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Analytical note

Determination of arsenic in water samples by Total Reflection X-Ray Fluorescence using pre-concentration with alumina ☆

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ABSTRACT

The determination of arsenic in water samples requires techniques of high sensitivity. Total Reflection X-Ray Fluorescence (TXRF) allows the determination but a prior separation and pre-concentration procedure is necessary. Alumina is a suitable substrate for the selective separation of the analytes. A method for separation and pre-concentration in alumina, followed by direct analysis of the alumina is evaluated. Quantification was performed using the Al–Kα and Co–Kα lines as internal standard in samples prepared on an alumina matrix, and compared to a calibration with aqueous standards. Artificial water samples of As (III) and As (V) were analyzed after the treatment. Fifty milliliters of the sample at ppb concentration levels were mixed with 10 mg of alumina. The pH, time and temperature were controlled. The alumina was separated from the slurry by centrifugation, washed with de-ionized water and analyzed directly on the sample holder. A pre-concentration factor of 100 was found, with detection limit of 0.7 $\mu g L^{-1}$. The percentage of recovery was 98% for As (III) and 95% for As (V) demonstrating the suitability of the procedure.

1. Introduction

The toxicity of arsenic species is widely known. In the agricultural field As is used as insecticide and pesticide [1,2]. The element can be found in chicken manure due to the fact that it is part of some chemicals used in the chicken feed [3]. The sources of arsenic are widely distributed and can be pigments, veterinary medicines for animal growth, mining operations and natural geological [1,4,5]. The contamination of crops, waters and soils can occur with the entry into the food chain [6,7]. The most toxic species are inorganic As (III) and As (V). The contamination of water sources with this toxic element can represent a serious public health problem. Water in most of the countries must be monitored to verify that As levels are below 10–50 $\mu g\, L^{-1}$ [1]. The determination of arsenic in water samples requires techniques with high sensitivity. Total Reflection X-Ray Fluorescence (TXRF) allows the determination of arsenic [8,9], but a separation and pre-concentration procedure may be necessary. Most of the current atomic spectroscopic techniques, e.g., Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Hydride Generation Atomic Absorption Spectrometry (HG-AAS) or Electro-Thermal Atomic Absorption Spectrometry (ETAAS), and TXRF, require generally the digestion of the sample. This is performed in order to avoid matrix interferences and, in some cases, for the appropriate transport of the analyte to the atomization/ionization system. Sample digestion invariably implies analyte dilution [10–15]. As (III) and As (V) are the most determined species in environmental waters, soils and sediments, while organic species are determined in biological tissues [16,17]. The concentration of species at low ranges demands a pre-concentration and separation step, since most of the available instruments still a lack the required sensitivity for direct determination and selectivity. The analytical methods frequently used for separation and pre-concentration [1] are solvent extraction [15], precipitation and co-precipitation, Ion Exchange Chromatography (IEC) [12], Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) [10]. A wide number of instrumental methods has been developed either for the determination of total As, in its methylated and inorganic forms in soils and sediments, waters, air, biological fluids and tissues. Among them the most commonly used include UV–visible spectrometry, electrochemical, HG-FAAS in continuum flow or in flow injection [11], AES, ICP-OES [7], ICP-MS [14], ETAAS [17], X-Ray Spectrometry [8,18], Neutron Activation Analysis (NAA)[1,10,11,17]. For speciation on line combinations of some separation techniques are employed (HPLC [1,12,17] and IEC) with the most sensitive detection methods. The most

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widely used procedures for the As analysis exploit the reduction of some compounds to arsine with $TiCl_3$, $SnCl_2$, HCl, hidracine, cystein and $NaBH_4$.

It is therefore convenient the development of analytical methodologies that may cope with the aforementioned problems, since in many cases the preparation procedure dilutes the analyte in a high extent rendering the solutions below the detection limit. To cope with this problem a procedure is necessary for the separation of the analytes from the matrix and their pre-concentration. Alumina is a well suited substrate for separation and pre-concentration of many elements [19], by the adsorption process. It is also a suitable substrate for the selective separation of analytes.

Alumina has been tested for speciation and fractionation of some analytes as As(III), As(V), Cr(III), Cr(VI) and Pt [19,20] by atomic absorption after an elution step. The advantages of TXRF are the possibility of the direct analysis without the elution phase. In this work a method for separation and pre-concentration in alumina is reported. This step is followed by the direct analysis of the alumina by TXRF. This procedure avoids the elution step required in other techniques such as HG-FAAS [11].

2. Materials and methods

2.1. Instrumental

The analysis was carried out in a Canberra XRF Spectrometer with a modified TXRF module designed at the Atominstitut der Österreichschen Universitäten, Vienna. The excitation was performed with the Kα (17,4 keV) line of a Molybdenum anode X-ray tube, operated at 40 kV and 20 mA. A carbon-molybdenum multilayer crystal was used for monochromation of the incident beam and a Si(Li) detector ($R_{Mn,5.8\ keV} = 180$ eV) was used for the detection of the fluorescence signal. The spectra were collected in a PC-based multichannel analyzer (Canberra S-100), with live collection times of 200 s. The spectral data analysis was conducted with the AXIL fitting program in the QXAS package supplied by the International Atomic Energy Agency.

