



Ultrasound-assisted extraction of gold and silver from environmental samples using different extractants followed by electrothermal-atomic absorption spectrometry

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ABSTRACT

Ultrasound-assisted extraction combined with electrothermal-atomic absorption spectrometry has been applied to the determination of silver and gold at $\mu\text{g g}^{-1}$ levels in different environmental samples such as soil, sediment, fly ash and industrial sludge. Two different extraction systems have been tried, i.e. acid mixtures (HCl, HF, and HNO_3) and thiourea in diluted H_2SO_4 medium. In both cases, an efficient cup-horn sonoreactor was used as ultrasonic device to accelerate the extraction process. This ultrasonic processor allows the use of any extractant including HF and simultaneous treatment of up to six samples. Recovery ranged from 81% to 107% for silver, and from 91% to 105% for gold. Optimal acid mixtures were 25% v/v HNO_3 + 25% v/v HF for Ag and 25% v/v HNO_3 + 25% v/v HCl for Au. The thiourea method required 0.6% m/v thiourea + 2% v/v H_2SO_4 . The latter method was considered advantageous since efficient Au and Ag extractions were obtained in a short time, and moreover, wastes generated were less harmful to the environment. Limits of detection for Ag and Au were 0.012 and 0.050 $\mu\text{g g}^{-1}$, respectively. Repeatability expressed as relative standard deviation ranged from 2 to 10% for both metals. Both extraction methods were applied to the determination of Au and Ag in sediments and soils located at different sampling points from Galicia (Spain).

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1. Introduction

Noble metals such as Ag and Au have many applications in industry, jewellery and medicine [1–3]. Some Au compounds are used as anti-inflammatory drugs in the treatment of rheumatoid arthritis, whereas silver compounds are involved in the treatment of infections. Au is also found in electronic apparatus. Moreover, Ag has applications in photography, industry and hard solder. Both noble metals are typically found at trace level in the environment, and as a consequence, sensitive techniques are required for their determination [4]. Different analytical techniques are available for determination of trace amounts of Ag and Au in geological and environmental samples such as electrothermal-atomic absorption spectrometry (ETAAS) [5], inductively-coupled plasma mass spectrometry (ICP-MS) [6,7], inductively-coupled plasma optical emission spectrometry (ICP-OES) [8,9]. Other less common techniques include instrumental neutron activation analysis (INAA) [10] and total reflection X-ray fluorescence spectrometry (TXRF) [11].

The most spread sample treatment prior to analysis of Au and Ag is microwave-assisted digestion (MAD) [12,13]. Thus, MAD is employed in the EPA method 3051A [14]. Several acid mixtures such as HNO_3 + HCl + H_2O_2 [15], HNO_3 + HCl [13,14], HNO_3 + HCl + HF and even HNO_3 + HClO_4 + HF [16] have been employed. In order to avoid

sample treatments with acids at high temperature and pressure, several workers have proposed less harsh conditions. Thus, Lopez-Garcia et al. [17] developed a slurry sampling method for determination of Ag and Au in soils and sediments by ETAAS. Firstly, slurries were subjected to mild heating in a domestic microwave oven (30 s) or alternatively in a heating steam bath (10 min) with a mixture of 3% v/v HNO_3 , 25% v/v HF and 50% v/v H_2O_2 for silver, and concentrated HF for gold.

On the other hand, it is well known that precious metals have a high affinity toward complexing agents such as sulphur or cyanide. Cyanidation (CN^-) has been traditionally used for the recovery of Ag and Au from ores [18], but in the last years, alternative leaching procedures have been developed in order to avoid the high toxicity of cyanide [19]. As an example, thiosulfate ($\text{S}_2\text{O}_3^{2-}$) in ammonia medium and in the presence of Cu (II) [20], thiocyanate (SCN^-) [21] and thiourea (H_2NCSNH_2) in different oxidizing media [22] have been employed for this purpose.

