

Analytical possibilities of generating volatile hydrides in optical emission spectrometry (HG-ICP-OES)

Part 1. Theoretical fundamentals of the process

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Introduction

In view of the growing awareness of the hazards of environmental pollution, monitoring of the content of chemical elements and toxic substances in the various components of the environment (air, water) and in food became a necessity. Compounds of arsenic form trace chemical constituents of ecosystems; seldom do concentrations thereof reach toxic levels, however, the closeness of the range of doses absorbed by organisms and of the toxic dose, requires, when one considers the widespread occurrence thereof, strict control [1].

The growing importance of analytical testing in research work [2], industrial process control and environmental quality assessment [3] has been observed in recent years; at the same time the requirements on the quality of test results are also growing. In modern world many important opinions and decisions depend on the results of chemical analysis. This applies to determination of both macro components, as well as elements and compounds present in trace amounts. These concentrations must remain under strict control and must be maintained at very low level. However, the problem of reliability of the results of inorganic trace analysis, despite the use of sophisticated instruments and application of well-defined procedures, still exists [4, 5]. Implementation of an appropriate quality control and assurance system in laboratory practice is becoming a matter of great importance [6, 7].

The Institute for Inorganic Chemistry in Gliwice has for many years been conducting research on the industrial applications of layered aluminosilicates. The results included the development of such processes as: modified process for obtaining bleaching clay with the use of acid activation of bentonite [12, 13], waste-free process for obtaining mineral sorbents from halloysite [14], as well as manufacture of organically modified clays by blending natural layered silicates (montmorillonite, halloysite or kaolinite) with an organic ammonium salt. Due to the ion-exchange properties of the clays, their inorganic cations are replaced with cations of organic compounds, and the products obtained (intercalates) are used in the manufacture of nanocomposites: polymer – layered silicate. The growing interest in the application of silicates and clays in nanotechnology stimulates the pursuit of sufficiently sensitive methods that would enable accurate and precise detection of the desired analytes in the materials mentioned.

Chemical analysis of materials with an aluminosilicate matrix, including various complex minerals, is still not a simple analytical procedure. Direct spectrometric determination of trace amounts of arsenic using optical emission spectrometry (ICP-OES) in solutions of inorganic matrixes studied, is characterised by relatively low sensitivity due to low efficiency of ionisation in plasma. The present paper, based on literature reviewed, assesses analytical possibilities of determining trace amounts of arsenic and other elements that form volatile compounds in environmental matter, with special consideration given to hydride generation.

Chemical characteristics and toxicological properties of arsenic

Arsenic is one of the elements the significance of which for the human organism is rising. Arsenic micro compounds of complex chemical properties arouse interest among scientists, becoming the subject of numerous studies. The reason for the way the presence and role of As compounds in the environment is now looked upon is the continuous development of analytical methods, toxicology, biochemistry, environmental chemistry and environmental protection [15].

Arsenic is widely distributed in human environment [16, 17]. It is present in more than 160 various minerals; the most common include orpiment (As_2S_3), realgar (As_4S_4) and arsenopyrite ($FeAsS$). Arsenic also occurs in the form of arsenides and arsenosulphides of heavy metals (Fe, Ni, Co, Cu). It belongs to group Va of the periodic table and exhibits amphoteric properties. Depending on the redox conditions in the environment, arsenic can have four oxidation states (As^3 , As^0 , As^{3+} , As^{5+}). However, it mostly occurs as As(V) in the form of $H_2AsO_4^-$ anion, and as As(III) in the form of H_3AsO_3 , which prevails under reducing conditions of low pH [15]. Depending on the concentration, exposure time, form of occurrence and oxidation state, the routes of absorption of arsenic compounds vary: digestive tract, skin, respiratory tract. Arsenic is a carcinogenic, mutagenic and teratogenic element; toxicity of arsenic compounds strongly depends on the form they are taken in. In general, the noxiousness of arsenic compounds is assumed to decrease in the following order:

$$AsH_3 > \text{inorg. } As^{3+} > \text{org. } As^{3+} > \text{inorg. } As^{5+} > \text{org. } As^{5+} > \text{arsenium compounds} > \text{metallic arsenic}$$

although there are inorganic As^{3+} compounds of low toxicity, as well as organic As^{5+} compounds much more toxic than the legendary white arsenic ($LD_{50} = 35\text{mg/kg}$).