2.2. Reagents

The As(III) stock solution in concentration of 10 mgL^{-1} was prepared from arsenic(III) trioxide (Sigma Aldrich) by dissolving in 1 mol L^{-1} KOH followed by acidification with 1 mol L^{-1} HCl similarly to Mihucz, et al.[20]. The As(V) stock solution 10 mgL^{-1} was prepared from potassium dihydrogen arsenate (Sigma Aldrich, Hungary). Titrisol®, 1000 mg ml^{-1} standard solutions (MERCK, Germany) were employed for preparation of calibration curves. Nitric acid (Riedel de-Häen, Germany) was used for cleaning quartz reflectors. Distilled, deionized water (16 MΩ cm) was employed for rinsing and dilution purposes.

2.3. Calibration

2.3.1. Calibration with aqueous standards

Aqueous, multi-element (V, Co, Zn, Se and Sr) standards were prepared by mixing and dilution of the corresponding stock solutions with distilled, de-ionized water to yield final concentrations of 5, 10 and 20 mg $ml^{-1}$of each element. Cobalt was selected as internal standard and added to standards and samples. Five µL of standards or samples followed by 5 µL of a 10 mg L^{-1} Co solution (Internal Standard) were deposited onto the reflector and vacuum dried. For quantification, the normalized sensitivities obtained with the standards were fitted by a continuous curve. (See Fig. 1).

2.3.2. Calibration using aluminum from alumina as internal standard

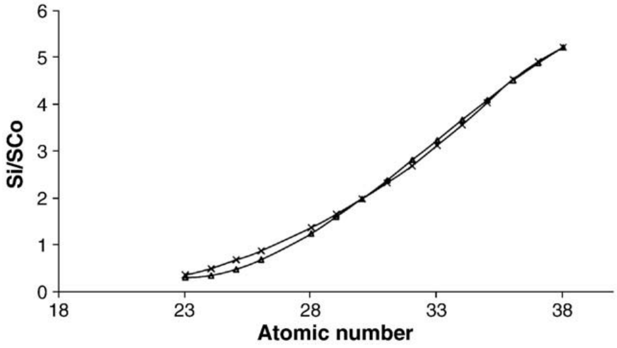

Fig. 1. Sensitivity curves using cobalt as internal standard for an aqueous matrix and an alumina matrix.

An amount of alumina (in the order of 1 mg, in a diameter of about 3 mm) was placed as a layer in the center of the quartz reflector with the aid of a needle, dried and weighed. The alumina on the sample carrier forms a thin layer in the central region which does not hinder the conditions for X-ray total reflection from the quartz substrate at the energy of the As Kα Fig. 2. The calibration was performed using the Al–Kα and Co–Kα lines as internal standard in the standard samples prepared on the alumina matrix, and compared to the calibration with aqueous standards (see Fig. 1).

2.4. Pre-concentration of arsenic

Artificial water samples of As(III) and As(V) were analyzed after the treatment. Fifty milliliters of the sample at ppb concentration levels (2, 20, 100, 200) were mixed with 10 mg of alumina. with a mechanical stirrer during the fixed contact time. It was not possible to use lower masses, and to have better enrichment factors due to the difficult management of small quantities of alumina in the centrifugation step. To enhance the enrichment factor is necessary to use higher water volumes. The pH (5.7), the time of contact (15–1440 min) and the temperature (47 °C) were controlled and varied for optimization. The selected temperature was enough high to have major reaction velocity, but enough low to avoid analyte loses). The alumina was separated from the slurry by centrifugation. The supernatant in the centrifuge tube was decanted and discarded and the alumina pellet at the bottom was washed with de-ionized water, which was further decanted. A mass of about 1 mg was placed on a previous weighed sample holder, dried and weighed. Then the alumina sample was directly analyzed on the sample holder, in the same way as with the alumina calibration standards. A typical spectrum of the alumina sample after the adsorption of the arsenic from

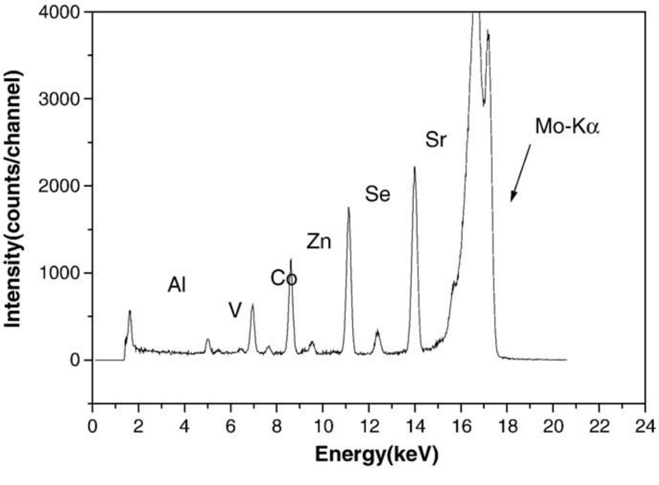

Fig. 2. Spectrum of calibration sample. Spike of the 10 mgL^{-1} multi-element solution on to 1 mg of alumina on sample holder.