Since the late 90s, ultrasound have been widely applied to assist metal extraction from a large variety of solid materials [23]. Ultrasound-assisted extraction (UAE) allows the release of metals in a short time using acids at low concentration. In addition, operation conditions involve atmospheric pressure and room temperature. Most studies on UAE have been performed using probe [24,25] or bath [26,27] ultrasonic processors. Whereas probe sonication has been proved efficient for UAE of a variety of elements, bath sonication usually needs longer times and concentrated acids for metal extraction [23,28,29]. However, probe sonicators are non-compatible

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with hydrofluoric acid, which is mandatory for achieving efficient extractions from samples containing silicates [30]. A novel ultrasonic processor, called cup-horn sonoreactor, has been recently applied to metal extraction from environmental and biological samples [31], showing interesting advantages such as sonication power approaching that of probes and capability of multitreatments using virtually any extractant composition.

Whereas a considerable amount of work has dealt with UAE of heavy metals and metalloids, UAE of noble metals has been scarcely addressed. So far, only two papers have been published on UAE of Ag from soil [28,32], yet in the latter high-ppm concentration levels were present. No work has been reported on the use of ultrasound for the extraction of Au from environmental samples.

The aim of this work is to develop a simple methodology for ultrasound-assisted extraction of Ag and Au at trace level from environmental samples using a cup-horn sonoreactor. Two procedures were developed and compared, *i.e.*, ultrasound-assisted acid extraction and ultrasound-assisted thiourea extraction. The quantification of both noble metals was carried out by electrothermal-atomic absorption spectrometry (ETAAS). Moreover, eleven real samples (river sediments and soils) were collected at different sampling points from Galicia, near the Miño River, and they were used as target samples for Ag and Au determination according to information from ancient history about the possible occurrence of Au traces in these locations.

2. Experimental

2.1. Reagents and standards

Ultrapure water was obtained from a PETLAB ultrapure water production system (Peter Taboada, Vigo, Spain). All chemicals used were of analytical-reagent grade. A silver standard solution (1000 mg L^{-1}) was obtained by dissolving the appropriate amount of AgNO_3 (Riedel-de Haën, Seelze, Denmark). A gold standard solution (1000 mg L^{-1}) in 10% v/v HCl was obtained from Prolabo (Leicestershire, England).

69% mass/volume nitric acid (Prolabo, Leicestershire, England), 37% mass/volume hydrochloric acid (Prolabo), 95% mass/volume sulphuric acid (Prolabo), 30% mass/volume hydrogen peroxide (Merck, Darmstadt, Germany) and 40% mass/volume hydrofluoric acid (Merck) were used for extraction after dilution with ultrapure water. Thiourea (H_2NCSNH_2 , Merck) and L-cysteine ($\text{HOCH}(\text{NH}_2)\text{CH}_2\text{SH}$, Merck) were diluted in ultrapure water.

All glass and plastic containers and materials were soaked in a 10% volume/volume HNO_3 solution for 24 h and rinsed with ultrapure water three times before use.

2.2. Certified reference materials

Five environmentally certified reference materials (CRMs) were used for both optimisation and evaluation of the proposed methodology. NIST SRM Montana Soil 2710, NIST SRM Montana Soil 2711, NIST SRM 2702 Marine Sediment, NIST SRM 2782 Industrial Sludge from the National Institute of Standards and Technology (United States) and BCR CRM 176R Fly Ash from the Community Bureau of Reference (Belgium) were analyzed. CRMs were used as received and no additional grinding was performed. Powdered samples were stored at 4 °C.

