reduction solution (4.7). Mix well, allow to stand at room temperature for 1 h and fill up to the mark with water. Allow to stand at room temperature for another hour prior to analysis. The solutions are diluted 25 times by this pre-reduction step.

8.2 Pre-reduction and calibration for the determination of antimony

Pipette 0 ml, 2,50 ml, 5,00 ml, 10,0 ml and 20,0 ml of antimony standard solution of 1 mg/l (4.15) into a series of 50 ml volumetric flasks and fill up to the mark with hydrochloric acid (4.2). Add 2,5 ml of these solutions, 2,5 ml of pre-reduction solution (4.7) and 2,5 ml of hydrochloric acid (4.1) to a series of 25 ml volumetric flasks and mix well. Allow to stand at room temperature for 2 h (pre-reduction does not occur immediately) and fill up with water prior to analysis. These solutions correspond to concentrations of 0 µg/l, 5,0 µg/l, 10 µg/l, 20 µg/l and 40 µg/l of antimony.

Pipette 2,50 ml of blank test solution (6.3.1) and test portion solution (6.2.1) into a series of 25 ml volumetric flasks and add 2,5 ml of hydrochloric acid (4.1) and 2,5 ml of pre-reduction solution (4.7). Mix well, allow to stand at room temperature for 1 h and fill up to the mark with water. Allow to stand at room temperature for another hour prior to analysis. The solutions are diluted 10 times in this pre-reduction step.

8.3 Pre-reduction and calibration for the determination of selenium

Pipette 0 ml, 0,50 ml, 1,00 ml, 2,50 ml and 5,00 ml of selenium standard solution of 1 mg/l (4.18) into a series of 100 ml volumetric flasks and fill up to the mark with hydrochloric acid (4.2). Add 5 ml of these solutions, 2,5 ml of hydrochloric acid (4.1) and 2,5 ml of water to a series of 25 ml volumetric flasks and mix well. Put the volumetric flasks without a stopper into a water bath (5.2) at 70 °C for 1 h (pre-reduction does not occur immediately). Remove the volumetric flasks from the water bath, leave them to cool down to room temperature and fill up to the mark with water prior to analysis. These solutions correspond to concentrations of 0 µg/l, 1,0 µg/l, 2,0 µg/l, 5,0 µg/l and 10 µg/l of selenium.

Pipette 5,00 ml of blank test solution (6.3.1) and test portion solution (6.2.1) into a series of 25 ml volumetric flasks and add 2,5 ml of hydrochloric acid (4.1) and 2,5 ml of water. Mix well and put the volumetric flasks without a stopper into a water bath (5.2) at 70 °C for 1 h (pre-reduction does not occur immediately). Remove the volumetric flasks from the water bath, leave them to cool down to room temperature and fill up to the mark with water prior to analysis. The solutions are diluted 5 times in this pre-reduction step.

If selenium contents in soil are below 1 mg/kg, the recovery rate should be checked by addition of known amounts of selenium.

8.4 Measurement of calibration and test solutions by hydride-generation atomic absorption spectrometry

Set up the instrument measurement parameters according to the manufacturer's instructions. With HGAAS the use of a background correction system is essential. Select wavelengths of 193,7 nm for arsenic, 217,6 nm for antimony and 196,0 nm for selenium. Set up the hydride-generation system using sodium borohydride ($NaBH_4$) solution (4.8) according to the manufacturer's instructions.

Once the hydride-generation system is stabilised, calibrate the system with fixed volumes (e.g. 10 ml for a batch system) of blank calibration solution and calibration solutions for arsenic (8.1), for antimony (8.2) or for selenium (8.3). Then measure the blank test and test portion solutions.

For each type of soil, it is mandatory to determine the corresponding extract solution, at least once, by means of the standard addition method. If the analytical results according to the standard addition method and the calibration curve method are equal, the calibration curve method can be applied. If the analytical results are different, matrix interferences are likely and the standard addition method shall be used for each corresponding soil extract solution.

Alternatively, it is possible to use the matrix check or quality control spike option.

The calibration shall be established from standard solutions for arsenic, antimony and selenium which give peak absorbances lower than the maximum absorbance specified for that wavelength and element.

9 Plotting the calibration graph

The software of modern instruments will usually plot a graph having the element concentrations of the calibration solutions (from which the blank calibration readings have been subtracted), in milligrams per litre, as the abscissa and the corresponding values of the peak height (or peak area) as the ordinate. If this facility is not available, then prepare such a graph using other software or by hand.