Theoretical fundamentals and sources of errors in determination of elements that form volatile hydrides - literature review

Modern analytical methods enable direct multi-element analysis of samples, when concentration of the determined component is above the quantitation limit of the method. This condition is not met in many analytical tasks. In such cases the sample is pre-treated using various methods of enrichment or separation of the determined component from the principal constituents of the matrix. In the end the concentration of the analytes in the sample matrix is increased to above the quantitation limit of the analytical instrument, the matrix composition is made less complex and interfering components are removed from the sample, which allows the sensitivity of the method to be increased. For these reasons the CVG (Chemical Vapour Generation) technique in combination with two variations of atomic absorption spectrometry: cold vapour generation (CV-AAS) for Hg determination and volatile hydrides generation (HG-AAS), as well as in combination with optical

emission spectrometry (ICP-OES), atomic fluorescence spectrometry (AFS) and mass spectrometry (MS) for elements that form volatile hydrides, has become the basic analytical technique for determining the elements mentioned [18, 20]. By enabling the isolation of analytes from the environmental or organic matrix, which often strongly interferes or distorts analytical results, it provides low detection limits and allows for direct and selective determination of analytes in the samples tested [21].

The first to propose the hydride generation technique was Holak, who in 1969 applied Marsh's method of arsine evolution in combination with atomic absorption spectrometry AAS [22]. In 1978 the volatile hydride generation technique was combined with inductively coupled plasma (HG-ICP-OES: *Hydride Generation Inductively Coupled Plasma Optical Emission Spectrometry*) – since then a rapid development of this technique applied in trace analysis is observed, and the great interest taken in it is reflected in the large number of review articles [21, 23–33].

Hydride generation is a technique of introducing analytes in gaseous form into an excitation source, applied in spectrometric methods to determine chemical elements, the ions of which react with a reducing agent in an acidic medium to form volatile gaseous hydrides stable at ambient temperature [21]. Elements that are capable of forming volatile hydrides include, in addition to As, also: Bi, Ge, In, Pb, Sb, Sn, Se, Te and Tl. These elements show variable valency, and the process of reducing metal ions to hydrides has several stages [34]. The reaction between the acid and the reducing agent generates nascent hydrogen [35], which reduces the ions of the elements to their respective hydrides. The hydrides generated in the sample are washed out with a carrier gas (argon, rarely nitrogen or helium), separated in a phase separator from liquid reaction mixture (and from other reaction by-products: H_2 , CO_2 , H_2O) and carried to an appropriate detection system – atomizing system (AAS, AFS) or excitation source (ICP, MIP, DCP, GD [36, 37].

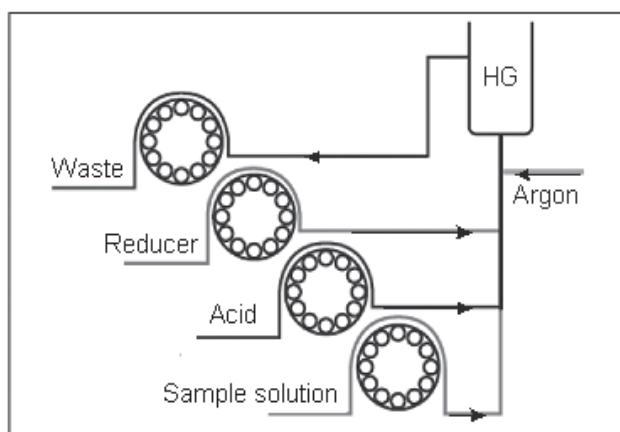


Fig. 1. Reactant flow diagram for an HG-ICP-OES system

The generation of a volatile hydride EH_n in a reaction of ions of element E, the oxidation state of which is $m+$, proceeds instantly in acidic aqueous solutions and can be described with the following equations [29]:

1. Formation of free hydrogen:



2. Reduction to hydrides:



The efficiency of hydride generation depends on a number of factors, such as: oxidation state of the element determined in the so-

lution; concentration and type of reducing agent; concentration and type of acid used; type and design of generator, material of which the separator and connecting tube between the separator and excitation/ionization source is made of; effect of the matrix and conditions of measurement [21, 29].

