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Review

Atomic Absorption Spectrometry in Determination of Arsenic, Antimony and Selenium in Environmental Samples

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Abstract

This paper reports determination of arsenic, antimony and selenium in different matrices using atomic absorption spectrometry, with atomisation in a graphite tube and with generation of hydrides. The actual state of atomic absorption spectrometry as the method of determining As, Sb and Se is described on the basis of literature data. The effects of interference in determinations by atomic absorption spectrometry, and the problems related to sample preparation to determinations (extraction, mineralisation, concentration) are discussed. The application of flow injection analysis in atomic absorption spectrometry with hydride generation is described. The effectiveness of atomic absorption spectrometry in speciation determinations of arsenic, antimony and selenium applied alone and in combination with chromatographic methods is shown.

Keywords: atomic absorption spectrometry, hydride generation, graphite furnace, arsenic, antimony, selenium

Introduction

Compounds containing arsenic, antimony and selenium occurring in trace amounts in various ecosystems have recently become a subject of close monitoring. Although these elements rarely, even in a polluted environment, reach a level of toxic concentration, a small difference between their admissible and toxic doses absorbed by living organisms in view of their common presence means their presence requires careful control [1]. The contents of arsenic, antimony and selenium compounds can also be an element of the monitoring of the spread of pollution and can bring the information on an enhancement of anthropopressure processes. Another important problem is determining the natural level of their presence implied by the hydrogeological conditions or - when anthropogenic changes cannot be excluded - a level of reference for the time of analysis. Results of such determinations are often used as reference for studying the tendencies of processes taking place in the ecosystems and their dynamics.

The total content of a given element does not give any information on the processes in which the element is involved in a given ecosystem, so does not inform on its actual toxicity, migration, bioavailability or accumulation. Only identification of the forms in which the element

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occurs in the natural environment (speciation) either as specific chemical compounds (individual speciation) or groups or classes of compounds (operational speciation) permits drawing conclusions on the element's essential relations and effects [2].

One of many methods of determination of the total contents and speciation analysis of arsenic, antimony and selenium on the level of their environmental concentrations is atomic absorption spectrometry (AAS). Particularly advantageous is this method in combination with generation of hydrides as it enables isolation of the element determined from the environmental matrix, often complex and interfering - especially when atomization is performed in a graphite furnace. The method allows group speciation analysis possible to perform in routine procedures. The paper presents atomic absorption spectrometry as the method for determining arsenic, antimony and selenium. Different methods of determination of arsenic, antimony and selenium and the achieved limits of determinability will be described in the second part of the paper (in preparation).

Determination of Arsenic, Antimony and Selenium by Atomic Absorption Spectrometry with Generation of Hydrides

Determination of Arsenic

Determination of arsenic in environmental samples has become of growing interest to many authors. It has been established that the presence of transient metals such as nickel, cobalt and copper has considerable effect on determining arsenic by AAS with generation of hydrides [3, 4]. The interfering effect of these metals appears at their high concentrations (a few thousand μg/mL) [4], when arsenic occurred at 5 ng/mL, the influence of Cu, Co, Ni and Se was significant at their concentrations 2000, 30000, 200 and 200-fold higher than that of arsenic. The interfering influence of these metals could be reduced by the use of alkaline samples [4]. This influence becomes more pronounced when supports other than hydrochloric acid are used (e.g. acetic acid, citric acid, tartaric acid, acetate or citrate buffers), but becomes significant at concentrations of the interfering metals (Cu, Ni, Fe) above 10 μg/mL [5]. Since in environmental samples the concentration of transient metals is even a few hundred times lower, their presence is not important for analytical determination of arsenic; it becomes important when the samples are metals or their alloys.

In determinations of environmental samples the subject of concern of many authors was to find a method of the analyte preconcentration in order to achieve a limit of detection close to the analyte concentration in natural environment.

Applying the cryogenic trap at the liquid nitrogen temperature after derivation by L-cysteine at room temperature or on microwave heating, the limits of detection of arsenates (V), arsenates (III), MMAA (monomethyloarsenic acid) and DMAA (dimethyloarsenic acid) were 57, 30, 98 and 42 pg, respectively, i.e. close to 50 pg/mL. Similar limits of detection of 19, 45, 61 pg were obtained for inorganic arsenic, MMAA and DMAA, respectively, in a 1 mL sample, applying the liquid nitrogen trap and separating different forms of arsenic on the basis of their boiling temperatures. About 10% loss of arsenic compounds was found when the samples were stored at minus 20°C, so their freezing in liquid nitrogen was recommended [6]. The application of liquid nitrogen trap after derivation with potassium iodide (the use of ascorbic acid and tin (II) chloride for reduction of arsenates (V) gave poorer results) gave the limit of detection of arsenates (III) and (V) of an order of 0.25 ng/mL. The effect of interference of the following metal ions was studied: Ni, Be, Cr, Ag, Pb, Cu, Sn, Zr, Sb, Fe. The use of sodium borohydride at higher concentrations (5 mol/L) reduced the interference, which was greater for determinations of As (III) than As (V) [7]. The use of microwave heating, cryogenic trap and citric acid for determination of As (III) and nitric acid for determination of inorganic arsenic, MMAA and DMAA, the limits of detection were in the range 20-60 pg/mL for the sample of 10 mL. This method was applied for samples of surface waters (river water) and reference materials [8].