10 Calculation

10.1 General

By reference to the calibration graph, the software calculates the concentrations of the elements corresponding to the absorbances of the test portion and the blank test solution. Calculate the mass fraction (w) of the element (E), expressed in milligrams per kilogram of dry matter, of the sample using Equation (1):

$$w(\mathrm{E}) = \frac{(\rho_1 - \rho_0)}{m} \cdot f \cdot \frac{V}{1000} \cdot C \qquad (1)$$

where

$w(\mathrm{E})$ is the mass fraction of the element in the sample, in milligrams per kilogram of dry matter;

ρ_1 is the element concentration, in micrograms per litre, corresponding to the absorbance of the test portion (6.2.1);

ρ_0 is the element concentration, in micrograms per litre, corresponding to the absorbance of the blank test solution (6.3.1);

f is the dilution factor of the test portion [when the test portion (6.2.1) is diluted];

V is the volume, in millilitres, of the test portion taken for the analysis (100 ml according to ISO 11466);

m is the mass of test sample taken, in grams;

C is the correction factor for the dry soil sample: $C = 100/w_{dm}$;

w_{dm} is the dry matter content of the soil, expressed as a percentage according to ISO 11465.

10.2 Calculation according to the method of standard additions

The software of a modern instrument may calculate the content of the element of interest directly. Alternatively, external software may be used. If these facilities are not available, plot a graph with the absorbance values on the ordinate and the element concentrations on the abscissa. The element content of the soil samples is calculated from the value of the negative intercept on the abscissa, taking into account the blank value and any dilution of the sample. Be sure that the analyte portions added do not exceed the linear region of the calibration curve.

11 Expression of results

Values shall be rounded to three significant figures.

EXAMPLE w(As) = 0,15 mg/kg

w(As) = 1,45 mg/kg

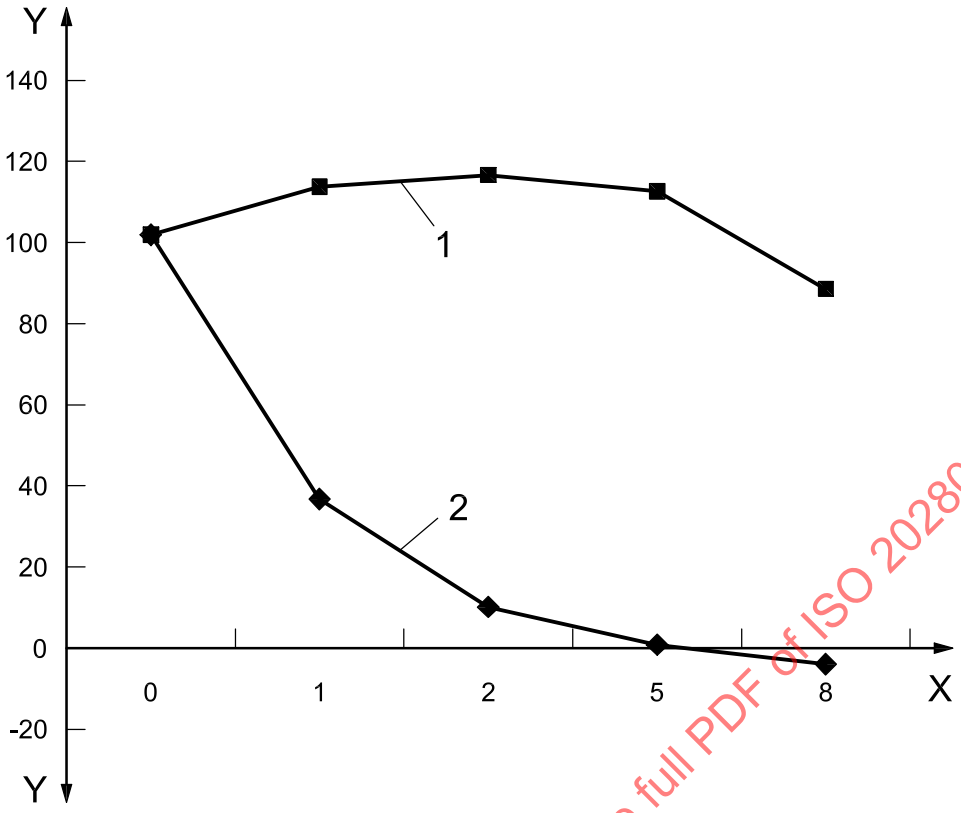
w(As) = 12,5 mg/kg

12 Interferences

Potential background absorption interferences due to high salt concentrations are eliminated by the instrumental background correction system. Background signals can be reduced with appropriate matrix modifiers and application of the platform technique, together with carefully designed temperature programmes.

Because of the high sensitivity of electrothermal atomic absorption, stringent precautions shall be taken to clean all glassware and avoid contamination of sample, standard and calibration solutions by foreign material and dust from the laboratory atmosphere.

However, during hydride formation, other elements are reduced to the elemental state (i.e. Cu, Ni, Fe, Pb) and can compete with the determined element reduction if they are at high concentration levels. In such cases, the standard addition method is more suitable than the direct calibration method. If the concentration of copper in the measuring solution exceeds 1 mg/l, the signal for selenium may be significantly reduced. This can be eliminated by adding 0,5 ml of a 1,10 phenanthrolin-monohydrate solution (4.19*)* to the measuring solution (see Figure 1).



