

Analytical Methods for Determining Arsenic, Antimony and Selenium in Environmental Samples

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Abstract

This paper presents a comparative description of different methods of determination of arsenic, antimony and selenium: spectrophotometric, electro-analytical (voltamperometry), activation analysis, atomic fluorescence and the methods of inductive or microwave-induced plasma in combination with different detection methods (emission or mass spectrometry). The description is based on literature data illustrating the present state of the metalloid determinations in different matrices. The limits of determination ensured by different methods are also compared. Much attention has been paid to methods combining chromatographic separation with selective detection, especially with the application of plasma generation methods (usually ICP-MS).

Keywords: spectrophotometry, electroanalysis, neutron activation, atomic fluorescence, plasma methods, arsenic, antimony, selenium

Introduction

Determinations of arsenic, antimony and selenium by atomic absorption spectrometry were described in a previous article [1]. The method of absorption atomic spectrometry is neither the only nor the best for determining arsenic, antimony and selenium. Depending on the kind of samples to be analyzed and the expected concentrations of metals to be determined, other methods can prove equally successful [2-6].

Spectrophotometric Methods

The spectrophotometric methods of determination of metals have been very popular but recently have

become obsolete, in particular for analyses of environmental samples, as they are time-consuming and do not ensure a sufficiently low detection limit. At present the methods are used for direct determination of inorganic metal compounds. They are based on more or less specific reactions of colour metal complexes which can be assessed on the basis of the absorption of a certain wavelength of radiation passing through a studied solution [7]. The too high detection limits of this method can be reduced by special sample preparation, e.g. extraction, sorption, chelation, in order to concentrate the metal to be determined. Speciation analyses are possible with the use of different reaction conditions (e.g. different pH values) or a combination of different methods [3].

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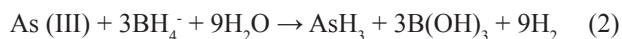
Spectrophotometric Methods of Determination of Arsenic

The molybdenum blue method [7,8] is based on the formation of molybdenum blue by ammonium molybdate (VI) with As(V) ions (in the environment of hydrazine sulphate). The sample to be determined is mineralised by inorganic acids, extracted by arsenic and then arsenic iodide is extracted by a mixture of chloroform with 10 M hydrochloric acid. The As (III) ions are oxidized by cerium sulphate to As (V), which takes part in the reaction of molybdenum blue formation and is detected at the wavelength 825 nm. In this method there is a possibility of interference from the presence of germanium, but this can be eliminated by co-precipitation with hydrated iron oxide or extraction with bromides applied by Rao [8].

The method based on the use of silver dithiocarbaminian (DDTC-Ag). In this method arsenic liberated from a solution as arsenic hydride forms complexes with DDTC in the presence of a strong reducing agent (sodium borohydride) and can be detected at a wavelength of 525 nm. Different kinetics of the reaction of hydride generation, depending on the pH of the environment, allows speciation determination of As (III) and As (V). At pH above 6 the hydrides are formed with As (III). At pH 1-4 As (V) is reduced to As (III)



and then hydrides are generated



The method is subjected to different interference, first of all from the elements forming volatile hydrides (Sb, Se, Sn, Te, Bi) but also from transition metals (Ag, Au, Cr, Cu, Ni, Pt), but only when present at concentrations much higher than natural. The interference can be eliminated by the addition of 1,10-phenantroline (Pt) or extraction of all other elements mentioned above by dithiozine prior to determination of arsenic. The limit of linearity of calibration curve 2-40 µg for 20 mL of sample, which corresponds to a detection limit of 100 ng/mL.

The method based on the formation of DDTC-Ag complex [7] has been recommended by International Standards ISO 6595 [9] for determination of total arsenic in water samples. After oxidation of organic compounds or sulphates by heating with potassium manganate and potassium sulphate peroxide, arsenic is reduced to As(III) by hydroxylamine hydrochloride and then As(III) is reduced to hydride by free hydrogen appearing in an acidic medium as a product of the reaction of hydrochloric acid with tin chloride. Arsenic hydride is absorbed in a solution of silver diethyldithiocarbamate in chloroform or pyridine. The red-violet complex formed as a product is determined at the wavelength of 510 or 525 nm. In this reaction interference from antimony can be expected as it forms a red complex with silver diethyldithiocarbami-

nate. The method is unreliable at its high concentrations of above 500 ng/mL. The method based on the reaction of complex formation with silver dicarbaminat was recommended for determination of antimony in samples of natural water [10].

The methods used for separation of arsenic from the solution or for the concentration of arsenic are: distillation after reduction to arsenic hydride, extraction of halogenides by CCl₄ from an acidic environment and extraction of the diethyldithiocarbamate complex with As (III) [7].

Spectrophotometric Methods for Determination of Antimony

A frequently used method is the one based on the formation of brilliant green after reduction of Sb(V) to Sb (III) by cerium sulphate and hydroxylamine hydrochloride. In this form Sb is determined at the wavelength of 620 nm. The extraction of antimony by surfactants (cetylpyridinium chloride (CPC) or Triton X-100) decreases the detection limit to 3 ng/mL [11].

Antimony also forms complexes with the bromopyrogallol (BPR) red, differing for Sb (III) and Sb (V) by optical absorption. The difference at wavelength of maximum absorbance is great enough to enable speciation determination of Sb (III) and Sb (V). With the use of a micellar system of sodium dodecylsulphate (VI) (SDS) and nonylphenoxypolyethoxyethanol (OP) at 80°C, it is possible to determine Sb (III) in the binary system Sb (III) / Sb (V) at 538 nm, reaching a detection limit of 40 ng/mL. The method tolerates 10-fold excess of Sb (V) and is resistant to interferences from transition metals and anions.

