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Review

Determination of Different Forms of Arsenic, Antimony and Selenium in Water Samples Using Hydride Generation

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Abstract

This paper shows speciation analysis of arsenic, antimony and selenium using hydride generation atomic absorption spectrometry. Determining different forms of given elements (forms on different oxidation stages: As(III)/As(V), Sb(III)/Sb(V), Se(IV)/Se(VI) and forms bound with organic matter) is based on different kinetics of hydride generation for forms on different oxidation degrees. This paper shows steps for speciation analysis as described in literature, the main procedures and reagent used in different studies.

Keywords: arsenic, antimony, selenium, speciation, hydride generation, atomic absorption spectrometry

Introduction

Speciation is the identification and quantitative determination of different forms or phases in which a given element occurs in a given substance, established in so-called speciation analysis [1]. In the context of the study of water environment, the form or phase of occurrence of a given element can be defined according to different criteria [2, 3]:

- as a certain compound or degree of oxidation of a given element, their identification and determination is the subject of individual or detailed speciation,
- as certain functional groups or forms of particular biochemical or hydrogeochemical functions: bioavailable, mobile, exchangeable forms and others,
- according to analytical procedures used for their identification and determination: reagents, instrumental procedures, etc.
- according to the physical distribution of substances: suspended and dissolved forms (similarly, according to cytological presence of elements - the forms of the elements as they occur in different cellular organs),
- combining compounds of similar properties, or a similar form, e.g. combining compounds with a given element at the same oxidation degree, e.g. the speciation analysis of As (III)/As(V); this is a pragmatic approach when it is impossible or too difficult to perform individual speciation analysis.

The significance of determination of not only the total

Corrspondence to: Prof, dr hab. J. Siepak content of a given element but its speciation forms follows from different toxicological effects of different speciation forms of a given element on the ecosystem. For example the inorganic compounds of selenium are a few hundred times more toxic than the methylated forms, a similar situation takes place for arsenic, while the compounds containing antimony (III) are more toxic than those containing antimony (V). The speciation analysis of arsenic, antimony and selenium by the method of atomic absorption spectrometry with generation of hydrides is based on the established different kinetics of the reaction of hydride generation by elements at different degrees of oxidation, depending on the pH of the reaction environment.

Speciation of Arsenic and Antimony

In the environment of weak organic acid (citric acid [4-8], acetic acid [4-7, 9], tartaric acid [4, 7]) or a buffer system of a relatively high pH (or in an alkaline medium at pH = 9 [10]), the appropriate hydrides are formed almost exclusively from the inorganic compounds with a given element at the 3rd degree of oxidation, whereas the compounds with a given element at the 5th degree of oxidation do not react. The reaction of hydride generation in the presence of a low concentration of hydrochloric acid (0.02 mmol/mL) is similar [6]. In the environment of a strong reducing acid (HC1) at pH < 1, the hydrides are formed with the element bonded in both inorganic and organic (monomethyloarsenic acid MMAA and dimethyloarsenic acid DMAA) compounds, irrespective of the oxidation degree of a given element, however, the compounds containing a given element at the fifth degree of oxidation react slower and in a smaller amount. The hydrides are formed as a result of reduction of arsenate (III), arsenate (V) and methyl derivatives of arsenic (MMAA, DMAA) [7, 11] and no other arsenic-organic compounds [12]. At a high concentration of HC1, reduction of methyl and dimethyl derivatives of arsenic also practically do not take place [4]. The generation of hydrides with the compound of As (V) is 10% less effective than with those of As (III). A two-stage mechanism of the reaction of the former has been suggested, including a reduction of As (V) to As (III) and then generation of hydrides [13]. The course of the reaction depends on the pH value of the environment of the reaction. The first stage of the reduction of As (V) to As (III) is much slower than the generation of hydrides at pH > 5, the reduction of As (V) requires a pH value close to 1. At this pH also a reduction of MMAA and DMAA takes place [13], and with increasing concentration of HC1 the yield of the reduction of the methyl derivatives decreases, reaching practically zero above the HC1 concentration of 5 mmol/mL [4]. The reduction of the methyl derivatives of arsenic gives [14]:

$$\mathrm{MMAA} \text{ -> } \mathrm{CH3AsH_2};\ \mathrm{DMAA} \text{ -> } \mathrm{(CH_3)_2AsH}$$

characterised by the melting points of 2°C and 35.6°C [7].

Methyl derivatives of antimony react in the same way and give [15]:

$$\mathrm{CH_3SbH_2} \text{ and } \mathrm{(CH_3)_2SbH}$$

A differentiation between the inorganic forms Sb (III) and Sb (V) is based on the selective reduction of antimony compounds, dependent on pH. The reduction of Sb (V) practically does nor occur at pH 6-7, in general at pH above 2, but in these conditions Sb (III) undergoes reduction [10]. An environment favourable for selective reduction of Sb (III) in the presence of Sb (V) is that of citric acid [16-18], tartaric acid [16,19] or boric or acetate buffer [16]. Moreover, the citric acid complex with Sb (V) does not undergo reduction and does not form hydrides [10]. Speciation determination of antimony has also been performed with the sequential use of three inorganic hydrochloric acids, phosphoric (V) acids and sulphuric (VI) acids [14]. In order to determine the total amount of antimony in a given sample a preliminary reduction of Sb(V) to Sb(III) is necessary. This is performed in the off and online systems by different reducing reagents tin (II) chloride [20], hydrochloric acid, potassium iodide, ascorbic acid, L-cysteine and their mixtures (Table 1). The content of Sb (V) is then found from the difference between the total content of antimony and the content of antimony compounds with Sb (III).

