



Room temperature trapping of stibine and bismuthine onto quartz substrates coated with nanostructured palladium for total reflection X-ray fluorescence analysis



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ABSTRACT

In this work, a novel method for determining Sb and Bi based on the trapping of their covalent hydrides onto quartz reflectors coated with immobilized palladium nanoparticles (Pd NPs) followed by total reflection X-ray fluorescence (TXRF) analysis is proposed. Pd NPs were synthesized by chemical reduction of the metal precursor using a mixture of water:ethanol as mild reducing agent. Silanization using 3-mercaptopropyltrimethoxysilane (MPTMS) was performed for the immobilization of Pd NPs onto the quartz substrates. Volatile hydrides (stibine and bismuthine) generated by means of a continuous flow system were flushed onto the immobilized Pd NPs and retained by catalytic decomposition. As a result of the high catalytic activity of the nanostructured film, trapping can be performed at ambient temperature with good efficiency. Limits of detection (LODs) were 2.3 and $0.70 \mu\text{g L}^{-1}$ for Sb and Bi, respectively. Enrichment factors of 534 and 192 were obtained for Sb and Bi, respectively. The new method was applied for the analysis of several matrices (milk, soil, sediment, cutaneous powder). Recoveries were in the range of 98.4–101% for both elements with a relative standard deviation of 2.5% ($N = 5$).

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1. Introduction

The chemical hydride generation (CHG) technique using sodium borohydride as reducing agent is one of the most used derivatization reactions to form volatile hydrides from several metals and metalloids [1]. One of the main advantages of CHG is its simplicity. Before analysis, volatile hydrides are usually retained by different ways in order to improve the sensitivity. Hydrides can be trapped using the so-called atom traps [2]. The most used atom traps are quartz tubes and tungsten coils. For hydrides trapping, devices are pre-heated in order to obtain the thermal decomposition of the hydride. After that, the device is heated again releasing the trapped analyte and it is transported to the detector for the analysis by atomic absorption spectrometry (AAS).

Additionally, an alternative trapping approach is the collection of the metal hydrides onto preheated graphite tubes, also called in-atomizer trapping, thus achieving an *in situ* preconcentration of the analytes prior to AAS determination. Sensitivity using this procedure can be increased by the use of graphite tubes modified with metals of high boiling point, e.g., Pd, Ir, Pt, Rh or Zr [3–6]. In general, the trapping temperature using modified graphite tubes is lower than that using unmodified graphite tubes for hydride deposition. It could be ascribed to the catalytic dissociation of volatile hydrides in contact with the preheated

metals in the graphite tube [7]. Although in-atomizer trapping provides improved efficiency and sensitivity, there are some critical drawbacks that inherent to this approach. For instance, since the graphite tube has to be preheated, metal hydrides could be thermally decomposed on the injection capillary resulting in memory effects.

Effective trapping of volatile hydrides onto macroscopic solid surfaces, e.g., graphite tubes or modified graphite tubes, quartz tubes, etc., occurs at moderate-high temperature. For quartz tubes, trapping temperatures in the range of 600–1000 °C are necessary to achieve efficiencies around 90% [8–11]. For trapping volatile hydrides on graphite, temperatures ranging from 300 °C to 800 °C, depending on the element, need to be employed [12,13]. When using modified graphite surfaces with noble metals (e.g., non-nanostructured Pd), temperatures around 300 °C are needed to achieve trapping efficiencies around 70–80% [14–17]. In this case, a catalytic dissociation of the metal hydride over the noble metal occurs.

Catalytic decomposition of covalent volatile hydrides onto noble metals at room temperature should be desirable in order to extend this preconcentration approach to other analytical techniques.

Nanomaterials represent a powerful tool for analyte trapping due to their large surface area, low resistance to diffusion and fast sorption kinetics, which can improve the trapping efficiency [18]. The catalytic activity strongly depends on the size, shape and composition of the nanoparticles (NPs). By decreasing the particle size, the surface atom fraction increases rapidly resulting in high surface-to-volume ratio and density of

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exposed active sites. This fact should result in an improved accessibility to specific sites and enhanced catalytic activity [19,20].

Total reflection X-ray fluorescence (TXRF) is a well-established multielemental technique that has been increasingly applied for trace element determinations in microsamples. The main characteristic of TXRF technique is that the primary X-ray beam strikes the sample at an angle of less than 0.1° causing the total reflection of the beam, thus reducing absorption as well as scattering and increasing instrumental sensitivity [21]. Sample preparation is a critical issue for quantitative TXRF analysis [22]. Extraction and preconcentration procedures before analysis are usually necessary in order to improve sensitivity. Generally, sample is deposited as a thin film onto a sample carrier (*i.e.* quartz reflector) and dried by evaporation or under vacuum before analysis. However, when analytes with low boiling point and high vapor pressure (*e.g.* Hg, Se, Sb, Cd, *etc.*) are analyzed, losses by evaporation from the sample carrier occur and worsened limits of detection are obtained. In the last years, different strategies were developed to improve sample preparation in TXRF for the determination of volatile analytes, *e.g.* Hg and Se, based on trapping or complexation of the analytes, thus avoiding losses by evaporation [23–26]. The use of nanoparticles as solid phase for direct trapping of volatile analytes onto sample carriers allows high extraction efficiency and preconcentration. This strategy was firstly described by our group with silver nanoparticles (Ag NPs) immobilized onto quartz reflector for trapping Se and Hg [27]. Ag NPs were also tried for trapping other volatile hydrides, *e.g.* bismuthine, stibine, but low trapping efficiencies were obtained (*i.e.*, 20% and 12% for Bi and Sb, respectively) resulting in poor sensitivity. Palladium nanoparticles (Pd NPs) were also tried, but problems with aggregation during chemical synthesis using conventional reducing agents (*e.g.*, NaBH_4) were observed, thereby yielding poor immobilization onto quartz substrates. A simple route for the synthesis of surfactant-free immobilized Pd NPs for their use as effective nanocatalysts for metal hydride decomposition was described by our group [28]. It was demonstrated that immobilization of Pd NPs onto quartz substrates provided an effective nanostructured film for trapping arsine. In the present work, quartz reflectors with immobilized Pd NPs are tried for trapping Sb and Bi hydrides at ambient temperature. For this purpose, a continuous-flow vapor generation system is coupled to the quartz reflector coated with Pd NPs. After preconcentration, the quartz reflector is directly placed onto the sample changer for analysis by TXRF without the need for a drying step. After full optimization of the system, usefulness of the novel approach to the determination of Sb and Bi in several matrices was demonstrated.