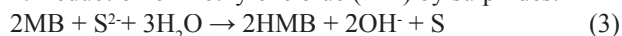
There are two methods of determination of antimony applied often [7]: one based on the use of rhodamine B and one using iodide ions. In the first a violet-pink association complex is formed between SbCl₆³⁻ and rhodamine B, which can be extracted by benzene or ethyl ether and shows a maximum absorption at 565 or 552 nm. In the second method, in an environment of sulphuric acid, antimony forms a green-yellow complex with iodide ions and the maxima of the complex absorption are at 425 nm and 330 nm. Due to the presence of bismuth the interferences can be eliminated by extracting antimony complexes by benzene. In the two methods, preliminary preparation of the sample is recommended by coprecipitation with hydrated manganese oxide, extraction of the chlorine complex by isopropyl ether in HCl environment, extraction of the iodide complex by benzene in H₂SO₄ environment and extraction of dithiocarbamate complexes in an acid environment. It is also possible to isolate antimony in the form of hydride, from a solution.

Spectrophotometric Method of Determination of Selenium

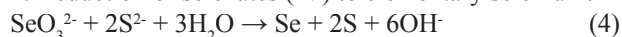
The method based on the reaction of selenium ions with methylene blue requires relatively simple instruments. However, more often the catalytic-spectropho-

tometric methods are used, in which different red-ox reagents are applied: p-hydrazinebenzosulfonic acid, phenylhydrazine, 3-fluorophenylhydrazine after the reaction of amine coupling to azides or reduction of sulphates. An interesting reaction is the catalytic reduction of methylene blue by sulphides to selenosulphides [12], which can be described as follows.

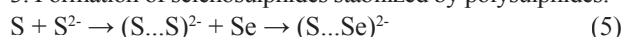
1. Reduction of methylene blue (MB) by sulphides:



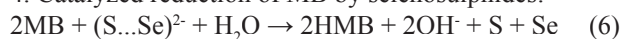
2. Reduction of selenates (IV) to elementary selenium:



3. Formation of selenosulphides stabilized by polysulphides:



4. Catalyzed reduction of MB by selenosulphides:



The sensitivity of the method can be enhanced to below 50 ng/mL, by applying a cationic surfactant such as cetyltrimethylammonium bromide (CTAB).

Popular reagents in spectrophotometric determination of selenium are ditizon, o-phenyldiamine and chromotropic acid. The methods based on the use of amines require a long reaction time (~2 hours), are not selective and are subjected to different interferences. A new reagent for spectrophotometric determination of selenium is 6-amino-1-naphtholo-sulphonic acid (J-acid), forming with Se (IV) at pH 1-2,5 a yellow complex showing a maximum absorption at 392 nm. The method is practically free from interference and allows achieving a detection limit of 80 ng/mL [13].

Selenium reacts with 2,3-diaminenaphthalene in the presence of bromide ions acting as a catalyst, forming a complex which can be extracted by cyclohexane in an acid environment. The maximum absorption of the complex is at 378.5 nm and the detection limit of the method is 12 ng/mL [14].

A classical method of determination of selenium [7] is based on the formation of a yellow complex between Se (IV) and 3,3'-diaminebenzidine (DAB) in acidic environment. The complex is extracted by toluene and shows a maximum of absorption at 420 nm. This reaction is specific for selenium. To improve the sensitivity of the method, selenium can be distilled after its reduction to hydride by precipitation in the metallic form and using tin chloride or hydrazine, or by extraction methods. This method has been recommended for determination of selenium in surface waters [10].

Electrocatalytical Methods

A well-known advantage of the electroanalytical methods is the fact that they permit determination of elements at the level of their natural occurrence in the environment (in particular voltamperometric methods)

Table 1. Electroanalytical methods of determination of arsenic [18].

Method	Reagent	Limit of detection ng/mL	RSD (%)
DPP	HCl	0.3	6.4
DPASV (Au)	HCl . HClO ₄	0.02 (20 min)	10
DPCSV	Cu(II). HCl	0.2 (1 min)	2.9
DPCSV	Se(IV). H ₂ SO ₄	2 (1.5min)	6.4
DPCSV	Cu(II)	0.2 (1 min)	8.3
SWCSV	HCl	0.005 (10 min)	8

and are usually suitable for speciation determination. The drawback of these methods is the possibility of their application to a relatively small number of elements and difficulties in determining a series of samples in different environmental matrices. The methods used for determination of elements in samples of different kinds include polarographic ones such as: the classical direct current polarography (DCP), alternative current polarography (ACP), square wave polarography (SWP), normal pulse polarography (NPP) and differential pulse polarography (DPP) and voltamperometric ones with linearly changing potential (LSV), cyclic and inverse.

Determination of Arsenic by Electroanalytical Methods

Determination of total arsenic by differential pulse cathode stripping voltamperometry (DPCSV) has been described by a few authors [15-17]. The limits of detection achieved were 0.05 ng/mL [15], 0.52 ng/mL [16] and 121 ng/mL [17], depending on the time and way of the analyte concentration on the electrode, and the results were in good agreement with those reported to be obtained by HGAAS [15]. Moreover, in determination of water samples [16] speciation analysis differentiating As (III) and As (V) was performed, based on the use of different electrolytes and oxidation of arsenic to As (V).

Li and Smart [18] have discussed different electroanalytical methods for determination of arsenic proposed in literature and developed by them (Table 1).

Determinations performed by direct current stripping voltamperometry with the gold electrode have been reported by Hua [19]. The speciation determination of As (III) and total arsenic after sample reduction proved to be of no avail because of the content of arsenic below the limit of detection of 0.15 ng/mL.

Determination of Antimony by Electroanalytical Methods

Using differential pulse anode stripping voltamperometry (DPASV) with a modified carbon electrode for determination of antimony, the detection limit is 1.0 ng/mL.