The analyte pre-concentration by co-precipitation of arsenic compounds with lanthanide or hafnium hydroxides on line enables routine determinations (about 30 samples per hour) at the limit of detection of 3 pg/mL. The interferences caused by selenium and copper appearing at concentrations above 1 ng/mL and I μg/mL, respectively, and the necessity of optimisation of many elements of the reaction system can create some problems [9]. The use of the complex of molybdenum and tetraphenylphosphine chlorine as a precipitating agent leads to similar results in determinations of As (III) and As (V in model solutions and reference materials) by the methods HGaAS and NAA [10].

The pre-concentration of arsenic compounds (As (V), MMAA and DMAA) with the use of ion-exchangers (anionit, analyte washed out with phosphoric acid (V) at pH 2) enables determination of arsenic in natural water samples at the limit of detection 0.1-0.6 ng/mL, by the method of standard addition [11].

The detection limit of about 0.1 ng/mg was achieved in determination of total arsenic in solid samples, applying extraction by xanthogeniane in hydrochloric acid environment followed by extraction of copper and iron by thiourea. The same solution was used in determination of reference materials [12]. Another idea was extraction by the system methanol/chloroform, followed by wet mineralization by sulphuric (VI) acid and nitric (V) acid. This procedure was applied for determination of arsenobetaine (AsB) in reference materials [13]. In solid samples the determinations can be performed after preliminary decomposition of the samples achieved by incineration at 550°C and extraction by hydrochloric acid, high-pressure wet mineralization (hydrogen peroxide and nitric (V) acid at 300°C) or mineralization (hydrogen peroxide and nitric (V) acid) at microwave heating [14]. The best effects in determination of arsenic in reference materials were obtained with sample incineration (applied also in [15]) and, moreover, this method was free of interferences from nitrates (III) [16]. Mineralization of biological samples was carried out with nitric (V), chloric (VII) and sulphuric (VI) acids [17].

The use of high-performance liquid chromatography (HPLC) for separation of arsenic compounds followed by selective detection by HGAAS, allows a direct speciation determination of arsenic in environmental samples. Analysis of solid samples was preceded by extraction of arsenic compounds by tripsin in an alkali environment (ammonium hydroxide), and after chromatographic separation the sample was mineralised on-line in a microwave system by hydrogen peroxide and nitric (V) acid, then the cooled sample (water and ice bath) was subjected to HGAAS analysis. The limits of detection achieved were 0.6 ng/mL for total arsenic (the linearity range up to 45 ng/mL) and 2.5; 5.3 and 3.3 for AsB, DMAA and MMAA, respectively, at linearity range 0-200 ng/mL [18]. The reaction system for generation of hydrides installed behind a column of chromatograph was applied in [19] for the izocratic conditions of separation of DMAA and gradient for separation of DMAA, MMAA and arsenates (V), which led to the limit of detection of 0.5 ng/mL in determinations of arsenic in samples of natural waters. The use of ionic chromatography (anion-exchange and exchange of ion pairs) in the HPLC system with HGAAS detection it was possible to separate AsB, DMAA, MMAA, arsenates (III), and arsenates (V) in different mobile phases.

A comparison was made of the results obtained without sample decomposition, with microwave mineralization of the sample behind the column and in the system HPLC-ICPMS [20].

In determination of arsenicbetaine in marine food sample (fruit of the sea) the limit of detection was 0.68-27.20 pg/mg for fresh sample extracted by the system methanol/water, with preliminary chromatographic separation (HPLC) and HGAAS detection. In this experiment the eluate from the chromatographic column was subjected to mineralization with microwave heating, then it was cooled in ice bath and passed to the hydride generation chamber [21]. In determinations of As (III), As (V), MMAA and DMAA the most important is pH of the reaction environment. The effect related to the analytic signal dependence on pH is compensated for by an addition of L-cysteine in the reaction of reduction of As (V), MMAA and DMAA to sulphur-organic compounds of As (III), taking part in generation of hydrides. The effect has been used to determine arsenic in samples of urine with the use of a chromatographic (GC) separation of arsenic compounds and mineralization with microwave heating [22].