Key

1 phenanthrolin added
2 without phenanthrolin

X copper (Cu) [mg/l]
Y selenium (Se) recovery [%]

Figure 1 — Recovery rate of a 5 µg/l selenium concentration at various copper concentrations with and without the addition of 1,10 phenanthrolin

13 Precision

An interlaboratory comparison (VDLUFA, 1997) yielded the data given in Table 3. Another one, conducted by the Federal Institute of Materials Research and Testing, BAM, Germany, in 2003, yielded the data given in Tables 4 to 9. Repeatability and reproducibility were calculated according to ISO 5725-2.

Table 3 — Precision data for the determination of arsenic, antimony and selenium in different soils using the hydride generation atomic absorption technique (pre-reduction according to 8.1 to 8.3)

Element	Sample	N_{lab}	w(ME) mg/kg	CV_r %	CV_R %	s_r mg/kg	s_R mg/kg
As	Soil 1	11	7,89	1,77	5,87	0,139	0,463
As	Soil 2	12	10,3	2,80	6,86	0,289	0,709
As	Soil 3	10	74,0	1,88	7,14	1,39	5,29
Sb	Soil 1	11	0,41	5,04	14,8	0,021	0,060
Sb	Soil 2	12	0,45	3,88	14,2	0,017	0,064
Sb	Soil 3	10	219	2,00	17,0	4,39	37,3
Se	Soil 1	10	0,17	6,51	14,5	0,011	0,024
Se	Soil 2	10	0,32	4,32	9,09	0,014	0,029
Se	Soil 3	11	0,67	4,36	22,0	0,029	0,146

N_{lab} is the number of accepted laboratories.
w(ME) is the mean metal content.
s_R is the reproducibility standard deviation.
s_r is the repeatability standard deviation.
CV_R is the relative-reproducibility standard deviation.
CV_r is the relative-repeatability standard deviation.

Tables 4 to 9 show precision data of an international interlaboratory comparison on arsenic, antimony and selenium determination in aqua regia extracts of soils using ETAAS and HGAAS. Calculations are according to ISO 5725-2 (3 replicates).

Table 4 — Arsenic — Electrothermal atomic absorption spectrometry

Sample	N_{lab}	N_{rej}	N_{res}	w(As) mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %	R mg/kg	r mg/kg
Soil 1	5	0	13	14,97	1,624	10,85	0,40	2,70	4,50	1,12
Soil 2	5	0	13	126,41	7,351	5,82	2,00	1,58	20,36	5,54
Soil 3	5	0	13	628,5	41,56	6,61	16,39	2,61	115,11	45,39

N_{lab} is the number of accepted laboratories.
N_{rej} is the number of laboratories not accepted.
N_{res} is the number of accepted results.
w(As) is the mean arsenic content.
s_R is the reproducibility standard deviation.
CV_R is the relative-reproducibility standard deviation.
s_r is the repeatability standard deviation.
CV_r is the relative-repeatability standard deviation.
R is the reproducibility limit.
r is the repeatability limit.

Table 5 — Arsenic — Hydride-generation atomic absorption spectrometry

Sample	N_{lab}	N_{rej}	N_{res}	w(Sb) mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %	R mg/kg	r mg/kg
Soil 1	10	0	28	11,59	1,05	9,06	0,45	3,88	2,91	1,25
Soil 2	8	1	22	120,2	14,29	11,89	4,83	4,02	39,59	13,38
Soil 3	9	1	25	614,6	43,46	7,07	22,58	3,67	120,38	62,55

N_{lab} is the number of accepted laboratories.
N_{rej} is the number of laboratories not accepted.
N_{res} is the number of accepted results.
w(As) is the mean arsenic content.
s_R is the reproducibility standard deviation.
CV_R is the relative-reproducibility standard deviation.
s_r is the repeatability standard deviation.
CV_r is the relative-repeatability standard deviation.
R is the reproducibility limit.
r is the repeatability limit.

Table 6 — Antimony — Electrothermal atomic absorption spectrometry

Sample	N_{lab}	N_{rej}	N_{res}	w(Sb) mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %	R mg/kg	r mg/kg
Soil 1	5	0	15	1,29	0,215	16,63	0,067	5,21	0,60	0,19
Soil 2	5	0	15	10,55	1,61	15,29	0,36	3,38	4,47	0,99
Soil 3	5	0	15	38,4	2,43	6,33	0,71	1,86	6,73	1,98

N_{lab} is the number of accepted laboratories.
N_{rej} is the number of laboratories not accepted.
N_{res} is the number of accepted results.
w(Sb) is the mean antimony content.
s_R is the reproducibility standard deviation.
CV_R is the relative-reproducibility standard deviation.
s_r is the repeatability standard deviation.
CV_r is the relative-repeatability standard deviation.
R is the reproducibility limit.
r is the repeatability limit.