Concentration of the analyte was achieved after 10 min [20]. Using the same methods with HCl and acetate buffer as electrolytes, the detection limits for determination of Sb (III) were 7.3 ng/mL and 73.2 ng/mL, respectively. For determination of Sb (V) it is recommended to use high concentrations of HCl [21]. The speciation analysis can be made determining directly the content of Sb (III) and the total antimony after reduction of the sample by hydrazine at elevated temperature; the detection limit obtained was 0.02 ng/mL [22].

The method of adsorption stripping voltamperometry (ASV), a speciation determination of Sb (III) and Sb (V), was made on the basis of the difference in the potential at which the corresponding peaks occurred [23]. The detection limits obtained were 0.21 ng/mL for Sb (III) and 0.56 ng/mL for Sb (V), after a 5-minute preconcentration.

The authors reported determination of Sb by the method of direct current stripping voltamperometry with a gold electrode, and speciation determinations with the use of different electrolytes [24].

Determination of Selenium by Electroanalytical Methods

Determination of the total content of selenium by the differential pulse cathode stripping voltamperometry (DPCSV) was described in [17], with the detection limit of 121 ng/mL. The method of differential pulse polarography (DPP) was used for determination of selenium Se (IV) in an environment of nitric acid, reaching high intensity of the diffusion current [25]. When applying a strongly basic (pH>9) electrolyte, the limit of determination was 0.08 ng/mL and the results of the determinations were comparable to those obtained by other methods [26].

For determination of Se(IV), the method of catalytic polarography was applied, ensuring the detection limit of 0.04 ng/mL. The speciation determinations were possible after reduction of Se(IV) by hot HCl [27]. Selective determination of Se (IV) was possible by the use of adsorption stripping voltamperometry (AdSV) at the detection limit of 0.1 ng/mL. The results were in good agreement with those obtained by other methods [28].

Neutron Activation Analysis

The methods of activation analysis are based on the phenomenon of radioactivity discovered by Irene and Frederic Joliot in 1934. In this phenomenon, referred to as activation, the radioactive nuclei are formed as a result of bombardment of a given substance with neutrons, ions or photons. Thus, formed isotopes can be identified on the basis of measurements of the energy of radiation and half-lifetime. Knowing the isotopes, we can also identify particular elements they were formed from. The quantitative analysis is based on the dependence of the radioactive activity of a given isotope and its concentration.

At present, the neutron activation analysis (NAA) using neutrons as activating particles, is one of the most

universal methods for determining chemical composition of different materials. A source of neutrons can be a nuclear reactor (which allows very low detection limits, of an order of 10^{-12} gram) or a generator of fast neutrons (allowing a possibility of determination of light elements (Al, Si) undetectable by other radiometric methods). This method's detection limit for determination of arsenic is 0,02 ng/mL. Speciation determinations are possible after appropriate sample preparation [29]. In determination of Sb (III) and Sb (V), with precipitation at a given pH, the detection limit obtained was of an order of pg/mL [30]. For As and Sb, using extraction by liquid solvents, the detection limits achieved were 5 ng/g and 6 ng/g, respectively [31]. For determination of the same substances with the use of ion exchange, the detection limits were 5 ng/g and 10 ng/g, for As and Sb, respectively [32]. An important advantage of the NAA method is the fact that the sample analyzed is not destroyed and can be used repetitively.

Atomic Fluorescence

This method is based on a similar principle as that of absorption atomic spectrometry, and thus construction of the analytical instruments is also similar. The radiation coming from a powerful source (electrodeless lamp EDL, laser) is absorbed by plasma generated by flame or an electrothermal atomiser. The absorption causes excitation of atoms, which emit radiation (fluorescence) on coming back to ground level. The wavelength of the emitted fluorescence can be the same as that of the excitation radiation (resonance fluorescence), higher (transition through an intermediate state) or lower (thermoluminescence). The intensity of the fluorescence radiation is proportional to the concentration of atoms in the plasma, which allows quantitative analysis (e.g. by a comparison with a standard curve). The intensity of the fluorescence radiation is measured at an angle to the path of the excitation radiation coming from the source, which eliminates the effect of the excitation radiation on the fluorescence intensity. However, the result can still be affected by scattering of the radiation by the sample.

The methods suitable for determination of elements heavier than sodium (elements of smaller atomic mass show very small fluorescence) are X-ray fluorescence (XRF) and the method with the sample excitation by fast protons (PIXE). In the method of XRF the sample is excited by X-ray radiation and then it emits secondary X-ray radiation (the so-called X-ray fluorescence). Each element emits a characteristic spectrum of radiation (qualitative analysis) and spectral line intensities are proportional to the content of a given element in the sample (quantitative analysis). In the method of PIXE, the atoms are excited by bombardment with fast protons and the sensitivity of the method is 100 times greater than that of XRF. The fluorescence methods allow reaching detection limits of an order of ppm-ppb.

Table 2. The limits of detection of As, Sb and Se obtained using different techniques of analyte introduction [37].

Technique	As		Sb		Se	
	DL ng/mL	RSD (%)	DL ng/mL	RSD (%)	DL ng/mL	RSD (%)
PN-T-MIP	500	4.8	250	4.0	540	4.2
GF-3F-MIP	50	1.8	20	2.0	46	1.5
HG-CT-3F-MIP	0.8	6.7	0.4	6.8	0.5	7.2
HG-GFT-3F-MIP	0.4	4.5	0.35	4.8	0.25	4.6

DL- the limit of detection, RSD% - relative standard deviation in percent.

In combination with hydride generation, the method of atomic fluorescence gives results comparable with those obtained by the other methods of metal determination [33]. The method of XRF with separation of the elements determined from the matrix eliminates interferences and permits a detection limits of an order of 10 ng/g [34] or 0.005 ng/mL [35]. The use of laser excitation allows determination of As, Se and Sb at the detection limits of 4 ng/mL, 2 ng/mL and 15 ng/mL [36].

