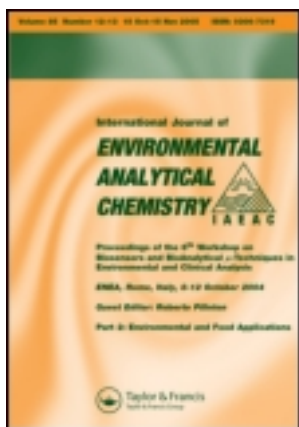


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Ultrasound-assisted extraction of antimony and cobalt from inorganic environmental samples using a cup-horn sonoreactor prior to their determination by electrothermal-atomic absorption spectrometry

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A simple, fast and reliable method is described for the quantitative extraction of Sb and Co from inorganic environmental matrices containing variable amounts of silicates prior to their determination by electrothermal-atomic absorption spectrometry. The method is based on the ultrasound-assisted extraction of both elements using the mixture 20% v/v HF + 20% v/v HNO₃ as extractant. The extraction procedure was carried out in closed Eppendorf vials immersed in a cup-horn sonoreactor for 20 min. Once extraction has been accomplished, the supernatant liquid is separated from the solid phase and subsequently transferred into the autosampler of the instrument. A two-level full factorial design (2⁴) was applied for screening optimisation of the variables influencing the ultrasonic extraction. These variables were: sonication time; amplitude of the ultrasonic energy; nitric and hydrofluoric acid concentrations. MLDs were 0.20 and 0.06 µg·g⁻¹ for Sb and Co, respectively. Between-batch precision values, expressed as relative standard deviations (*n* = 3), were less than 5.5 and 9.6% for Sb and Co, respectively. The method was evaluated using a wide variety of inorganic certified reference materials, such as SRM 2702 (Marine Sediment), SRM 2782 (Industrial Sludge), BCR 176R (Fly Ash), SRM 1633b (Coal Fly Ash) SRM 2710 (Montana Soil) and SRM 2711 (Montana Soil).

Keywords: ultrasound-assisted extraction; cup-horn sonoreactor; antimony and cobalt; environmental samples; electrothermal-atomic absorption spectrometry

1. Introduction

Ultrasound-assisted extraction (UAE) of trace elements from finely powdered solid samples dispersed in diluted acid solutions was developed at the end of the 1990s as an extension of the slurry sampling technique in electrothermal-atomic absorption spectrometry (ETAAS) [1,2]. Advantages of the novel approach were soon identified. Ultrasonic devices used for slurry mixing and homogenisation can also achieve an efficient analyte separation from the matrix, and consequently, interference effects caused by the latter can be overcome. Thus, lower background and decreased build-up of carbonaceous residues into graphite tubes have been reported [2]. In addition, sedimentation and volumetric

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errors inherent in the slurry technique are removed, since analytes are present in the liquid supernatant obtained after centrifugation. Advantages of UAE include the use of room temperature and atmospheric pressure as compared to more intensive sample pre-treatments for inorganic trace analysis such as microwave-assisted acid digestion. More importantly, diluted acids can be sufficient for quantitative extractions provided that efficient ultrasonic processors are employed [3]. Several studies have shown that UAE of trace metals from inorganic matrices entails many difficulties. For environmental matrices containing a significant fraction of the metals occluded in the aluminosilicate matrix, metal release is troublesome unless HF is added to the extractant so as to destroy the silicate lattice [4]. Several elements have been extracted from environmental matrices by using ultrasound such as Cd [2,5–13], Pb [5–9,11–15], Cu [5,6,8,9,11–14], Cr [7–9,11–13,16], Ni [7–9,11–14,16], Zn [8,9,11–14], As [11,14,17] and V [9,14,16] among the most studied elements. Nevertheless, others such as Co [8,14], Mn [7,8], Ag [5], Ba [14], Sr [14], Fe [9] and Tl [11] have been less commonly extracted from solid samples.

When ultrasonic baths are used for UAE, high acid concentration and long extraction times are often needed in order to obtain complete extractions [4,18]. The use of probe sonication allows shortening the extraction time, but this system is unsuitable when HF is needed for efficient extraction [19].

Although bath and probe ultrasonic processors are of widespread use for UAE applications, a recent study in our lab has shown that the cup-horn sonoreactor could meet in a better way the requirements for efficient metal extraction from inorganic samples such as sediment, soil, fly ash, etc. [7]. The latter system allows multitreatments to be performed at much higher ultrasonic power than that of ultrasonic baths and, in contrast to probe systems, addition of HF to break down the silicate matrix is feasible. Apart from the most studied metals mentioned above, little attention has been paid to other essential elements such as Co or toxic elements such as Sb.