In discussion of works devoted to determination of arsenic by AAS with generation of hydrides, we cannot disregard the attempts made with the flow-injection system (FLA), used instead of the flow system or the batch system - now of decreasing interest. Using the flow-injection system the limits of detection were much lower 0.04 ng (0.1 ng/mL) than those achieved with the use of the flow system 4 ng (1 ng/mL) and the batch system 0.6 ng (0.06 ng/mL); moreover, at a small use of the sample volume 0.4 mL in FIA, 4 mL in the continuous system and 10 mL with the batch system [23]. The authors of this work provide a list of references concerning determination of arsenic in the injection systems for generation of hydrides in AAS. The detection limits reported by different authors vary from 0.06 ng/mL to 0.15 ng/mL for samples of natural waters, 0.15-0.4 ng/mL for extracts from biological material samples or soil samples to the analysis rate of 20-220 samples per hour depending on the analytical system used [23]. The injection method, similarly to the flow method, permits carrying out the mineralization of the sample and reduction of As (V) to As (III) in the online system at the limit of detection of 0.20 ng/mL with the use of potassium iodide and L-cysteine for the reduction of As (V) to As (III), achieving the determined amount of As (III) of 0.25 ng/ml [24]. Because of low use of the sample the injection method was successfully applied when the sample was prepared off-line, e.g. mineralised [16].

The speciation study by AAS can be performed directly using different condition in the reaction of hydride generation and arsenic compound reduction from (V) to (III) by different reagents. Determination of As (III) was performed in a medium with HCl at a very low concentration (~ 0.03 mol/L) and total arsenic was determined after on-line reduction of As(V) to As(III) by potassium iodide.

The performance of some on-line reduction systems in different temperatures (100 - 140°C) has been compared and no interference from Cu, Ni, Co and Se has been detected. The detection limit in determination of the total contents of arsenic was 37 pg/mL, while for the selective determination of As(III) it was 111 pg/mL [25]. The authors of 5] applied the on-line reduction (80 s in a loop heated to 80°C) by potassium iodide for determination of the total content of arsenic reaching the limit of detection of 0.6 ng/mL. The determination of As (III) carried out at pH 6 in w citrate buffer ensured a similar detection limit. The reduction of As (V) to As (III) by L-cysteine [26, 27] (in a few minutes) enables speciation determination of As (III) and As (V) in samples of natural waters (river, sewage and mineral), at the detection limit of 0.01 ng/mL [28]. Direct speciation determinations in the flow-through systems can be also performed with injection sample supply [7, 8, 25, 29].

The AAS with generation of hydrides seems suitable for analysis of the majority of environmental samples, in combination with different methods of preconcentration [6, 7, 9-12, 30, 31], mineralization [13, 16], and separation [18-21]. An interesting idea was to replace the chemical generation of hydrides by their generation in electrochemical reactor in the electrode reaction of As (III), which requires reduction of As (V) to As (III), by potassium iodide or L-cysteine. Significant interferences from Ni, Cu, Co and Cr appear at their concentrations of 0.1 mg/mL, but they do not affect determination of environmental samples [32, 33]. Another proposition is a simplification of the construction of the hydride generation chamber so that hydrides are generated on a glass sinter to whose surface the sample and the reagents are supplied and the hydrides are carried by the stream of carrier gas to the atomiser [34]. The analytical possibilities in the study of environmental samples are improved when the sample is not supplied as a solution but as a homogeneous slurry [23]. This method has been applied for determination of arsenic in tobacco leaves, reaching a relative standard deviation (RSD) of 7.6% and a good agreement with the values in certified reference materials [35]. The application of hydride concentration on the

walls of the graphite tube followed by atomization allows a detection limit of about 0.15 ng for 1 mL sample [36].

Another group of papers report results of determinations of arsenic in different natural samples. Results of speciation analysis As(III)/ As (V) in water samples from Poznan lakes are given in [37], the total content of arsenic in surface waters from different areas in [38, 39] and underground waters in [40]. The detection limit achieved in the studies was 0.15 ng/mL, which permitted determination of arsenic in water environment.

The use of AAS with hydride generation in routine determinations in commercial laboratories is described in the document ISO 11969 [41] in Polish translation PN-ISO 11969 [42]. The document recommends off-line As (V) reduction to As (III) by potassium iodide and mineralization by sulphuric (VI) acid and hydrogen peroxide.

Determination of Antimony

The presence of transition metals Fe, Co, Ni, Cu in the sample may affect the process of hydride generation when antimony is reduced by sodium borohydride and thus cause a decrease of the antimony analytical signal. However, the interferences appear at high concentrations of the metals, of an order of a few tens [43], much higher than the environmental concentrations. There is also a possibility of other interferences from the other metals forming hydrides, which can form binary systems in gas phase, but they can be reduced by using multielement standards [44].

The determination of antimony in solid samples is performed after mineralization (microwave heating [45]) or extraction of antimony compounds. Similar to determination of arsenic [12], good results are obtained after extraction with xantogenian, separation of Fe, Pb, Sn and other metals by extraction with cyclohexane in acid medium, followed by reduction of Sb (V) to Sb (III) by potassium iodide in order to determine the total content of antimony at the detection limit of 20 ng/g sample [46].