Plasmic Spectrometric Methods

The plasmic spectrometric methods are based on the emission of electromagnetic radiation by elements excited e.g. in high temperature. Each element emits radiation of characteristic wavelengths (allowing qualitative analysis) and intensity proportional (at a given temperature) to the concentration of this element (allowing quantitative analysis). Emission of radiation by an atom of a given element is related to changes in the energy states of electrons from the outer electronic shell. An appropriately high quantum of energy (thermal, electric) provided to the atom makes one or more electrons jump to a higher energy level, causing the atom's excitation. The higher the energy of excitation, the greater the richness of the electronic transitions and the complexity of the emission spectrum.

A sample to be studied is transformed into aerosol by nebulizer or in a spark ablation system in which a fragment of the sample is evaporated from its surface and introduced into plasma. In such a form it is introduced into a stream of neutral gas (e.g. argon) to which a high frequency signal (27-90 MHz) is applied through inductive coupling (electrodeless). The energy of the signal heats up the gas (argon + the sample) to 10,000°C - the state of plasma, in which most atoms are ionized (formation of Me^+ , Me^{2+} etc.). The excited atoms emit radiation and on the basis of this emission spectrum the chemical composition (quantitative and qualitative) can be established. The method based on plasma excitation and analysis of the emission spectrum is known as ICP-AES (inductively coupled plasma - atomic emission spectrometry).

Another solution is based on the phenomenon of ionization of atoms in a plasma state at high temperature and

the possibility of identification of the ions using mass spectrometry (ICP-MS *inductively coupled plasma - mass spectrometry*). The sensitivity of the method of ICP-MS is the same or higher than that of GFAAS.

The ICP methods, both AES and MS, and MIP methods allow determination of a few elements in a wide range of concentrations, in the same sample in a few minutes, so they are superior in performance. Moreover, the use of an ultrasonic nebulizer (USN), instead of a pneumatic one, decreases the limit of detection from 5 to 20 times (with the use of a pneumatic nebulizer only 10% of the sample was introduced into the plasma studied). Table 2 gives a comparison of the limits of detection obtained for different techniques of analyte introduction. However, the ICP method is susceptible to different kinds of interference, which have to be eliminated by different instrumental and chemical solutions.

Determination of Arsenic

The application of the method of hydride generation before the introduction of analyte to the plasma enables a separation of the elements under determination from the interfering matrix. The results obtained by ICP-AES are comparable to those in HGAAS determinations, with the detection limit of 0.2 ng/mL [38]. The detection limit achieved when using the method of atomic emission spectrometry (AES), with inductively coupled plasma (ICP) was 0.1 ng/mL and with microwave excitation and generation of hydrides prior to the introduction of the analyte - it was 0.25 ng/mL. The use of a trap concentrating the hydrides, the detection limits for ICP and CMP were 0.02 ng/mL and 0.002 ng/mL, respectively. Using helium instead of argon, the detection limit can be 1.5-2 times decreased in the method with microwave plasma excitation and atomic emission spectrometry (MIP-AES) [39]. The detection limits achieved with generation of hydrides and their concentration in a graphite furnace or in a cold trap (liquid nitrogen temperature) were 0.4 ng/mL and 0.8 ng/mL [37]. Using mass spectroscopy (MS) the detection limit was 0.08 ng/mL, after hydride generation and reduction [40]. The determinations with hydride generation can be performed in the continuous flow of the analyte and in the batch system, getting comparable results at the

Table 3. Performance of different analytical methods of determination of selenium [6].

Method	Calibration range ng/mL	Linearity	DL ng/mL	RSD %	Time of analysis hours (20 samples)
AFS	0-5	0.998	0.28	3.1	12
HGAAS	0-5	0.997	0.038	3.8	6
FI-HGAAS	0-50	1	0.29	7.9	5
HG-ICP-AES	0-40	0.999	0.40	1.9	3
HG-ICP-MS ⁷⁷ Se	0-1	0.999	0.030	12.3	3
HG-ICP-MS ⁸² Se	0-1	1	0.032	8.7	3

DL stands for the detection limit, RSD% - relative standard deviation in percent.

detection limit of 4 ng/mL [41], or with injection supply of the analyte (FIA) [42]. Introduction of the analyte and hydride generation can be used irrespective of the method of detection: AES [37-39], or MS [40, 42-44]. Mass spectrometry ensures the detection limit of 0.006 ng/mL without preliminary concentration of the analyte [42, 45]. Improvement of the detection limit and reduction of the interference can be achieved by applying electrothermal evaporation of the sample in combination with ICP-MS, which decreases the detection limit down to 0.03 ng/g sample [46]. The sample evaporation is performed in a graphite furnace similar to that used in GFAAS in the conditions used in this method (temperature program and modifiers). With the use of a graphite furnace for on-line concentration of hydrides and the method of ICP-MS the detection limit was achieved to be 0.02 ng/mL [47].

Determination of Antimony

Applying the selectively pH-dependent extraction of Sb(III)/(V) complexes, it was possible to separate different forms of antimony oxidation and the limits of detection (for AES) were: 3 ng/mL and 5 ng/mL for Sb (III) and Sb (V), respectively [48]. Applying the technique of hydride generation and their capture in a graphite furnace of a cryogenic trap, the detection limits were 0.35 ng/mL and 0.4 ng/mL, respectively [37].

In the method of ICP with generation of hydrides, the interferences from other elements present in the analyte even in a few hundred excess are negligible [43]. Using the method of mass spectrometry for determination of antimony in solid samples after their deep wet mineralisation the detection limit obtained was 6 ng/g, and the results were in good agreement with the certified values [43]. Mass spectrometry applied together with the generation of hydrides allow reaching a detection limit of 0.06 ng/g [40]. The continuous or batch introduction of the sample can be replaced by the injection supply (FIA), in which much smaller volumes of the sample are needed. The detection limit of 0.001 ng/mL was achieved after the preliminary reduction of the sample and the injection loop volume of 500 μ L [42].