The valency of the elements determined has a great effect on measurement sensitivity. Elements in lower oxidation states form hydrides more readily. Therefore, when determining total element content, the form of the element in the sample analysed must be uniform [38, 39]. This step of initial reduction is a serious analytical problem and a potential source of errors [21, 29]. In the case of arsenic, in a weak organic acid medium (citric, tartaric, acetic acid) almost all of the hydrides are formed from inorganic compounds containing As(III), whereas compounds of As(V) do not react. On the other hand, in a strong reducing acid medium (HCl), at $pH < 1$, hydrides are formed from both inorganic and organic compounds (methylarsonic and dimethylarsonic acid) containing arsenic in the oxidation state of III and V, with the latter reacting more slowly and to a lesser extent [11]. Arsenic hydrides are formed exclusively by the reduction of arsenates(III), arsenates(V) and methyl derivatives of arsenic; other organoarsenic compounds do not form hydrides [21].

The initial reduction step can be effected in various ways, both in offline and online arrangements, using various reducing agents [21]. The most common, according to the literature, agents used to reduce As(V) to As(III) include: potassium iodide (KI) [41–43, 62], L-cysteine ($C_3H_7NO_2S$) [61, 62, 44–46], thiourea (CH_4N_2S) [34, 41, 47] and mixtures of potassium iodide with ascorbic acid ($KI + C_6H_8O_6$) [42, 48, 49, 61] or strong inorganic acid ($KI + HCl$) [50, 51]. It should be emphasized that multi-element analysis requires selection of a versatile initial reduction procedure to enable eventual selective determination of all analytes in the matrix of the tested sample. The differences in hydride generation kinetics, strongly dependent on the form of the element in the sample, became the basis of speciation analysis, which enables analytical differentiation between the various forms of elements [52–55].

In general, various reducing agents are used for hydride generation: Zn/H^+ , $Mg/Ti^{3+}/H^+$, Al/H^+ , $SnCl_2$; however, the most widely used is sodium tetrahydroborate(III), and its advantage over the other reductants consists in providing high efficiency of hydride generation, increased reduction reaction rate and decreased level of blank test. The applied reductant concentration depends on the method of hydride generation and acid concentration; a 0.05–10% $NaBH_4$ solution stabilized with NaOH or KOH is usually used [21, 29, 50].

Hydrochloric acid (0.02–10 mole/L) is commonly used for decomposing sodium tetrahydroborate (III) [21, 29, 50]. Aside from HCl, organic acids have also been used, such as: acetic and tartaric [56], citric and sulphosalicylic [57], oxalic [58], as well as other inorganic acids: nitric [59, 60, 61], sulphuric [60, 61], perchloric acid [62], and mixtures of acids, e.g. $HCl + HNO_3$ [63].

The designs of hydride generators also vary: in practical analysis the most widely used are those systems, where gaseous phase is separated from the sample solution and simultaneously the gaseous reaction products (hydrides, hydrogen and water vapour) are transferred to the excitation source (GLS - Gas Liquid Separator) [21, 29]. Fig. 1 shows a typical media flow diagram for a phase separating generator combined with ICP.

Of high importance in hydride generation is the connection between the separator and the excitation/ionization source. The generated hydrides may decompose on the internal surfaces of the generator and the conduit between the generator and the excitation source. It should be borne in mind that the stability of hydrides of the elements of group V of the periodic table, one of which is arsenic, decreases with increasing metallic character of the elements. It has been found that the degree of interaction between

the hydride and the surface of glass or other material is inversely proportional to carrier gas flow rate, and is directly proportional to generator size and internal surface area of the transfer conduit. The smaller is the dead volume between the hydride generator and the excitation/ionization source, the better [21, 29].

