Compendium for sampling and analysis in execution of the Materials Decree and the Soil Decree

Antimony, arsenic and selenium with hydride – atomic absorption spectrometry (Hydride-AAS)

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CMA/2/I/B.6

Contents

1 SCOPE

The method is new and describes a procedure for the determination of arsenic, antimony and selenium including the organically bound forms. The method is applicable for ground water, digests and eluates.
Higher concentrations can be measured by a suitable dilution of the water sample.

2 PRINCIPLE

The method is based on the atomic absorption measurement of arsenic, antimony and selenium generated by the thermal decomposition of arsenic(III)hydride, antimony(III)hydride and selenium(IV)hydride. Under the conditions of this method, only As(III), Sb(III) and Se(IV) are quantitatively converted to the hydride. To avoid errors in determination, other oxidation states of the relevant elements need to be converted to the oxidation states as mentioned above. As(III), Sb(III) and Se(IV) are reduced to gaseous hydride (AsH_3, SbH_3, SeH_2) by reaction with tetrahydroborate in a hydrochloric acid medium.

The absorbance of arsenic is determined at 193.7 nm, antimony at 217.6 nm and selenium at 196.0 nm.

> Note: As an equivalent determination technique (after pre-reduction and hydride generation) the ICP-AES technique may be used (see CMA/2/I/B.1) or atomic fluorescence spectrometry (AFS).

3 NOTES

- For the preservation and treatment of water samples refer to CMA/1/B.
- The samples are collected in polyethylene or borosilicate glass containers that are first cleaned with nitric acid (10% v/v) and rinsed with ultrapure water.
- Most organic materials interfere with the determination of the different analytes. They shall be removed prior to the analysis by a suitable digestion method.
- Special precautions should be taken when disposing the sodium borohydride solution. To prevent possible explosions, the remainder should be broken down with an excess of sulphuric acid before disposal in a suitable way.
- Serious contamination problems may occur when taking samples and while storing these samples. This may be caused by insufficient cleaning of the containers, loss of metals due to adsorption and/or precipitation in the sampling containers attributed to insufficient acidification of the sample solutions.
- Only use containers and a filtration system that has been rinsed with acid and ultrapure water.
- Metal salts and standard solutions of metals
    - Many metal salts are very toxic.
    - Carry out operations in a fume hood.
    - Wearing gloves and safety goggles is strongly recommended.
- Acids
    - Acids are corrosive and harmful
    - Always wear gloves and safety goggles when handling acids
    - Work in the fume hood with concentrated acids.

4 EQUIPMENT AND MATERIAL

4.1 EQUIPMENT

Atomic absorption spectrometer fitted with a hydride system, and a suitable radiation source for the determination of arsenic, antimony and selenium, for example electrodeless discharge lamp or a hollow cathode lamp with a background correction facility.

4.2 GLASS MATERIAL

4.2.1 All glass material shall be rinsed immediately before use with hot, dilute nitric acid (10% v/v) and with ultrapure water.
4.2.2 Digestion flasks, temperature resistant and suitable for containing the sample-acid mixture
4.2.3 50 or 100 ml volumetric flasks
4.2.4 Reflux condenser
4.2.5 Absorbers, to capture volatile components in case of open digestion, they are filled with dilute nitric acid or dilute aqua regia
4.2.6 Boiling stones or rough glass beads
4.2.7 Electric heater

4.3 GAS SUPPLY

Argon or nitrogen

5 REAGENTS AND SOLUTIONS

The reagents used have an ‘analytical quality’ purity.

Other standard concentrations and solutions may be applied as long as they are suitable for this application.

The analyte content in the water and the reagents shall be negligible, compared with the lowest concentration to be determined.

5.1 Ultrapure water: (electrical conductivity less than 0.1 mS m-1, equivalent to a resistance greater than 0.01 MΩ m at 25°C). It is recommended to use water from a water purification system that supplies ultrapure water with a resistance greater than 0.18 MΩ m (usually expressed by suppliers as 18 MΩ cm).
5.2 Hydrochloric acid (HCl) d= 1.15 g/ml
5.3 Nitric acid (HNO_3) d= 1.4 g/ml
5.4 Sodium hydroxide (NaOH)
5.5 Sodium tetrahydroborate solution

Dissolve 1 g of sodium hydroxide in about 20 ml of ultrapure water. Add 3 g of sodium tetrahydroborate ($NaBH_4$) and dilute to 100 ml with ultrapure water.
Prepare the solution on the day of use.

Note: for flow-through systems, it is recommended to follow the manufacturer's instructions. A solution containing 0.5% of sodium tetrahydroborate and 0.5% of sodium hydroxide is suitable. This solution is stable for at least a week.