Applying the method of ICP-MS and the electrothermal evaporation of the sample, the detection limit achieved was 0.01 ng/g [46]. The evaporation was realized in a graphite furnace, similar to that used in GFAAS, in the conditions used in this method (temperature program, modifiers). The detection limit obtained in ICP-MS determinations with the use of a graphite furnace for on-line concentration of generated hydrides was 0.005 ng/mL [47].

Determination of Selenium

A comparison of performance of the analytical methods used for determinations of Se in environmental samples (bottom sediments) is illustrated in Table 3. The data show that the method of ICP-MS is characterised by a similar performance to AAS, provided that generation of hydrides is applied in each of them. The interference due to transition metals can be eliminated by removing the metals on ion-exchange resin (cationit) and on-line. Having removed the transition metals and applied hydride generation, the method of ICP-AES ensured the detection limit of 0.4 ng/mL [49]. Applying organic compounds (such as simple alcohols, polyalcohols, organic acids) as modifiers the detection limit can be decreased to 0.2 ng/mL [50]. In determination of selenium by any method with hydride generation, an important step is to reduce selenium to Se (IV). In determinations by the method of ICP-AES using HCl as reducer, the detection limit of 1.5 ng/mL was achieved [51], the same as when the ICP-MS method was used [52]. Applying generation of hydrides followed by their capture in a graphite furnace or cryogenic trap, the detection limits were 0.25 ng/mL and 0.5 ng/mL [37]. When the injection sample supply was used with generation of hydrides and mass spectrometry, the limits of detection of Se(IV) and Se(VI) were 0.012 ng/mL and 0.016 ng/mL [49].

Chromatographic Methods (Hyphenated Techniques)

Chromatographic methods, in particular gas chromatography (GC) and high-performance liquid chromatography (HPLC) provide more detailed information than the

above-described methods. The latter give total content of a given metal in the sample or the fractions at different degrees of oxidation [53], whereas chromatographic distribution allows identification of specific compounds, both organic and inorganic, containing a given metal. Unfortunately, the detectors used in chromatographic methods, such as electron capture detector (ECD), thermal conductivity detector (TCD), flame ionisation detector (FID), photoionisation detector (PID), spectrophotometers (UV-Vis, IR, UV) or fluorimeters (RF) are non-selective to compounds of different metals and usually do not have sufficiently low detection limits [54, 55]. The situation is improved by the use of atomic absorption spectrometers specific for metals [55-59] or plasmic spectrometers with emission or mass detection [58-65] and with different sources of excitation: microwave-induced plasma (MIP), capacity-coupled plasma (CCP), capacity-microwave coupled plasma (CMP), inductively-coupled plasma (ICP), directly-coupled plasma (DCP) [54], or atomic fluorescence detector [66].

A combination of a chromatograph with a spectrometer acting as a selective detector permits determination of organometallic compounds on the level of their occurrence in the natural environment and identification of particular compounds. The authors of [67] determined As (III), As (V), monomethylarsenic acid (MMAA), dimethylarsenic acid (DMAA), arsenobetaine (AB) and arsenocholine (AC) in model solutions simulating natural samples, applying a system of HPLC-ICP-MS. The results of the chromatographic determinations with the use of C_{18} (HPLC) were comparable with those obtained by HGAAS and ICP-MS. The detection limits were 10 ng/mL for arsenates (III), 15 ng/mL for DMAA, AB, MMAA and 20 ng/mL for arsenates (V), applying the HGAAS detection [60]. With the use of an ion-exchange column for HPLC with ICP-MS detection, the detection limits were: 0.12 ng/mL for As (III) and AC, 0.04 ng/mL for As (V), 0.08 ng/mL for MMAA, 0.06 ng/mL for DMAA and AB [61], 1.3 mg/kg for As (III), DMAA, MMAA or 1.7 mg/kg for As (V) in determinations of solid samples extracted with phosphoric acid. Using liquid chromatography with HGAAS detection and membrane (PTFE) separation of gas from liquid phase, the following detection limits were reached: 0.7 ng/mL; 1.1 ng/mL; 1.2 ng/mL and 3.0 ng/mL for determinations of arsenates (III), DMAA, MMAA and arsenates (V) [57]. For determinations of different arsenic compounds with the microcapillary HPLC and ICP-MS detection, the detection limits varied from 0,1 to 0,9 ng/mL, but the sample volume of 1 μ L was required for individual analysis [68]. The use of different columns and mobile phases for speciation determination of antimony is compared in [58]. The authors consider the anion-exchange, cation-exchange and reverse-phase columns working with FAAS or ICP-MS as detectors, and report agreement between the results of chromatographic analyses and in direct ICP-MS.

Speciation analysis of organic selenium compounds and selenium amino acids was performed in

Table 4. Speciation analysis of organic selenium compounds [2].

Form	Matrix	Detection
Gas chromatography		
DMSe, DMDS _e	water	AAS
DMSe, DMDS _e	air	FID
DMSe, DMDS _e	gas samples	SCD, MS, ETAAS, FID, MIP
Liquid chromatography		
TMSe ⁺ , Se(IV), Se(VI)	water	ETAAS, IDMS, ICP-AES, HGAAS
TMSe ⁺ , Se(IV), Se(VI)	clinical samples	NAA, HGAAS, ETAAS, ICP-MS

the system HPLC-ICP-MS [33]. Similar detection limits of about 1ng/mL were obtained for determination of Se (IV), Se (VI), selenomethionine (SM) and selenocysteine (SC) by HPLC combined with FAAS detection (with the use of a slit concentrator STAT) or ICP-MS detection [59]. Performances of gas and liquid chromatography methods for speciation analysis of organic selenium compounds are compared in Table 4.

In a combined analytical system HPLC-ICP-MS a simultaneous speciation analysis of arsenic, antimony, selenium and tellurium was performed differentiating between different forms of oxidation and methyl compounds of these metals, achieving the detection limits from 0.01 ng/mL to 1.8 ng/mL, depending on the compound determined [64].