Typical interferences that occur in the hydride technique include [21, 24, 25, 29, 50]:

- *Spectral interference* associated with a group of chemical elements that form volatile species under the conditions of hydride generation; these elements include primarily transition group metals: Cd, Co, Cr, Cu, Fe, Ni, Zn, Ag, Au, Pd, Rh – present in the samples in concentrations 10-100 times higher than those of the analytes,
- *Kinetic interference* – for instance, dependence of relative analyte signal sensitivity on the volume of analysed sample,
- *Oxidation state interference* – e.g. the value of signal intensity measured for As(V) is by 20-30% lower than for As(III),
- *Chemical interferences*:
 - effect of inorganic acids used to prepare sample solution on efficiency of hydride generation – HF, even at low concentrations, may decrease the measured signal intensity of the analyte; the effects of HCl, H₂SO₄, HNO₃ are weaker in the case of arsenic than in the case of antimony [64],
 - effect of strong oxidizers: S₂O₈²⁻, MnO₄²⁻, Cr₂O₇²⁻, S²⁻ [66],
 - effect of difference in the oxidation state of the analytes in the measured sample and in the standard sample,
 - effect of the matrix – a matrix that contains heavy metals may form with the element determined scarcely soluble compounds or may cause adsorption or decomposition of the hydride formed on the precipitate, hindering thereby the transfer of the hydride to the excitation source,

Tests conducted by numerous researchers [50, 65÷67] suggest that alkali metals and alkaline earth metals, and some other elements: B, Al, Ti, V, Zr, Si and anions: CO₃²⁻, C₂O₄²⁻, Cl⁻, CN⁻, Br⁻, I⁻, NO₂⁻, NO₃⁻, S²⁻, SCN⁻, SO₃²⁻, SO₄²⁻ have little or no effect on the determination of volatile hydride-forming elements.

Authors of another publication [50] enumerate efficient methods of interference elimination, such as:

- addition of complexing agents: EDTA and DTPA [68÷72], KCN, KCNS [73]; thiourea and FeCl₃ [74, 75], sulphanilamide [76], L-cystine [36], L-cysteine, L-histidine [69], 1,10-phenanthroline [71], tartaric acid and other,
- treating the sample solution to remove interfering elements on ion-exchange resins [77÷79] or on activated carbon [80],
- separating the matrix by precipitating metal hydroxides [81] or coprecipitating with various carriers (lanthanum nitrate [82, 83], lanthanum hydroxide [84]),
- increasing acid concentration or volume of the solution analysed, changing reaction medium, maintaining short times of contact between the sample and the reducing agent, fast removal of gaseous reaction products [29],

The ICP technique, like other spectrometric methods combined with hydride generation, requires digestion and quantitative transfer of mineral compounds and elements, both free and bound to the material tested, to the solution. Depending on the nature of the matrix, various digestion methods may be used. The hydride generation processes determine the analytical procedures applied – separate, chemical interrelations of formation of the individual hydrides dictate the preparation procedures specific for the given analyte [50].

The literature data indicates that when silica determination is not required, then samples of silicates and aluminosilicates are subjected to a wet digestion process in a mixture of concentrated mineral acids (HNO₃, HClO₄, H₂SO₄, aqua regia, H₃PO₄) preferably with hydrofluoric acid HF added [85, 86]. Although the degree of dissociation of the latter is low (in a 1M solution about 10% of HF is in the form of

HF₂⁻ ions, and only 1% in the form of F⁻), the extremely strong complexing properties of fluoride ions make it very efficient in breaking Si – O bonds [87]. The other acids destroy the organic matrix and other, non-silicate constituents of the sample (sulphides, oxides, etc.). In an open system, the removal of the main element in the form of a volatile silicon fluoride enhances the quantitation of the remaining analytes (trace amounts in particular) by eliminating all possible disadvantageous interactions of silicon [88]. Likewise, the evaporation of the sample with hydrofluoric acid mixed with other acids provides another advantage consisting in the removal from the reaction mixture of fluoride ions (in the form of SiF₄), which cause much interference in spectrometric determination of elements.