The reaction of arsenic compounds with cysteine can be described as follows [21]:

1. reduction of As (V) prior to the reaction with borohydride:

$$2\ \mathrm{Cys\text{-}SH} + \mathrm{R_nAsO(OH)_3\text{-}n} \text{ -» } \mathrm{Cys\text{-}S\text{-}S\text{-}Cys} + \\ + \mathrm{R_nAs(OH)_{3\text{-}n}} + \mathrm{H_2O}$$

2. the reaction of As (III) with cysteine leading to cysteine complexes:

$$\mathrm{R_nAs(OH)_{3\text{-}n}} + \mathrm{(3\text{-}n)Cys\text{-}SH} \text{ -» } \mathrm{R_nAs(\text{-}SCys)_{3\text{-}n}} + \\ + \mathrm{(3\text{-}n)H_2O}$$

The arsenic compound reaction with potassium iodide occurs according to the scheme:

$$\mathrm{2KI + Na3AsO4 + 4\ HC1} \text{ -> } \mathrm{I_2 + NaAsO_2 + NaCl} + \\ + \mathrm{KC1 + 2H_2O}$$

and with hydrochloric acid according to:

$$\mathrm{2HC1 + Na3AsO_4} \text{ -> } \mathrm{Cl_2 + Na_3AsO_3 + H_2O}$$

Speciation of Selenium

The compounds containing selenium at the 6th degree of oxidation do not undergo reduction in the environment of a strong reducing acid (HC1) at pH < 1 and the hydrides are formed almost exclusively from the inorganic compounds containing Se(IV). The 60% reduction of Se (VI) to Se (VI) in the environment of HC1 (4-7 mol/L) at room temperature takes 7 days [22], while at elevated temperature (90-100°C) it is faster [23, 24]. The course of the reduction of Se (VI) to Se (IV) can be described as [25]:

$$HSeO_4^- + 3H^+ + 2Cl^- \rightarrow H_2SeO_3 + Cl_2 (aq) + H_2O$$

The time of the reaction usually varies from 20 to 45 minutes [23,26]. Considering the possibility of the formation of volatile chlorides, it is recommended to conduct the reduction of selenium (VI) compounds by HC1 in a closed system, at temperatures of about 140°C; however, too long heating can lead to the appearance of elemental selenium [22, 27]. The use of a closed system heated with microwave radiation in this process of reduction decreases the possibility of analyte loss [28, 29].

The reduction of Se (VI) to Se (IV) can also be realised with the use of hydrobromic acid [30, 31], a solution of potassium bromide and hydrobromic acid [30] or a 20% solution of potassium iodide KI with HC1 and thiourea (the latter system restricts the interference of transition metals - Ag, Au, Fe, Ni, Co, Pt, Pd, Os) [26].

In order to determine the total content of selenium a preliminary reduction of Se(VI) to Se(IV) is needed (Table 1). The reduction can be performed in the off and online systems with the help of HC1. The content of the compounds with Se (VI) is found from the difference between the total content of selenium and the content of selenium compounds with Se(IV) [10, 23].

Table 1. The reagents used for reduction of compounds of arsenic, antimony and selenium.

Reducing reagent	References
As	
L-cysteine	11, 21, 41, 44-50
L-cysteine + HCl	32, 46, 51
KI	41, 52-54
KI + ascorbic acid	5, 6, 7, 20, 32, 34, 43 ,46, 52, 55-57
Sb	
L-cysteine	48
L-cysteine + HCl	46, 51
KI + ascorbic acid	16, 46, 58
KI + HCl	18
Se	
HBr (HCl) + KBr	30
HBr	30, 31
HCl	30, 33, 54, 56, 59-63

Determining Forms Bound to Organic Matter

Determining the content of the elements bound to organic matter requires a preliminary mineralisation of the sample in order to release a given element from the