Other Analytical Methods

The above described and discussed methods of determination of arsenic, antimony and selenium are not all analytical methods used for this purpose but have been chosen as most often applied. The other methods mentioned in literature include direct mass spectrometry (dual MS-MS) [69], molecular absorption spectrometry [70], capillary electrophoresis as a method for separation of compounds prior to detection by ICP-MS [68], or ion-exchange chromatography [71, 72] with ICP-AES or MS detection.

A Comparison of the Methods of Determination of Arsenic, Antimony and Selenium

The authors of [73], devoted to determining inorganic and organic compounds in water, compared the performance of analytical methods for determination of arsenic, antimony and selenium. They analyzed the spectrophotometric methods, absorption and emission spectroscopies, electroanalytical and combined (chromatography with different detection techniques) methods described above.

Table 5. Speciation determinations of arsenic in environmental samples [3].

Method	Forms determined	Samples	DL range ng/mL
UV-vis	As(III), AsT	water, sediments, model samples	2-100
EQ	As(III), As(V), AsB, AsC, AsT, MMAA, DMAA	model samples, reference, clinical	0.1-18
HG-AAS	As(III), As(V), MMAA, DMAA	water, soils, clinical	0.01-2
ETAAS	As(III), AsT	water, sediments, model	0.02-10
HPLC-HG-AAS	As(III), As(V), MMAA, DMAA, AsB, AsC	water, sediments, clinical, model	0.3-6
HPLC-ICP-MS	As(III), As(V), MMAA, DMAA, AsB, AsC	water, sediments, biological, model	3-21
NAA	As(III), As(V)	water, biological, reference	0.02

DL - detection limit

The Standard Methods recommend HGAAS, GFAAS, the spectrophotometric method with silver dicarbamate and ICP for determination of arsenic, FAAS, GFAAS, HGAAS for determination of antimony, the spectrophotometric method with 2,3-diaminonaphthalene, fluorimetric method, GFAAS and ICP for determination of selenium, and the ways of sample preparation for analyses.

Speciation analysis of arsenic has been described in details in ref. [3]. The paper presents different procedures of determination of different forms of arsenic and the detection limits of the methods described from the lowest to the highest reported in literature for a given form

of arsenic in different kinds of environmental samples, Fig. 1 and Table 5. The authors [6] present different analytical methods of selenium determination: fluorimetry, HGAAS, FI-HGAAS, HG-ICP-AES, HG-ICP-MS, RNAA. They describe the procedures of sample preparation, give the basic parameters of the analytical methods and relevant instruments, Table 6. A comparison of gas and liquid chromatography, in combination with different methods of detection, for speciation analysis of organic compounds of selenium is made [2] and the detection limits ensured by different methods and dependent on the environmental matrix are given.

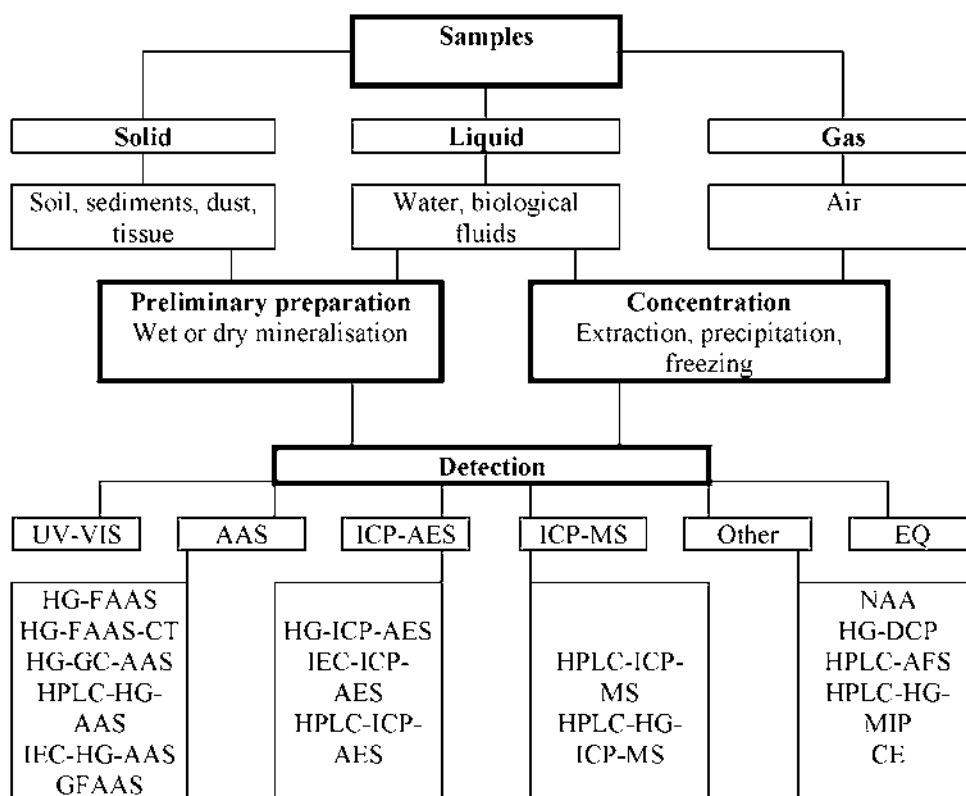


Fig. 1. Different procedures of speciation analysis of arsenic in environmental samples of different types [3].

Table 6. A comparison of selected methods for determining selenium [6].

Analytical technique	Matrix	DL ng/mL
Spectroscopic methods		
UV-VIS	plants	80 000
AFS	sediments	0.28
XRF	water	0.06
HGAAS	tissues	0.02
ETAAS	urine	0.02
ICP-AES	sediments	0.4
MS	water	0.01
Electrochemical methods		
ASV	water	80 000
CSV	water	0.002
DPP	tissues	0.005
Radiochemical methods		
NAA	food products	0.5

DL - detection limit

Table 7. Speciation analysis of selenium [4].