The speciation analysis of antimony concerns mainly the separation of Sb (III) and Sb (V) compounds [45, 47]. For determination of total content of antimony, Sb (V) compounds are subjected to reduction by potassium iodide [47], potassium iodide with addition of ascorbic acid [45] or L-cysteine [26, 28], and the determination procedure is performed in the presence of hydrochloric acid [47]. Determination of Sb (III) was performed in the presence of citric acid, whose concentration was optimised (6% for the injection system and 4% for the continuous system), reaching a detection limit of 0.007 ng (25 *y.L)* for the injection system and 0.21 ng/mL for the continuous system [47]. The application of the injection system for determination of antimony has been discussed in [23]. Speciation determination was performed after pre-concentration of antimony compounds on ion-exchange columns (detection limit 1.5 pg/mL) and graphite cell walls (detection limit 5-20 pg/mL). When determining antimony directly from solid samples extracts, the detection limit achieved was 0.08 ng/mL extract [23]. Replacement of a continuous system by injection supply of the sample means that much smaller volume of the sample is required for determination. In the examples illustrating the use of the injection system for determination of antimony in natural waters the detection limit varied from 2.1 to 0.06 ng/mL, depending on the volume of the injection loops (50-850 µl), with the precision of 10.0-0.8%.

Speciation analysis Sb (III)/Sb (V) has been made for water samples from Poznan lakes [37], while total content of antimony was determined in surface waters from different areas [38, 39] and underground waters [40]. A detection limit of 0.15 ng/mL permitted determinations of antimony in natural water samples.

Speciation analysis is facilitated when the sample is used not as a solution but as a slurry and hydrides are generated from the sample in this form [23, 45]. According to another proposition hydrides are generated on the surface of glass sinter and carried by a carrier gas to the atomiser [34]. The limit of detection can be further reduced by concentration of hydride on the walls of graphite tube covered with zirconium at 500°C-750°C, or with Nb-Ta-W at 600°C-750°C, when the limit of detection can reach 0.010 ng for a 1 mL sample [36].

Determination of Selenium

The recommended analytical conditions for routine determinations of selenium in commercial laboratories are given in the document ISO 9965 [47]. According to this document the reduction of Se (VI) to Se (IV) should be carried out by hydrochloric acid at a temperature below 100°C, with mineralization by sulphuric (VI) acid and hydrogen peroxide. Similar to arsenic [4, 5, 25] and antimony [43] determinations, some interferences from the transient metals Cu, Ni, Fe [48, 49] can appear when these metals occur in concentrations much higher than in ordinary environmental samples. In determinations of selenium, interference can also be due to elements forming volatile hydrides such as As, Bi, Sb, Sn (similar to other elements determined by the method with generation of hydrides [44]). An approximate mechanism of the interference can be expressed as [50]:

$$M + H_2Se \Leftrightarrow MSe + H_2 \qquad M = As, Bi, Sb, Sn.$$

The disappearance of free atoms in the absorption chamber of the atomiser (quartz tube) is caused by a change in the character of the surface as a result of deposition of interfering substances on the walls. Moreover, bismuth is deposited in the tubes supplying the analyte also leading to interference related to the sample transportation - the loss of the element analysed as a result of distribution of hydrogen selenide. Interference in the periodic system is greater than in the flow-through system. However, it should be noted that the tolerance of particular interfering substances (a ± 10% change in peak height) varies, according to different authors, from 0.01 - 800 µg/mL, so at concentrations higher than environmental ones [50]. Moreover, interference can be compensated for by multi-element calibration [44].

Low concentrations of selenium in environmental samples require a determination method with low limits of detection, which could be used (on- or off-line) after

preliminary concentration of the analyte. The application of aluminium microcolumn to concentrate the analyte washed out from the column to the system of hydride generation allows a 50-fold concentration of the analyte for samples of 25 mL volume and a detection limit of 6 pg/mL. The use of this column and on-line reduction enables speciation determinations [51]. The concentration of hydrogen selenide in a cryogenic trap leads to detection limits below 2 pg/mL for a sample of 30 mL volume. Selenoorganic compounds are mineralised by disulfide peroxide in the presence of strong acid [52]. Using co-precipitation of selenium (IV) compounds with lanthanum hydroxide (like in determination of arsenic [9]) and solving the precipitate in hydrochloric acid to generate hydrides, the detection limit achieved was 1 pg/mL for the sample volume of 6.7 mL.

The procedure was used for determination of selenium occurring at levels below 0.01 ng/mL in drinking waters [53]. The procedure was improved by on-line addition of the precipitating substance [54].