5.6 Potassium iodide – ascorbic acid solution
Dissolve 5 g of potassium iodide (KI) and 5 g of L(+) ascorbic acid ($C_6H_8O_6$) in 100 ml of ultrapure water.
Prepare the solution on the day of use.

Note: The use of ascorbic acid can be omitted if a 20% solution of potassium iodide is used.

5.7 Arsenic stock solution: 1000 mg/l
Place 1.320 g arsenic(III) oxide (As_2O_3) in a 1000 ml volumetric flask. Add 2 g of sodium hydroxide and dissolve in a small quantity of ultrapure water. Dilute to volume with ultrapure water.
This solution is stable for at least 1 year.

Arsenic stock solutions are commercially available. If the stock solution contains As(V), the standard solution shall be treated in the same way as a sample for the reduction step.

5.8 Antimony stock solution: 1000 mg/l
Dissolve 2.743 g of potassium antimony tartrate ($K(SbO)C_4H_4O_6.1/2H_2O$, dried for 2 hours at 105°C) in approximately 100 ml of hydrochloric acid. Transfer the solution into a 1000 ml volumetric flask and dilute with ultrapure water.
This solution has a limited shelf life.

Antimony stock solutions are commercially available. If the stock solution contains Sb(V), the standard solution shall be treated in the same way as a sample for the reduction step.

5.9 Selenium stock solution: 1000 mg/l
Place 1.4053 g selenium(IV)dioxide in a 1000 ml volumetric flask. Add 2 g of sodium hydroxide and dissolve in a small quantity of ultrapure water. Dilute to volume with ultrapure water.

Selenium stock solutions are commercially available. If the stock solution contains Se(VI), the standard solution shall be treated in the same way as a sample for the reduction step.

5.10 Arsenic standard solution 1: 10 mg/l As
Pipette 10 ml of arsenic stock solution into a 1000 ml volumetric flask. Add 20 ml of hydrochloric acid and dilute to volume with ultrapure water. This solution is stable for about 1 month.

If a stock solution of arsenic(V) is used, arsenic(V) shall be reduced to arsenic(III) before diluting to 1000 ml.

5.11 Arsenic standard solution 2: 0.1 mg/l As
Pipette 10 ml of arsenic standard solution 1 into a 1000 ml volumetric flask. Add 20 ml of hydrochloric acid and dilute to volume with ultrapure water. Prepare the solution on the day of use.

5.12 Antimony standard solution 1: 10 mg/l Sb
Pipette 10 ml of antimony stock solution into a 1000 ml volumetric flask. Add 20 ml of hydrochloric acid and dilute to volume with ultrapure water. This solution has a limited shelf life.

5.13 Antimony standard solution 2: 0.1 mg/l Sb
Pipette 10 ml of antimony standard solution 1 into a of 1000 ml volumetric flask. Add 20 ml of hydrochloric acid and dilute to volume with ultrapure water.
Prepare the solution on the day of use.

5.14 Selenium standard solution 1: 10 mg/l Se
Pipette 10 ml of selenium stock solution into a 1000 ml volumetric flask. Add 20 ml of hydrochloric acid and dilute to volume with ultrapure water.
This solution is stable for approximately 1 week.

5.15 Selenium standard solution 2: 0.1 mg/l Se
Pipette 10 ml of selenium standard solution 1 into a 1000 ml volumetric flask. Add 20 ml of hydrochloric acid and dilute to volume with ultrapure water.
This solution is stable for approximately 1 week.

5.16 Independent standard solutions
It is recommended to prepare or buy a stock solution of arsenic, antimony and selenium which contains the relevant analyte in the highest oxidation state. From these stock solutions suitable standard solutions are prepared to control both the digestion and measurement process in order to determine the pre-reduction yield and to control all steps.

5.17 Antifoaming agent, for example n-dodecane ($C_{12}H_{26}$)

6 PROCEDURE

Various procedures are described in the standard methods to carry out the aqua regia digestion and the pre-reduction. The method described below is based on the ISO and the NEN standard methods.
Other digestion methods with aqua regia are described in CMA/2/I/A.6.1.
Other pre-reduction methods can be used if equivalence with the method below is demonstrated.

6.1 AQUA REGIA DIGESTION IN AN OPEN SYSTEM

Add a test portion of about 50 ml ± 0.1 ml sample to the digestion vessel.

Add 12.0 ml ± 0.2 ml of hydrochloric acid followed by 4.0 ml ± 0.2 ml of nitric acid. The boiling point of this mixture is equal to 103 °C at 101.3 kPa.

The volume ratio sample to aqua regia is equal to approximately three, but a volume ratio up to four is allowed. The amount of sample, and as a result also the amount of acid, can be reduced, if necessary.

If excessive foaming occurs, add one or more drops of antifoaming agent (5.17).

Swirl and allow the mixture to stand until any visible reaction has stopped.