Form	Samples	Analytical method	DL ng/mL
Se(IV)	water	DPP	10
Se(VI)	water	DPCSV	0.04
Se(IV), Se(VI)	water	MFS	0.005
Se(IV), Se(VI)	soil	GLC-ECD	0.002
Se(IV)	soil	SCIC-LC-CD	110
Se(VI)	soil	SCIC-LC-CD	60
Se(IV), Se(VI)	water	HG-QFAAS	0.003
Se(IV), Se(VI)	water	IC-HG-AAS	0.010
Se(IV), Se(VI)	sediments	HG-AAS	0.010
Se(IV), Se(VI)	model	LC-ICP-AES	0.054
TMSe ⁺	model	LC-ICP-AES	0.014
DMSe, DMDS _e	air	GC-AAS	0.0002
DMSe	air	GC-GFAAS	0.0001
DMDS _e	air	GC-GFAAS	0.0002
SeM, SeC	blood	LC-MS	-
Se(0)	model	HG-ICP-AES	0.6
Se total	model	HG-UV-DAD	1 000
Se total	water	ID-MS	0.010
Se total	biological	HG-ICP-MS	0.0013

DL - detection limit

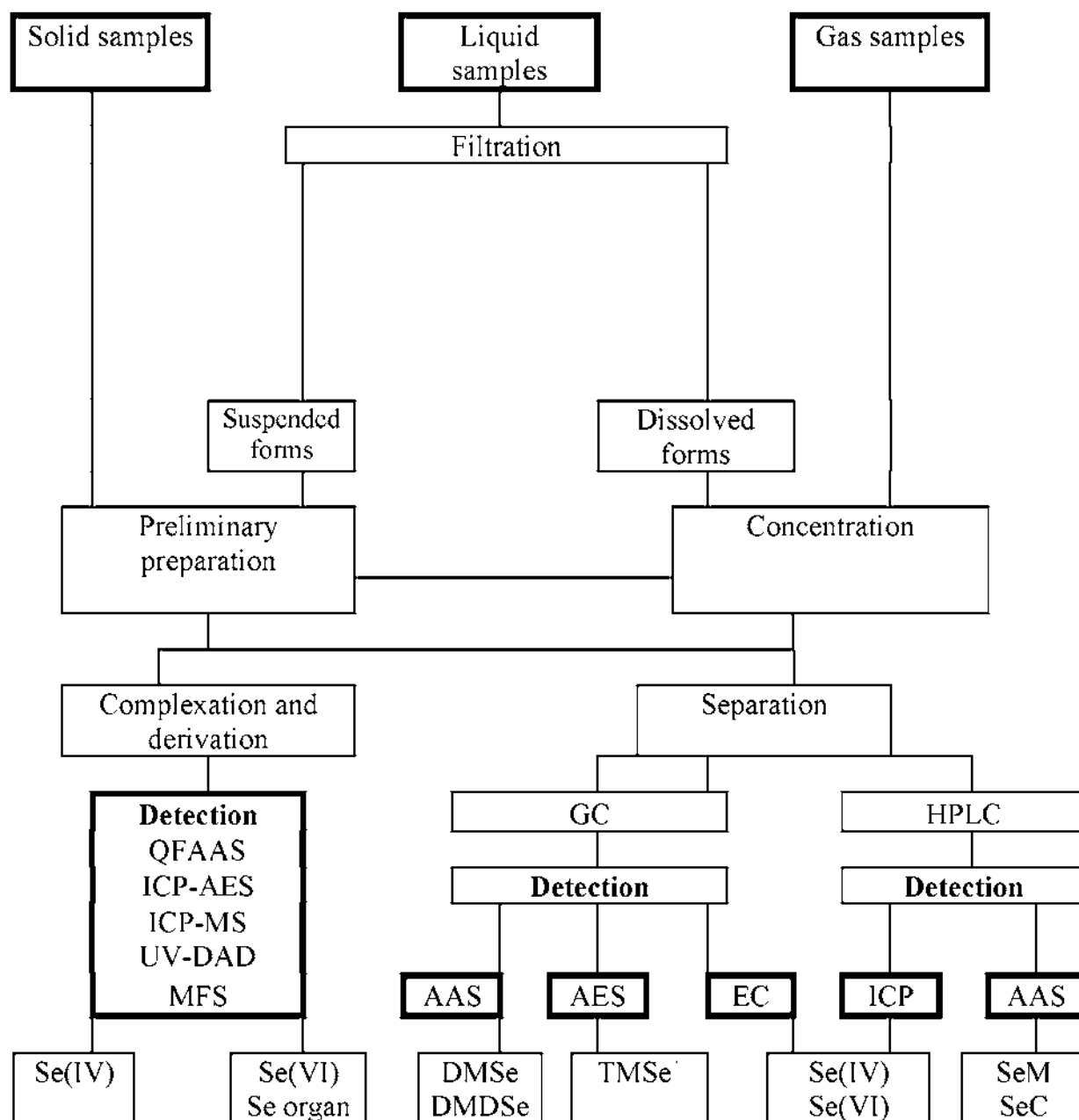


Fig. 2. Analytical procedures of speciation analysis of selenium in environmental samples [4].

A similar comparative presentation of the methods of speciation analysis of selenium has been made in [4]. The detection limits (Table 7) and analytical procedures of determination of selenium in different kinds of environmental samples are given in Fig. 2.

The authors [5] discuss problems related to speciation analysis of selenium in environmental samples. They present sample preparation procedures, a comparison of analytical methods and the detection limits achieved (Table 8).

Tables 9-11 give a brief characterisation of the above-discussed analytical methods and references concerning speciation analysis.

Summary

This paper presents results illustrating the possibilities of selected analytical methods in determining arsenic, antimony and selenium. The significance of knowing the level of these elements in environmental, technological and pharmaceutical samples is reflected in the number of devised methods of their determinations, ensuring the possibility of optimisation for particular cases. The accessibility of a variety of instrumental and methodical solutions permits the choice of a technique best for expected levels of concentration.