Selective determination of Se (IV), Se (VI) and Se (-II, 0) at a level of pg/mL [55] was achieved when applying analyte concentration and ion-exchangers. The same group of researchers proposed optimisation of the analyte concentration for determinations with hydride generation and proposed a procedure for determination of total selenium and selenium (IV) in samples of surface waters reaching the detection limit of 5 pg/mL [56]. The application of strong anionite in the system for hydride generation allowed getting the detection limit of 0.12 pg/mL for a 10 mL sample. The system has been successfully used for analyses of natural water samples [57]. Another possible solution is concentration of selenium formed as a result of decomposition of selenowodoru on the walls of the graphite tube at 700°C. The detection limit obtained was 36 pg for a 2 mL sample. The method was applied for determination of selenium in selenosugars after their mineralization by disulfate peroxide [58]. Using a similar procedure of concentration in the graphite tube at 250°C, the obtained detection limit was 0.06 pg/mL for a 1 mL sample. The method was validated for reference materials and then applied for determination of selenium in urine samples [59].

Determination of elements in solid environmental samples must be preceded by their mineralization or extraction of a given element. Mineralization can be performed by a combination of nitric (V) acid, sulphuric (VI) acid and hydrogen peroxide at microwave heating [49]. For decomposition and mineralization of organic tissues (fish) three procedures have been proposed:

a) with magnesium nitrate and nitric (V) and hydrochlo ric acids,
b) with sulphuric (VI) and hydrochloric (VII) acids and in a closed bomb with nitric (V) acid.

The determinations were performed for reference materials and environmental samples for selenium concentrations at a level of 1 µg/g sample getting similar results for each method [60]. The reference materials made of clinical samples were mineralised by nitric (V) and sulphuric (VI) acids in a closed microwave heated system [61]. The microwave heating under reflux in the presence of a mixture of mineral acids and hydrogen peroxide has been discussed in [14]. The performance of the two methods (i.e. that with microwave heating and that with heating under reflux in determination of selenium) was compared in [14]. The determination of selenium was performed at its concentration below 0.5 µg/g sample. In analysis of biological samples a mixture of nitric (V), sulphur (V) and hydrochloric (VII) acids was applied for deep mineralization [17]. For extraction of selenium compounds from geological samples the following two procedures were applied: heating at 110°C with nitric acid for 3.5 hours or extended (24h) heating with aqua regia in water bath. Moreover, the authors of [62] compared the effectiveness of procedures of selenium extraction from geological samples by different mineral acids (nitric (V), sulphuric (VI) and hydrochloric and their mixtures.

The separation of the speciation forms of selenium was performed using a liquid chromatograph HPLC and detection by AAS with hydride generation. Different selenium compounds were separated on an anion-exchange column. For the compounds of Se (IV), Se (VI) and trimethylselenium the obtained detection limits were 1.4, 2.2 and 1.2 ng [63]. The chromatographic separation of selenium compounds was reported in many works [51, 56, 64]. In another approach the speciation determination of selenium (Se (IV), Se (VI) and organic selenium compounds) was performed on the basis of different boiling points using a cryogenic trap [52] or on the basis of different kinetics of hydride formation for Se (IV) and Se (VI) compounds after mineralization of organic compounds [17].

Similar to determinations of arsenic and antimony, many authors have used the injection system of sample supply [65]. With the use of sample concentration by co-precipitation [53, 54] and ion-exchange [57] the achieved detection limit was 0.001 ng/mL and 0.12 ng/mL, respectively. The content of selenium was also determined in human blood serum by the direct method at a detection limit of 1.2 ng/mL [66]. Different authors applying different methods of sample preconcentration reported having achieved the detection limit of 1-2 pg/mL at a frequency of analysis of 33-50 samples per hour. In determination of selenium in biological and clinical samples, (extracts after mineralization) the detection limit obtained was of an order of 1 ng/mL at a frequency of analysis of 90 samples per hour. Table 1 presents the main analytical problems discussed in the hitherto published reports, for different kinds of samples studied.

Determination of Arsenic, Antimony and Selenium by Atomic Absorption Spectrometry with Atomization in Graphite Furnace

Determination of Arsenic

Absorption atomic spectrometry with atomization in graphite furnace allows determination of arsenic at a level of a few ng/mL. The detection limit in direct determinations is ~2 ng/mL, the method requires optimisation (temperature programme and modifiers) taking into

Table I. A survey of references concerning particular analytical problems related to determination of arsenic, antimony and selenium by hydride generation atomic absorption spectrometry.