On the other hand, however, this approach carries a serious risk: some metals, such as As, B, Ti, Nb, Ta, Ge, Sb, may form volatile fluorides and, in an open system, some or all of them may escape [87]. For this reason microwave digestion in closed vessels is gaining interest as a method of decomposing silicate and aluminosilicate samples: shorter digestion times and smaller amounts of acids used mitigate the risk of sample contamination. The disadvantageous effects of silicon and fluorine, however, are not avoided. Pre-treatment of solid samples by creating a suspension in a liquid medium (slurry sampling) seems to be an interesting alternative [89].

For the determination of arsenic and other volatile hydride-forming elements, *Terashima* [90] digested geological samples in a mixture of concentrated mineral acids: HClO₄+HNO₃+HF (1:0.75:1 v/m) with 2% KMnO₄ solution added. *Rubeska* [91] digested rock and soil samples with a HF+HClO₄ mixture with KMnO₄ added, and sulphide mineral samples in *aqua regia*. *Smith* [92], prior to determination of arsenic, fused solid samples containing silica and organic matter with MgO+KOH in nickel crucibles in a muffle oven at 550°C. *Herman* [93], prior to spectrometric determination of selenium in glass, solubilised the samples using a mixture of acids: HCl+HNO₃+HF (1:1:2.5 v/m), binding excess hydrofluoric acid with boric acid. *Hall and Pelchat* [84] digested geological samples to simultaneously determine As, Bi, Sb, Se and Te in a HF+HClO₄+HNO₃+HCl mixture, while *Nash and Maskall* used microwave energy to decompose environmental samples [94]. *Paper* [95] compares two digestion methods of biological and environmental samples for spectrometric determination of As, Se, Sb, Bi and Sn using HNO₃ in a closed system and HNO₃+HClO₄+H₂SO₄ mixture in an open system. It was indicated that the use of large amounts of reagents for sample pre-treatment leads to increased blank test values and higher detection limits.

Summary

To summarise the literature reviewed, it should be stated that transforming the elements determined into gaseous form and introducing them into the excitation or ionization source has a number of advantages over the conventional spraying of a liquid sample. The major advantages include: more efficient sample transfer (nearly 100%); elimination of the atomizer - spray chamber system; high determination selectivity achieved by suppressing matrix interferences; low detection limits and ability to conduct speciation analyses.

The HG-ICP-OES technique allows obtaining desirable linear calibration curves with wide dynamic ranges (6 orders of magnitude) as compared to 2 orders of magnitude offered by HG-AAS. Moreover, this technique is free from interferences in the gaseous phase, which are characteristic of quartz atomizers used in AAS and result from the high temperature of plasma [36]. One disadvantage of the method may be plasma instability, which occurs when unreacted acid is introduced into the plasma together with the hydrides [62, 96].

It should be emphasized that irrespective of all of the advantages of the hydride generation method, its application will always require optimising a number of parameters [29, 36] in order to attain maximum hydride generation efficiency. Such optimisation may include:

- finding optimum conditions associated with the concentration of the acid and reducing agent used (as valency of the elements determined has a significant effect on measurement sensitivity);
- determining the effect of matrix on the concentration and remaining available quantity of reducing agent (when compounds contained in the matrix are reduced to a metal or hydride);
- providing efficient means of hydride transfer to the excitation source, with consideration given to the stability of the hydride, which can undergo decomposition on the walls of transfer conduits;
- finding measurement conditions that will ensure appropriate sensitivity and precision of spectrometric determination (plasma discharge power, plasma gas flow rate, plasma burner position, selection of analytical lines, quantitation limit).

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