2. Experimental

2.1. Apparatus

TXRF measurements were carried out by means of a TXRF spectrometer model S2 Picofox™ (Bruker AXS Microanalysis GmbH, Berlin,

Germany). Gilson's Minipuls 3 peristaltic pumps (Gilson Inc., Middleton, USA) with head speed adjustable from 0 to 48 rpm, equipped with Tygon® tubes were used for the continuous-flow hydride system.

A MC5 Sartorius microbalance (Sartorius AG, Göttingen, Germany) was used for weighing.

A Speedwave™ MWS-2 microwave digester (Berghof, Eningen, Germany) with a maximum microwave power of 1000 W and equipped with DAK-70 high pressure digestion vessels (100 mL) was used for digestion of samples.

A field emission transmission electron microscope (FETEM) model JEOL JEM-1010 (JEOL, Seoul, Korea) was used for obtaining TEM images.

2.2. Standard and solutions

All chemicals were of analytical reagent grade. High-purity deionized water obtained from an Ultra Clear™ TWF EDI UV™ water system (Siemens, Barsbüttel, Germany) was used throughout. Nitric acid 65% (m/v) (Panreac, Barcelona, Spain) and RBS 50® solution (Sigma-Aldrich, Steinheim, Germany) were used for cleaning the sample quartz reflectors.

For the synthesis of Pd NPs, $\text{Pd}(\text{NO}_3)_2$ 40% Pd basis (Aldrich, Dorset, United Kingdom) and absolute ethanol (Prolabo, Fontenay-sous-Bois, France) were used.

Stock standard solutions (1000 mg L^{-1}) were prepared by dissolving SbCl_3 99.5% (m/m) (Analyticals Carlo Erba, Milano, Italy) and $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$ 71.5% (m/m) (Merck, Darmstadt, Germany) in high-purity deionized water and an appropriate acidic medium. Diluted working standards were prepared fresh daily from the stock solutions.

Milk samples, *i.e.* full-cream, full-cream with Ca and vitamins and full-cream without lactose, were analyzed. These samples were purchased in supermarkets and are representative of what is commonly consumed.

NIST 2711 (Montana II Soil), NIST 2702 (Inorganics in Marine Sediment) certified reference materials (CRMs) from the National Institute of Standard and Technology of the U.S. Department of Commerce (Washington D.C., U.S.A.) and Talquistina® powder (Lacer, Barcelona, Spain) were also analyzed.

2.3. Sample preparation

For sample preparation, microwave-assisted digestion was performed. 3 g of milk were weighted in a TFM® vessel. Then, 5 mL of concentrated HNO_3 were added. A three-step microwave program was applied (Step1 130°C , 5 min, 400 W; Step2 150°C , 5 min, 400 W; Step3 145°C , 5 min, 400 W). After cooling to ambient temperature, 1 mL of concentrated H_2O_2 was added and the three-step microwave program was run again. The same procedure was followed for Talquistina® powder, using 100 mg of sample. For CRMs, a 100 mg portion was accurately weighed and microwave-assisted digestion with

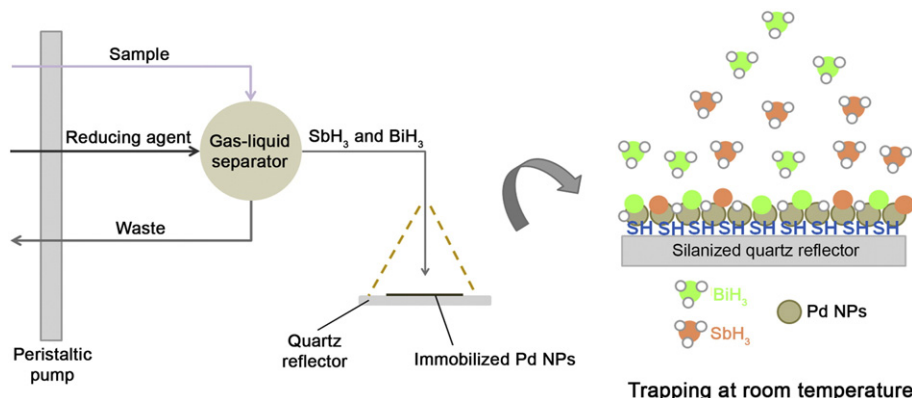


Fig. 1. Schematic diagram of the coupling between the membrane gas-liquid separator and the quartz reflector with immobilized palladium nanoparticles.

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