Analytical problem	Samples	References
As		
Interferences	model, reference materials	3, 4
Concentration	model, water, biological material, sediments	6, 7, 9-12, 30, 31,
Extraction and mineralization	biological material	13, 16
Injection analysis	model, clinical and biological materials	7, 8, 16, 23, 24, 29, 30, 69
Speciation analysis	model, water, biological, clinical materials, sediments	5-7, 10, 11, 13, 18-22, 25, 29, 30-32, 67, 68
Detection in chromatography	model, water, biological material	19-21, 29
Sb		
Interferences	model,	43, 44
Concentration	reference materials	36
Extraction and mineralization	soil	46, 62
Injection analysis	water, soil, clinical and biological materials	23, 47
Speciation analysis	water, clinical, sediments	26, 28, 45, 47
Se		
Interferences	model, water	44, 50
Concentration	water, model	48, 51-55
Extraction and mineralization	grunty, biological	14, 44, 49, 60-62
Injection analysis	model, water, clinical, biological, soil	23, 53, 54, 57, 66
Speciation analysis	water, model, clinical	51, 55-59, 63
Detection in chromatography	model, clinical	63

regard the type of the sample [69]. In environmental samples the concentration of arsenic is often below the detection limit of a given analytical method, therefore, many authors are concerned with the techniques of sample preconcentration. Using for this purpose tionalid supported on polyacryl resin as a sorbent, the detection limits obtained were 0.02 ng/mL for As (III) and 0.3 ng/mL for As (V). Moreover, taking advantage of the fact of selective absorption of As (III), speciation measurements were performed in samples of river, well and mine water [70]. The preconcentration of arsenic compounds was also performed using sorption on polyuretane foam with dicarbaminiane, which gave a detection limit of 0.06 ng/mL in determinations of water samples [71]. Another method of analyte preconcentration is based on ion-exchange, which has been used (in the hydride generation version) for speciation determinations of reference materials [72]. Other authors applied extraction of arsenic compounds in the form of molybdenium-arsenic acid by izobutylmethyl ketone (IBMK) and for determination of the organic phase they achieved the detection limit of 0.58 ng/mL, for 1% absorption [73].

For determination of arsenic in solid state biological samples the method of extraction by chloroform and tetrahydrofurane was used, the organic phase was introduced in pulses to the graphite furnace. The characteristic mass of 26 pg arsenic in a 20 µL sample was obtained, which corresponds to the detection limit of ~ 1.3 ng/mL [74]. The solid samples were dissolved in hydrofluoric acid in a closed system heated by microwaves, and then by boric acid. The conditions of determination were optimised using nickel, gallium and palladium salts as modifiers. The detection limit obtained was 2 ng/mL [75]. Solid samples were also decomposed by a mixture of nitric (V) acid and hydrochloric (VII) acid with the addition of potassium iodide or hydrasine. After the interference study and optimisation of analytical conditions the detection limit obtained was 0.30 ng/g sample [76]. The authors of [77] applied the decomposition by nitric acid (V) and potassium permanganate (VII), while those of [78] applied direct pulse introduction of slurry to a graphite furnace reaching the detection limit of 1 µg/g [78].

The speciation determination concerning mostly a discernment of As (III) and As (V) was performed after selective sorption of As (III) compounds on polyacryl resin [70], or sorption of the complex As (III)-DDTP (ammonium diethyldithiophosphate) on a gel column with the phase C-18, reaching the detection limit of 0.15 ng/mL [79]. The authors of [80] applied selective retention of As (V) compounds in ion chromatography. The ion-exchanger was an organocyan system and in the spectrometric determinations a number of modifiers were used (Pd, Mo, Zr, W), they finally recommended the use of Pd+W+citric acid. The method was applied for analysis of water samples. For selective determination of As (III) and As(V) the authors of [81] used extraction by ammonium butyldithiophosphate, obtaining the detection limit of 6 pg/mL for the two forms of arsenic. The above procedures were used to determine arsenic in natural waters [81].

Many authors have been concerned with interference from different elements or chemical compounds in different analytical systems in methods of arsenic determination [82]. Results of a study on interference from phosphates in thermal decomposition of arsenic compounds and molecular phosphorus (P_2) in spectra have been discussed in [83]. It should be noted that the interference appears at concentrations of phosphates at a level of a few tens or a few hundreds µg/mL [84]. The authors of

[85] present a comprehensive study of all kinds of interference: those following from molecular absorption of As_2, or related to the processes taking place in the atomiser, the effect of the surface (ordinary graphite, glassy graphite), the effects related to modification of the matrix (Ni, La), and the effect following from the use of a platform. A more detailed study on the effects related to molecular absorption (As_4, As_2) is presented in [86]. The interference related to the matrix can at least partly be controlled by the modifiers. Spectral interference due to molecular absorption can be eliminated by applying background correction [87] (a particular case based on the use of a deuterium lamp is described in [88]). The effectiveness of the background correction technique with a source of continuous radiation (deuterium or wolfram lamp) and that based on the Zeeman effect has been compared in [89]. The latter was proved very effective in reducing interference due to aluminium and phosphorus. The effect of frequently used nickel and palladium modifiers involves the formation of NiAs, $NiAs_2$ and PdAs of the boiling points ~ 800°C (for the compounds with nickel) and ~ 900°C-1100°C for PdAs, in the phase of thermal mineralization. Similar compounds are formed with copper and cobalt, when these two are used as modifiers. The inter-element bonds are formed at a slow (100°C/s) temperature increase [90]. The mechanism of the reaction of palladium was studied by mass spectrometry coupled with AAS, revealing the formation of $Pd_nAs_mO_l$, compounds undergoing decomposition to PdAs in the process of atomization and later to free As atoms As [91].

