Determination of As, Sb and Hg in water samples by flow injection coupled HR CS ETAAS with an in situ hydride generator

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ABSTRACT

A chelating sorbent which employs magnetic nanoparticles (MNPs) functionalized with 1,5-bis(di-2-pyridil) methylene thiocarbohydrazide (DPTH-MNPs) was used to develop a simple method for the analysis of trace amounts of metal ions (As, Sb and Hg) present in environmental samples combining on-line magnetic solid phase extraction (MSPE) with atomic spectrometry. The application of hydride generation with high resolution continuum source electrothermal atomic absorption spectrometry (HR CS ETAAS) improves the sensitivity of As, Sb and Hg determination.
This method has proven to have a high sensitivity with detection limits of 0.25 μg L^{-1}, 0.003 μg L^{-1} and 0.22 μg L^{-1} for As, Sb and Hg, respectively. Besides, the proposed method was applied in the sequential determination of the 3 elements mentioned above with a sample throughput of about 16.7 h^{-1}, thereby, reducing the time of analysis and the volume of reagents and sample required. This method was applied to determine the target elements in a TMDA 54.5 and TM 24.3 certified reference materials, and seawater collected from Malaga Bay. The results showed good agreement with the certified values.

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1. Introduction

Heavy metals are serious pollutants because of their toxicity, persistence, and non-degradability in the environment. For example, mercury is one of the most harmful pollutants [1–3]. It is easily accumulated in organism and will cause deleterious effects on human beings when the content goes beyond the allowable limit. Arsenic is known to be one of the most toxic elements and has serious effects on plants, animals and human health [4]. As a cumulative toxic element, antimony has chemical and toxicological properties similar to those of arsenic. Hence, the monitoring of Hg, Sb and As in environmental samples is of great importance. Concentration of these elements in water should be constantly monitored to ensure that their maximum permissible concentrations intended for human consumption are not exceeded. Coupled techniques based on the combination of a separation method with an element-selective detection system have become reliable in analysis [5].

Since concentrations in waters are expected to be very low [6, 7], for the determination of mercury, antimony and arsenic, highly sensitive analytical detection techniques are required. A variety of atomic spectrometry techniques have been employed for the determination of trace metals in various samples. However, the concentration of heavy metals in real samples are usually lower than the detection limit of most of these techniques; and complex or high salinity matrices in real samples might seriously interfere with the determination of target analytes.

Solid phase extraction (SPE) in the on-line column operation mode has attracted more attention due to the prominent advantages in terms of automation, and extremely low sample and reagents consumption which contribute to the green analytical procedures. These on-line SPE procedures usually make use of a packed column filled with a suitable sorbent. Since the adsorbent material plays a crucial role in solid-phase extraction, the research of new material is of continuing interest [8–14].

Magnetic nanoparticles (MNPs) as sorbents have two main uses in analytical chemistry are separation and pre-concentration of chemical species (mainly by magnetic solid-phase extraction, MSPE), and as sensors and biosensors [15] Magnetic solid phase extraction (MSPE) with magnetic particles (MPs) as the adsorbents has aroused great interest in analytical community in recent years. Superparamagnetic iron oxide particles as sorbents in SPE have received increasing attention, because they are attracted to a magnetic field but do not retain any magnetism after the field is removed [16–21]. On-line MSPE using MNPs as the sorbent is one of the latest developments. These automatic pre-concentration techniques offer several advantages such as simplicity of operation, higher sample throughput, improved analytical characteristics and reduced sample and reagent consumption [22]. The advantages of use of MNPs are: (1) reduced analysis time, (2) being more environmentally friendly and (3) requiring fewer reagents. Moreover,

these nanometer-sized metal oxides are relatively inert, in chemical term, and are unsuitable for samples with complicated matrices [23, 24]. Therefore, a suitable coating is essential to overcome such limitations. MNPs packed in a microcolumn could be immobilized controllably by an external magnetic force (magnet knotted reactor (MKR)) during both column preparation and operating period.

Moreover, chemical cold vapour generation (CVG) acts as an effective sample introduction method for trace elements determination using atomic spectrometry, easily achieving simultaneously matrix separation and greatly improved detection power [25–27]. Undoubtedly, hydride generation atomic spectrometry is currently the most popular technique for routine determination of trace amounts of elements, which generate volatile species because of the enhanced concentration detection limits. Furthermore, matrix separation, analyte concentration and potential delineation of species lead to enhanced accuracy, precision and reliability.

However, due to differences in the HG reaction conditions required for effective formation of the corresponding hydrides, determination of more than one hydride-forming element is not an easy task. Typically have to be proceeded by careful optimization of the experimental parameters, being appropriate for all hydride-forming elements examined, therefore, development of a universal procedure is the most desired but also demanding and challenging. Hence, most of the works are focused on single-element analysis [28–31].

In this work, silica coated magnetic nanoparticles (MNPs) modified with 1,5-bis(di-2-pyridil) methylene thiocarbohydrazide (DPTH-MNPs) was used as SPE sorbent. So, a flow injection, magnetic solid phase microextraction (FI-MSPME)/cold vapour generation system coupled to a high resolution continuum source electrothermal atomic absorption spectrometer (CVG HR CS ETAAS) method for the determination of trace amounts of Hg, Sb and As in environmental water samples has been developed. In this work, a magnet based MKR designed to contain DPTH-MNPs was placed in the injection valve of the FI manifold. For the quality control of the analytical performance and the validation of the developed method, the analysis of two certified samples, TM 24.3 and TMDA 54.5, Fortified Lake Waters was addressed. The results showed good agreement with the certified values.