> *Note*: If suspended solids make it impossible to deliver a representative test portion of a known volume, deliver the test portion otherwise, for instance by weighing. Calculate the volume from the determination of its mass, possibly corrected for the mass and density of solids..

Connect the digestion vessel to the reflux condenser and connect the absorber.

Place everything in the temperature-controlled heating apparatus and increase the temperature to boiling point.

Maintain this temperature for at least 2.5 hours.

If a selenium determination should be carried out, go to paragraph 6.2.

If only antimony and arsenic should be determined, carry out the following procedure:
- After digestion, allow the digestion vessel to cool. Add the contents of the absorber, if used, to the digestion vessel.
- Rinse the absorber and the reflux condenser with ultrapure water and add everything to the digestion vessel. Dilute to 100 ml with ultrapure water.
- Go to paragraph 6.3.

6.2 PRE-REDUCTION STEP FOR SELENIUM

Add 20 ml of hydrochloric acid to the contents of the round-bottomed flask and boil the liquid again for a minimum of 15 minutes.

After digestion, allow everything to cool and add the contents of the absorber, if used, to the digestion vessel.

Rinse the absorber and the reflux condenser with ultrapure water and add everything to the digestion vessel. Dilute to 100 ml with ultrapure water.

6.3 PRE-REDUCTION STEP FOR ANTIMONY AND ARSENIC

Add to 25 ml of the digested solution (with or without the pre-reduction step for selenium) 2.5 ml of the pre-reduction solution (KI/ascorbic acid) (5.6). The solution is mixed and analysed after a minimum of 2 hours and a maximum of 24 hours.
One should take into account the dilution that occurs during this step. (factor 1.1)

6.4 MEASURING

6.4.1 BLANK SOLUTION

Pipette 2 ml of hydrochloric acid into a 100 ml volumetric flask and dilute to volume with ultrapure water.
Treat the blank in exactly the same way as the sample.

6.4.2 CALIBRATION SOLUTIONS

Using the standard solution 2, prepare at least 5 calibration solutions covering the expected working range.

For example, for the range 1 µg/l to 10 µg/l, pipette 1 ml, 3 ml, 5 ml, 8 ml and 10 ml of standard solution 2 into a series of 100 ml volumetric flasks. To each of these flasks, add 2 ml of hydrochloric acid and dilute to volume with ultrapure water. These solutions correspond to concentrations of 1 µg/l, 3 µg/l, 5 µg/l, 8 µg/l and 10 µg/l of the relevant analyte.

Prepare the calibration solutions daily.

Treat the calibration solutions in exactly the same way as the samples.

6.4.3 INDEPENDENT CONTROL SOLUTION

Prepare this solution from the independent stock solution in an identical way as the calibration solutions at a concentration level that is roughly in the middle of the working range.

6.4.4 CALIBRATION AND MEASURING

Set all instrumental parameters of the atomic absorption spectrometer in accordance with the manufacturer's operating manual (wavelengths As: 193.7 nm; Sb: 217.6 nm; Se: 196 nm).
Follow the manufacturer's instructions for the settings on the gas-liquid separator.
Optimize the position of the absorption cell in order to obtain maximum transmission of the light beam.

Pass a stream of argon or nitrogen through the system and set the instrument to zero.

Measure the absorption given by the solutions in the following order:

- blank solution
- calibration solutions
- samples

Repeat the procedure using separate portions of each solution. Use the mean of these results.

7 CALCULATION

Establish the calibration curve using the software or manually, by setting the measured absorption values of the calibration solutions as a function of the corresponding element concentration.
Calculate the concentration in the solution by comparing the absorption response of the sample solution with those of known standard concentrations obtained from the calibration procedure.

All dilution steps shall be taken into account.

8 REFERENCES

- ISO 11969:1996 Water quality – Determination of arsenic – Atomic absorption spectrometric method (hydride technique)
- ISO 9965:1993 Water quality – Determination of selenium – Atomic absorption spectrometric method (hydride technique)
- NEN 6432:1993 Water – Determination of arsenic content by atomic absorption spectrometry (hydride generation technique). Destruction with nitric acid and hydrochloric acid.
- NEN 6433:1993 Water – Determination of antimony content by atomic absorption spectrometry (hydride generation technique). Destruction with nitric acid and hydrochloric acid.
- NEN 6434:1993 Water – Determination of selenium content by atomic absorption spectrometry (hydride generation technique). Destruction with nitric acid and hydrochloric acid.
- ISO/FDIS 20280:2005 Soil quality – Determination of arsenic, antimony and selenium in aqua regia extracts with electrothermal or hydride generation atomic absorption spectrometry.
- CMA/2/I/B.1 *Elements with inductively coupled plasma atomic emission spectrometry (ICP-AES)*, https://esites.vito.be/sites/reflabos/2014/Online%20documenten/CMA_2_I_B.1.pdf
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