Determination of Antimony

Determinations of antimony are also not free from interference similar in nature to those in determining arsenic discussed in [82, 83, 86, 88, 89, 91]. The spectral interferences due to the presence of P_2 molecules are described in [83]. Interference related to the presence of iron and aluminium together with the methods of their elimination by background correction with a source of continuous radiation or based on the Zeeman effect are described and compared in [89]. The background correction with a source of continuous radiation does not eliminate the influence of titanium, aluminium and iron, which are, however, eliminated by the Zeeman effect based correction. A study of the optimisation of the analytical method (the temperature programme) is reported in [92].

The limits of detection offered by AAS with atomization in a graphite furnace are of a few ng/mL, therefore often for determination of environmental samples the analyte must be pre-concentrated to decrease this limit. The use of extraction to polyuretane solid state with dithiocarbaminate the detection limits of 0.06 ng/mL were achieved and the method was applied for determination of antimony in water [71]. Selective determination of Sb (III) forming complex with lactic acid was possible after extraction by lactic acid and malachite green because Sb (V) did not undergo extraction, and the detection limit obtained was 0.01 ng [93]. Applying complexation with ammonium pyrolidinodithiocarbaminate (APDC) on-line and elution with ethanol the detection limit was decreased to 0.021 ng/mL. Spectrophotometric analysis of one sample was performed parallel to preconcentration of the next sample to be studied, which shortened the time of analysis [94]. The determination based on selective pH-dependent sorption of Sb (III) and Sb (V) were carried out for the samples of water and snow reaching the detection limit of 30 pg/mL [95]. Using activated aluminium oxide as a sorbent and extraction by HC1, a concentration coefficient of 400 was obtained at 80% recovery [96].

To analyse solid samples, the element studied should be first transferred to a liquid phase by extraction or mineralization of the sample. Another approach, based on pulse supply of slurry into the graphite furnace, applied to determination of Sb in soil and sediment samples led to a detection limit of 0.03 μg/g [78]. The pulse supply of slurry into the graphite furnace was also applied in determinations of dust and volatile ashes mineralised by nitric acid (V) [97]. The results of antimony determination in a solid sample of wolfram oxide using direct atomization were compared with those obtained by the method involving dissolution of the sample in ammonium hydroxide with an addition of tartaric acid. The detection limits obtained were 0.1 and 1 mg/g sample, respectively [98].

Determination of Selenium

The optimisation of the analytical method for determining selenium has been discussed in [69]. With the optimised temperature programme and optimum choice of a modifier the detection limit obtained was 1.5 ng/mL. Validation of the analytical procedure and a comparison of different methods of determination of selenium (AAS with atomization in the graphite furnace, AAS with hydride generation and pre-concentration of hydrides in the graphite furnace) are presented in [99]. The parameters of the analytical method, characterisation of the calibration and the influence of matrix have been discussed. For determination by AAS with atomization in the graphite furnace the detection limit was 1-2 ng/mL. A comparison of different methods of selenium determination (AAS with atomization in the graphite furnace, AAS with hydride generation and Inductively Coupled Plasma with emission detection and mass spectrometry) has been performed in the aspect of determination of biological samples [100]. The detection limit obtained for AAS with atomization in the graphite furnace was 14 ng/mL, which was much better than for ICP-AES (76 ng/mL) and slightly worse than for ICP-MS (6 ng/mL) and HGAAS (8 ng/mL). The detection limit of AAS with atomization in the graphite furnace and HGAAS obtained for analysis of biological samples were 11 and 10 ng/mL, respectively [101].

The detection limits of direct determinations, usually of an order of ng/mL, are often insufficient for determinations of environmental samples, which means that it is necessary to apply preliminary concentrations of the analyte off- or on-line. When using sorption of Se (IV) complex with bizmuthiole on active carbon we could determine Se (IV) and after reduction of Se (VI) by HCl we could also get the content of total selenium in samples

Table 2. A survey of references concerning particular analytical problems related to determination of arsenic, antimony and selenium by hydride generation atomic absorption spectrometry.