2. Experimental

2.1. Instrumentation

All experiments in this work were carried out using a HR CS ETAAS, ContrAA 700, commercially available from Analytik Jena AG (Jena, Germany) and equipped with both a graphite furnace and flame atomizers. The optical system comprises a xenon short-arc lamp (GLE, Berlin, Germany) operating in "hot-spot" mode as the radiation source, a high-resolution double echelle monochromator (DEMON) and a linear CCD array detector with 588 pixels, 200 of which are used for analytical purposes (monitoring of the analytical signal and BG correction), while the remainder are used for internal functions, such as correcting for fluctuations in the graphite tube atomizer and both solid sampling and liquid sampling autosampler. The lines selected for the absorbance measurements were 193.696 nm (As), 217.5815 (Sb) and 253.6519 nm (Hg). The peak volume selected absorbance (PVSA) was equivalent to three pixels (central pixel ± adjacent ones) for Sb and Hg and five pixels for As (central pixel ± two adjacents). The graphite furnace heating programs for the determination of As, Sb and Hg are provided in Table 1.

Two four-channel peristaltic pump (Minipuls 3, Gilson, Villiers le Bel, France) were used for the continuous-flow vapour system with a Rheodyne Type 50 six-port rotary valve and a gas–liquid separator. The FI system and the ETAAS instrument were coupled and operated completely synchronously. Schematic diagram of the continuous flow system used for determination of the different CV forming elements studied is shown in Fig. 1.

Table 1
Optimized furnace program used for Sb, As and Hg determination.

Step	Temperature/°C	Ramp time/°C s^{-1}	Hold time/s	Argon flow rate/L min^{-1}
As (193.696 nm)				
Conditioning	150	300	2	0
Drying	155	50	80	2
Atomization	2200	1000	6	0
Cleaning	2200	0	4	2
Sb (217.582 nm)				
Conditioning	150	300	2	0
Drying	155	50	80	2
Atomization	2100	1000	6	0
Conditioning	2100	0	4	2
Hg (253.6519 nm)				
Conditioning	65	300	0	0
Drying	65	0	80	2
Atomization	1050	1000	5	0
Conditioning	1100	1000	10	2

The magnet knotted reactor containing the DPTH-MNPs was a PTFE tube (500 mm × 0.5 mm i.d.) packed with 50 mg of DPTH-MNPs and knotted round a circular Nd/Fe/B magnet (Outer diameter: 26.75 mm; Inner diameter: 16 mm; Height: 5 mm; Holding strength: 81.4 N) and sandwiched between other two identical circular magnets; at both ends of the PTFE tube, polyethylene frits (Omnifit, Cambridge, UK) were fixed to prevent material loss.

Tygon pump tubings were used to deliver samples, reagents and withdraw waste. The reaction coil and connections were made of 0.8 mm i.d. PTFE tubing. The element vapours generated in the reactor were transported to the graphite tube through a PTFE transfer line connected to a gas–liquid separator with a PTFE membrane of 0.5 mm pore diameter.
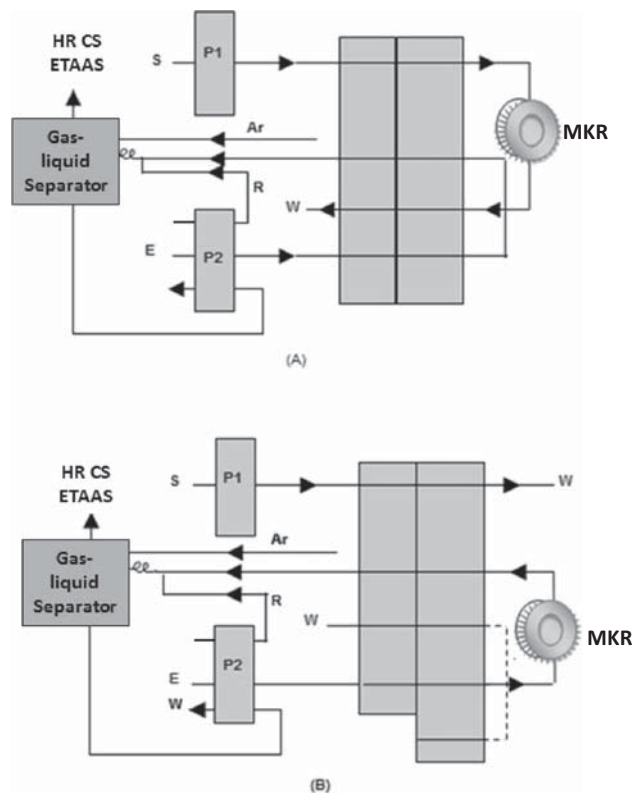

Fig. 1. Schematic diagram of the FI system for the pre-concentration and separation of Sb, As and Hg; P1 and P2, peristaltic pumps; MKR, magnet knotted reactor; S, sample; R, reductant; E, Eluent; W, waste. (A) pre-concentration step and (B) elution step.