Certificates for CRMs ensured a particle size less than 70 μm in SRM 2702, less than 74 μm in SRM 2710 and SRM 2711, less than 75 μm in 2782 and less than 105 μm in BCR 176R. The certified silicon contents of SRM 2710, SRM 2711 and SRM 2782 are 28.9% mass/mass, 30.4% mass/mass and 20.3% mass/mass, respectively. Concentration ranges for the major components for SRM 2710, SRM 2711, SRM 2702 and SRM 2782 are as follows: C (2.1–3.4%), Al (1.4–8.4%), Fe (1.31–7.91%),

except for SRM 2782 where the concentration is 26.9%), Na, K or Ca (0.32–2.88%), Mg (0.26–1.1%), Mn (0.03–1.0%), Ti (0.09–0.9%), P (0.08–0.5%) and S (0.04–1.5%). No data were found for BCR 176R.

2.3. Sampling points and sample pre-treatment

Eleven sampling points along 88 km were selected according to previous information [33,34]. The sampling points are shown in Fig. 1. Six river sediment samples were collected at the Miño River (Ourense), Arenteiro River (O Carballiño), Arnoia River (Arnoia), Miño River (Salvaterra de Miño), Louro River (Tui) and Lagares River (Vigo). Miño River is the longest river of Galicia and Arnoia River and Louro River are some of their tributaries. Another type of target samples are soils, which in some cases belong to ancient gold ores. Soil samples were collected at Rivas (O Irixo), Brués (Boborás), O Lago (Maside), Sampaio (Ribadavia) and Oleiros (Salvaterra de Miño).

Samples were selected according to information from the literature, trying to cover two kinds of Au ores in Galicia, primary and secondary deposits. Primary deposits refer to the Au found in rocks or hydrothermal veins due to chemical processes at high temperature in shear zones of the Earth crust. Secondary deposits are river deposits. In the case of Ag, this noble metal usually appears in gold ores. In addition, Ag appears linked to sulphur in hydrothermal veins [33,34].

2 kg of sample (sediment or soil) were collected at each sampling point using a plastic scoop and kept in polyethylene containers. Once in the laboratory, samples were dried at 60 °C in a heater until a constant weight for *ca.* 24 h for soil samples and 48 h for river sediments. After that, they were sieved using nylon sieves to collect the fraction with a particle diameter less than 50 μm , and then stored in polyethylene bottles at room temperature in a desiccator.

2.4. Instrumentation

All measurements were carried out with a Thermo Electron Corporation® series M5 atomic absorption spectrometer (Cambridge, UK) equipped with a deuterium background corrector. A Thermo GF95 graphite furnace and a Thermo FS95 furnace autosampler for silver and gold were used. In addition, a hollow cathode multi-elemental lamp of Ag/Au was employed as radiation source (Thermo Scientific, Cambridge, UK). The instrumental parameters are given in Table 1. Longitudinal-heated graphite tubes with integrated L'vov platform were provided by the same manufacturer.

A cup-horn sonoreactor UTR 200® (dr. Hielscher Company, Teltow, Germany) with 200 W of maximum output power and $24 \pm 1 \text{ kHz}$ of operating frequency was employed for ultrasound-assisted extraction of Ag and Au from the different samples.

A microbalance MC5 Sartorius (Goettingen, Germany) with 1 μg readability was used for weighing the samples. A Denver (Norfolk, United Kingdom) microcentrifuge was used for a rapid separation of liquid and solid phases.

2.5. Ultrasound-assisted extraction procedure and thermal programs

A portion of solid material (3–30 mg) was weighed into an Eppendorf vial depending on the analyte concentration and 1 mL of the suitable extractant (mixture of diluted HNO_3 , HCl, HF or thiourea solution) was added to the vial. Ultrasound energy was applied for the required time at a sonication amplitude of 60% by means of the cup-horn sonoreactor. This system was previously filled with ultrapure water so that ultrasound waves could be efficiently transmitted [35]. After sonication, centrifugation was carried out for 2 min at 5000 rpm according to previous experiments. Determination of silver and gold was performed in the supernatant. Blanks were treated in the same way. 15 μL of standard or sample was injected onto the L'vov platform of the graphite tube.

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