Analytical problem	Samples	References
As		
Interferences	model, clinical, water	69, 82-87, 89, 90
Concentration	biological, water	70-72
Extraction and mineralization	biological, industrial	74-77
Speciation analysis	water	70, 73, 79-81
Sb		
Interferences	biological, model	83, 89, 92
Concentration	clinical, water, model	71, 94-96
Extraction and mineralization	water	93
Speciation analysis	water	93, 95
Se		
Interferences	model	69, 82, 83, 89
Concentration	biological, water	71, 102, 103
Extraction and mineralization	biological	104
Speciation analysis	sediments, water	102, 105

of water and sediments [102]. Having performed extraction of the analyte to polyuretane solid phase with dithiocarbaminate and desorption by isobutyl-methyl ketone, for water samples the detection limit achieved was 0.08 ng/mL [71]. The application of ion-exchange (anionit) and pulse supply of slurry of the ionite to the graphic furnace led to the detection limit of 0.05 ng/mL at 100-fold concentration of natural water samples [103]. For analysis of solid state biological samples the method applied involved mineralization by nitric acid and microwave heating, then extraction by diethylodithiocarbaminate solution in chloroform, which allowed determination of the organic phase at the detection limit of 2 ng/g for a sample of 2 g [104].

AAS with atomization in the graphite furnace has been used as a selective method for detection in chromatographic determinations. The application of separation of selenates (IV) and (VI) by ion chromatography ensured the detection limit of 8 ng for Se (IV) and 11 ng for Se (VI) in a sample of 100 µL [105].

A number of authors have been concerned with different kinds of interferences (due to the presence of specific elements, compounds and different analytical systems) affecting the method [82]. The problems with interference caused by the presence of phosphates in thermal decomposition of selenium compounds and molecular phosphorus (P_2) in the spectra, have been discussed in [83]. Interference appears at the phosphate concentrations of a few tens or a few hundred µg/mL. The use of background correction with a source of continuous radiation does not eliminate the effect of phosphorus or iron, which can be removed on the background correction with the Zeeman effect [88]. The application of the Zeeman background correction in determining clinical samples is discussed in [106].

One of the most important problems in determination of selenium is the choice of a proper modifier for specific analyses. For direct determination of selenium in fruit juices the following modifiers have been considered Ni/Cu, Pd/Mg, Pt/Mg, Pt/Ni, Pt/Cu, choosing finally Pt/Ni one for which the detection limit obtained was 28 pg for a sample of 10 µL [107]. For determination of selenium in fly ash two modifiers were used: a cadmium-palladium one, reaching a detection limit of 7 ng/mL solution after mineralization by nitric (V) acid and hydrochloric (VII) acid [108] and a mercury-palladium one - reaching a detection limit of 7.45 ng/mL solution [109]. The use of a palladium modifier (reduced by ascorbic acid) for determinations of selenium in highly pure iron led to a detection limit of 0.01 µg/g sample [110]. The mechanism of platinum and rhodium modifiers involving a formation of PtSe and RhSe of higher temperature of atomization was studied in [111]. The performance of palladium, nickel and copper as modifiers in determination of selenium was analysed in [112], whose authors finally recommended the use of thermally reduced palladium [113]. The performance of the metals Pd, Pt, Rh, Ru, Ir as modifiers was studied in [114] whose authors reported similar maximum temperatures of thermal mineralization of about 1200°C when applying all the modifiers considered. In [115] the effect of the presence of magnesium, copper, nickel, palladium and Cu/Mg and Pd/Mg in determinations of selenium in model samples was compared and the use of the system Pd/Mg was recommended. The studies of using different modifiers (Mg/Ni/Pd) for determination of selenium (arsenic and antimony) by graphite furnace atomic absorption spectrometry and atomic absorption spectrometry with hydride generation and in-situ preconcentration in graphite tube were described [116]. The performance of palladium as a modifier was also studied by mass spectrometry in [91]. The results indicated the formation of palladium-selenium compounds $Pd_nSe_mO_l$], undergoing decomposition to PdSe and then to free Se atoms. Table 2 presents the main analytical problems discussed in the above quoted papers and the kinds of samples they refer to.

Atomic absorption spectrometry has been widely used in determinations of arsenic, antimony and selenium. It seems rather complementary to than competing with other methods for determination of these elements, in particular those based on plasma generation (ICP or MIP). The possibility of speciation determination offered

by GFAAS (Table 2) and the method with hydride generation (Table 1) ensures a special position of this method among the other analytical methods, especially in determinations of environmental samples. Recently, a new approach to speciation determinations of arsenic antimony and selenium has been proposed, based on a combination of chromatographic techniques for separation of different species with their selective detection by AAS with hydride generation. This approach is very promising and will determine the direction of development of both analytical equipment and methods.

Summary

This paper presents determinations of arsenic, antimony and selenium by the method of atomic absorption spectrometry, with atomization in a graphite tube and with generation of hydrides. These experimental methods enable determination of the elements studied on a very low level of concentrations (ng/ml), which means that the majority of samples can be subjected to the measuring procedures without preliminary preparation. Thanks to the accessibility of atomic absorption spectrometry, it has been applied for determination of arsenic, antimony and selenium in a wide range of samples.

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