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The new concept of hyphenated analytical system: Simultaneous determination of inorganic arsenic(III), arsenic(V), selenium(IV) and selenium(VI) by high performance liquid chromatography–hydride generation–(*fast sequential*) atomic absorption spectrometry during single analysis

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Abstract

The paper presents a new conception of determination of inorganic speciation forms of arsenic: As(III) and As(V) as well selenium Se(IV) and Se(VI) by means of the high performance liquid chromatography hyphenated with a detection by the atomic absorption spectrometry with hydride generation (HPLC–HG–AAS). The application of optimization procedure conditions of chromatographic separation of arsenic and selenium speciation forms (using anion-exchange Supelco LC-SAX1 column and phosphate buffer at pH 5.40 as a mobile phase) as well as the use of the atomic absorption spectrometry as a detector, which enables work in fast sequential mode, allowed to develop original detection methodology of simultaneous determination of arsenic As(III), As(V) and selenium Se(IV) and Se(VI) speciation forms within a 220 s single analysis. The obtained detection limits were 7.8 ng mL^{-1} for As(III); 12.0 ng mL^{-1} for As(V); 2.4 ng mL^{-1} for Se(IV) and 18.6 ng mL^{-1} for Se(VI) and precision 10.5%, 12.1%, 14.2% and 17.3%, respectively, for 100 ng mL^{-1}. The described method was used for ground water analysis.

Keywords: Speciation analysis; HPLC–HG–AAS; On-line pre-reduction; Arsenic; Selenium; Ground water

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1. Introduction

Speciation analysis procedures of metalloids are complicated and sometimes lead to an approximated content determination of individual speciation forms. Therefore there is an interest in analytical techniques, which allow a direct determination of the speciation forms by hyphenated techniques, which in one system group use two (or more) independent techniques—usually separation and selective determination techniques [1].

Separation of determined species takes place in a chromatographic system—gas chromatography as well as high performance liquid chromatography or capillary electrophoresis. Spectrometric methods commonly used for determination total element contents: atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), atomic fluorescence spectrometry (AFS), methods with plasma induction: inductively coupled plasma (ICP), microwave induced plasma (MIP) and with emission detection (AED) or mass spectrometry (MS) are applied as detectors [2].

All of these detection methods can be coupled with hydride generation as a method of determination of total element content releasing from the environmental matrix sample. Additionally, the plasma methods surpass the atomic absorption spectrometry in terms of the possibility to perform multi-elements detection. The application of spectrometric

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methods connected with hydride generation technique as a detector in gas and liquid chromatography increases possibility of species determination of arsenic and selenium [3].

The hyphenated systems: high performance liquid chromatography with hydride generation inductively coupled plasma mass spectrometry detection (HPLC–HGICP-MS) [4,5], high performance liquid chromatography with hydride generation atomic fluorescence spectrometry detection (HPLC–HGAFS) [6–10] as well as high performance liquid chromatography with hydride generation atomic absorption spectrometry detection (HPLC–HG–AAS) [11–22] enable determination of content of arsenic inorganic As(III) and As(V), organic monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), arsenobetaine (AsB) and other speciation forms. These methods are competitive to the systems coupled with direct detection: high performance liquid chromatography with inductively coupled plasma mass spectrometry detection (HPLC–ICP-MS) [23,24]. The possibility of determination of inorganic forms, what is available not only for hydride generation technique but also for organic derivatives of arsenic was obtained through the *on-line* mineralization of organic matter: e.g. by microwave heating, supported by UV radiation and sometimes additionally by the initial reduction of arsenic forms to As(III).

In case of selenium species determinations, determination of its organic forms is of the biggest interest because of its physiological importance. Among the hyphenated methods, the plasma methods with domination of inductively coupled plasma mass spectrometry (ICP-MS) systems are most frequently used [25–27]. However, a determination of selenium Se(IV) and Se(VI) inorganic species can be carried by use of atomic fluorescence spectrometry (AFS) or atomic absorption spectrometry (AAS) systems in connection with hydride generation techniques as detectors by use of the initial reduction *on-line* of Se(VI) forms [28,29]. Additionally, the application of selenoorganic compounds mineralization performed *on-line* allows to determine organic speciation forms of selenium also in hydride generation atomic absorption spectrometry (HG–AAS) systems [30].

Possibilities of multi-element determinations, i.e. the determination of dozen or more elements in one sample during a single analysis are a future of the hyphenated techniques. Therefore, plasma methods: inductively coupled plasma (ICP) or microwave induced plasma (MIP) have advantage over more simple and cheaper atomic absorption spectrometry method (AAS) [31]. However, the occurrence of AAS instruments enabling simultaneous multi-element determinations [32] or fast sequential determination of many elements during one analysis is also available in the connection with hydride generation techniques [33]. In the future this can change of metalloids analytic methods.

The article presents simultaneous determination of inorganic speciation forms of arsenic As(III) and As(V) and selenium Se(IV) and Se(VI) by means of the hyphenated technique of the high performance liquid chromatography with detection of the atomic absorption spectrometry with hydride generation (HPLC–HG–AAS). The original concept of the method of simultaneous arsenic As(III), As(V) and selenium Se(IV), Se(VI) species determination during a single analysis and on-line pre-reduction techniques was developed.

2. Experimental

2.1. Instrumentation

The hyphenated high performance liquid chromatography with hydride generation atomic absorption spectrometry detection (HPLC–HG–AAS) system is shown in Fig. 1

2.1.1. HPLC system

The HPLC system consisted of a Shimadzu liquid chromatograph (LC-10A) equipped with a HPLC pump (LC-10AT), vacuum degasser unit (GT-104) and anion-exchange column Supelco LC-SAX1 compartment (250 mm × 4.6 mm i.d., resin particle size 5 μm) thermostatted by column oven (CTO-10ASvp). The chromatographic run was isocratic at 3 mL min^{-1} with an injection volume of 200 μL. PEEK transfer tubing of the eluent from the LC column to the hydride generation unit was inserted into a Tygon sleeve.

2.1.2. HG system

The continuous hydride generation system (VGA-77, Varian) consisted of a manually controlled four channel peristaltic pump with Tygon tubing (0.6 mm i.d.), one reaction coil (PTFE tubing 0.8 mm i.d., 75 cm length) and three ways connectors. The gas–liquid separator was made from glass and the interior dead volume was 3 mL.

2.1.3. AAS detection

All measurements were performed with a Model SpectraAA 220FS spectrometer (Varian, Australia). For the atomization of the arsenic and selenium hydrides (detected at 193.7 and 196.0 nm, respectively), a heating controller, electrothermally heating mantle and a quartz tube (ETC-60, Varian) heated to 900 °C, were used. A spectrometer is adapted to work in a fast sequential mode as described by the producer. In a spectrometer optical system four lamps are installed still in the fixed positions. A rotary mirror, which movement is coordinated with an automatic choice of the suitable analytical wavelength and the slit value, makes the choice of the radiation source. By the simultaneous activation of two or more lamps it is possible to reset quickly (approx. 1–2 s) an optical system of a spectrometer to the sequential elements determination within the same sample.

The chromatograms were displayed on the screen of a personal computer by using the signal graphics option of the AAS software (Varian), and as a separate print out of the screen. Peak areas or height were calculated by the AAS software.