Table 8. Analytical methods of determining selenium [5].

Method	DL ng/mL
Atomic absorption spectrometry	
GFAAS	0.5-2
HGAAS	0.05-0.1
HGAAS with concentration	~ 0.001
FI-HG-GFAAS	~ 0.001
GC-GFAAS	0.1 ng
HPLC-GFAAS	0.76-1.76 ng
Atomic emission spectrometry	
HG-ICP-AES	0.055-1.2
HPLC-ICP-AES	14-141 ng
IC- HG-AES	20
GC-MIP-AES	0.0025-0.062 ng
Atomic fluorescence spectrometry	
HG-ND-AFS	~ 0.001
HG-ICP-AFS	0.003 ng
HPLC-ND-AFS	0.2-0.3
LEAFS	$1.5 \cdot 10^{-5}$
Inductively coupled plasma with mass spectroscopy	
ICP-MS	~ 0.001
HG-ICP-MS	0.001-0.0064 ng
ETV-ICP-MS	0.001 ng
GC-ICP-MS	0.02
HG-GC-ICP-MS	-
LC-ICP-MS	0.03-0.2 ng
Gas chromatography	
GC-FID	0.005 ng
GC-ECD	~ 0.001
GC-FCD	0.006-0.022 ng
HG-GC-PID	0.025 ng
Fluorimetry	
DAN-FD	0.01-0.05
HPLC-FD	$1.5 \cdot 10^{-4}$ - 10^{-5}
Electrochemical methods	
DPP, DPV	0.01-2
CSV, DPCSV	0.0005-0.1
HPLC-ED	-
HPLC-IAPD	0.02-0.03 ng
Mass spectrometry	
GC-MS	-
LC-ES-MS	-

DL - detection limit

Speciation analysis providing more information about toxicity, bioavailability, migration of elements and the impact of industrial technologies has begun replacing simple determinations of total contents in environmental samples. Methods combining the use of selective analytical methods such as ICP-MS, AFS or MIP with chromatographic separation of different species containing a given element have become increasingly available. The necessary laboratory equipment and analytical units are not only constructed in laboratories, but in ready-made commercial equipment.

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The Most Often Used Acronyms

AAS	Atomic absorption spectrometry
ACP	Alternative current polarography
AFS	Atomic fluorescence spectrometry
ASV	Adsorption stripping voltamperometry
CCP	Capacitive induced plasma
CMP	Capacitive-microwave induced plasma
DAD	Diode array detector
DCP	Direct current polarography
DPASV	Differential pulse anode stripping voltamperometry
DPCSV	Differential pulse cathode stripping voltamperometry
DPP	Differential pulse polarography
ECD	Electron capture detector
ETAAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
FIA	Flow-injection analysis
FID	Flame- ionisation detector
GC	Gas chromatography
GFAAS	Graphite furnace atomic absorption spectrometry
HGAAS	Hydride generation atomic absorption spectrometry
HPLC	High-performance liquid chromatography
IC	Ion chromatography
ICP-AES	Inductively coupled plasma with atomic emission spectrometry
ICP-MS	Inductively coupled plasma with mass spectroscopy
LIF	laser induced fluorescence
MIP	Microwave induced plasma
NAA	Neutron activation analysis
NPP	Normal pulse polarography
PID	Photoionisation detector
RF	Fluorometric detector
XRF	X-ray fluorescence

Table 9. Analytical methods of determining arsenic.

Method	Kind of samples	Speciation	References
UV-VIS	metals, model	-	8, 9, 74
CSV	soil, water	+	15, 16, 18
SCCS	water	-	19
DPP	geological reference materials	-	17
AFS	model	+	33
XRF	biological reference materials	-	34
NAA	water, geological reference materials	+	29, 32
HG-ICP-AES	water, reference materials	+	38, 41
HG-MIP-AES	model	-	37, 39, 56
ICP-MS	food products	-	44
EV-ICP-MS	water, reference materials, model	-	46, 47
HG-ICP-MS	water	-	40, 42, 45
HPLC-ICP-MS	model, water, sediments, biological	+	60-63, 65, 66
HPLC-AFS	biological, water	+	66
HPLC-HGAAS	water	+	57
CE-HG-ICP-MS	water	+	68, 75
MS	reference materials	-	69
DAD MAS	model	-	70
IExC	model	+	71
LIF-ICP	model	-	36

+ a reference concerning speciation analysis

Table 10. Analytical methods of determining antimony.

Method	Kind of samples	Speciation	References
UV-VIS	water, model	+	11
CSV	water, model	+	21-23
SCCS	water, reference materials	+	24
DPP	biological, soil	-	20
AFS	biological	-	76
NAA	water, biological, geological	+	30-32
ICP-AES	water	+	48
HG-MIP-AES	model	-	37, 69
EV-ICP-MS	water, model	-	45-47
HG-ICP-MS	geological, water	-	40, 42, 43
HPLC-ICP-MS	soil, model	+	58, 65
DAD MAS	model	-	70
LIF-ICP	model	-	36

+ a reference concerning speciation analysis

Table 11. Analytical methods of determining selenium.

Method	Kind of samples	Speciation	References
UV-VIS	water, model	+	11
CSV	water, model	+	21-23
SCCS	water, reference materials	+	24
DPP	biological, soil	-	20
AFS	biological	-	76
NAA	water, biological, geological	+	30-32
ICP-AES	water	+	48
HG-MIP-AES	model	-	37, 69
EV-ICP-MS	water, model	-	45-47
HG-ICP-MS	geological, water	-	40, 42, 43
HPLC-ICP-MS	soil, model	+	58, 65
DAD MAS	model	-	70
LIF-ICP	model	-	36

+ a reference concerning speciation analysis

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