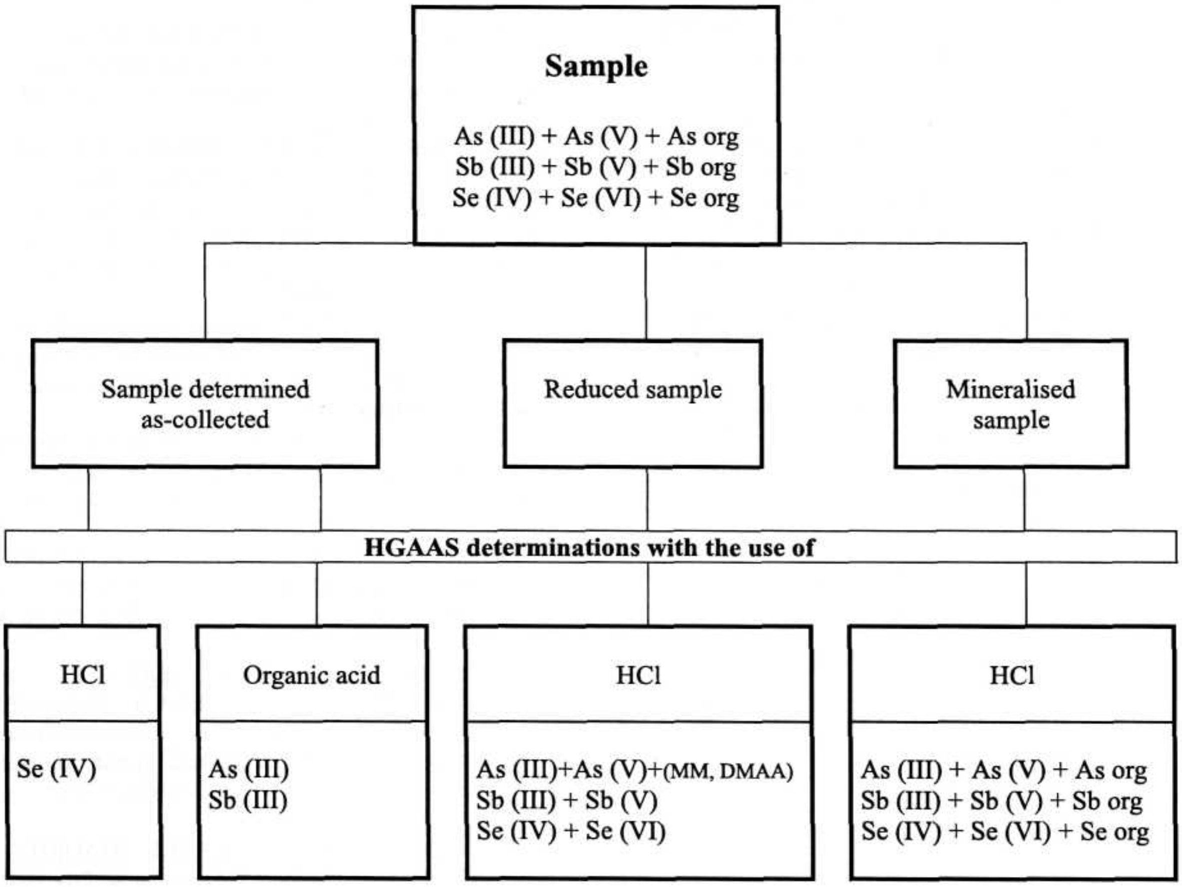

Fig. 1. A scheme of speciation analysis by HGAAS.

organic compounds. The mineralisation should always precede the determination of a given element by the method of hydride generation atomic absorption spectrometry (HGAAS). Different methods of mineralisation of water samples have been proposed: heating with oxidising reagents (nitric acid (V) [32], sulphuric acid (VI) [16, 33, 34, 35], aqua regia [36], persulphates [4, 36, 37, 38], permanganates [36]) in open systems under reflux [33, 34] or in closed systems (Teflon bombs [26]) often heated by microwave radiation [4, 23, 32, 35, 38-40], mineralisation with the use of UV radiation and oxidising reagents [23, 27, 35, 41, 42]. An important problem related to mineralisation of organic compounds is elimination of interference due to the oxidising reagent. The use of nitric acid (V) or hydrochloric acid and nitric (V) acid together can lead to a decomposition of arsenates (III) by the formed nitrogen oxides or nitrosil chloride [43]. Moreover, the presence of a strongly oxidising reagent disturbs the preliminary reduction of As (V), Sb (V) and Se (VI).

Conclusion

The general cycle of operations needed to perform a speciation analysis by the method of atomic absorption spectrometry with generation of hydrides can be described by the scheme presented in Fig. 1, (the differentiation between the suspended and dissolved fractions in the physical speciation analysis has been disregarded):

1. Determination of the content of As (III), Sb (III) and Se (IV) in as-collected samples, without any preliminary treatment,
2. Determination of the contents of As, Sb and Se in the samples subjected to preliminary reduction by different methods, determination of the total content of Sb and Se in inorganic compounds, determination of the total contents of As in inorganic compounds and in MMAA and DMAA, depending on the conditions of determination,
3. Determination of the total content of As, Sb and Se in samples after mineralisation of organic compounds and reduction,
4. Calculation of the contents of As (V), Sb (V), Se (VI) and elements in the organic matter [10].

The above scheme of the speciation analysis refers to the groups of the fractions under determination. It does not allow a determination of particular chemical compounds but the contents of a given element at a certain degree of oxidation As(III), As(V), Sb(III), Sb(V), Se(IV), Se(VI). The application of different processes (mineralisation, reduction) for separation of the determined fractions means that the procedure can be treated as operational speciation analysis. The results of speciation analysis give more information than the results of determination of an element's total concentration [2, 64].

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