UAE of Co from inorganic samples has been addressed in a few studies. Ashley *et al.* [4] used an ultrasonic bath of $1 \text{ W} \cdot \text{cm}^2$ and 60 min sonication time. Recoveries obtained were dependent on the type of acids and their concentrations, namely, 52–58% using 25% v/v HNO_3 , 48–58% using 25% v/v $\text{HNO}_3:\text{HCl}$ (1:1), and 68–100% using $\text{HNO}_3:\text{HCl}$ (1:1) v/v. Hristozov *et al.* [8] obtained a 72% recovery of Co from sewage sludge using an ultrasonic probe of 20 kHz and 400 W power. The sonication time was 20 min, and the extractant was $\text{HNO}_3:\text{HCl}$ (1:1). Canepari *et al.* [20] obtained a 55% recovery of Co from sediments using an ultrasonic bath of 28–35 kHz and 80–180 W power for 20–30 min with 0.1 M acetic acid as extractant. Ilander *et al.* [14] obtained a 104% recovery of Co from coal fly ash using an ultrasonic bath at 35 kHz and 650 W power for 18 min with *aqua regia* and 5% v/v HF as extractant. As we can note, incomplete extractions are typically reported even using concentrated acids. No studies have been published on the UAE of Sb from inorganic matrices, and only one paper by Balarama and Arunchalam [21] tackles the extraction of Sb, among other metals, from lichen and mussel samples by applying probe sonication.

The main goal of this work is to assess a cup-horn sonoreactor as a novel ultrasonic processor for the extraction of Co and Sb from typical inorganic matrices (i.e. sludge, soil, sediment, fly ash). The work is aimed at achieving a simple, expeditious and efficient sample pre-treatment prior to ETAAS determination. Sonochemical parameters influencing the ultrasound-assisted extraction are optimised using a two-level full factorial design. The method was evaluated using several certified reference materials.

2. Experimental

2.1 Reagents

All chemicals were of analytical-reagent grade. High-purity deionised water was obtained from a PETLAB ultrapure water purification system (Peter Taboada, Vigo, Spain). 65% mass/volume HNO_3 (Merck, Darmstadt, Germany), 37% mass/volume HCl (Darmstadt, Merck), 40% mass/volume HF (Merck) and 30% mass/volume H_2O_2 (Merck) were used for extraction after suitable dilution. An antimony standard solution of 1000 mg/L prepared from SbCl_3 in 5 mol/L HCl was provided by Panreac (Barcelona, Spain). A cobalt standard solution of 1000 mg/L was prepared from $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Fluka, Steinheim, Germany) in diluted H_2SO_4 . A solution of 1300 mg/L Pd used as matrix modifier was prepared by dissolving the appropriate amount of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Merck). All glassware, plastic ware, pipette tips and storage bottles were soaked in 10% (v/v) HNO_3 for 24 h and rinsed with high-purity water at least three times prior to use.

2.2 Certified reference materials

The following certified reference materials (CRMs) were employed for optimisation and validation of the extraction method. The CRMs used were: NIST SRM 2710 Montana Soil, NIST SRM 2711 Montana Soil, NIST SRM 2702 Marine Sediment, NIST SRM 2782 Industrial Sludge, NIST SRM 1633b Coal Fly Ash are all from National Institute of Standards and Technology (USA), and BCR CRM 176R Fly Ash from the Community Bureau of Reference (Belgium). 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 for SRM 2702, less than 74 μm for SRM 2710 and SRM 2711, less than 75 μm for 2782, less than 90 μm for SRM 1633b and less than 105 μm for BCR 176R. The certified silicon contents of SRM 2710, SRM 2711, SRM 2782 and SRM 1633b were 28.97% mass/mass, 30.44% mass/mass, 20.3% mass/mass and 23.02% mass/mass, respectively.

2.3 Apparatus

A Thermo Electron Corporation® series M5 Atomic Absorption Spectrometer (Cambridge, UK), equipped with deuterium background corrector, was employed in combination with a Thermo GF95 graphite furnace and a Thermo FS95 autosampler for Sb and Co. A monoelemental hollow cathode lamp of Sb and a multielemental hollow cathode lamp of Co/Mo were employed as radiation sources (Thermo scientific, Cambridge, UK) operating at the current intensity recommended by the manufacturer. Measurements based on integrated absorbance (peak area) were made at the analytical wavelengths of 217.6 nm for Sb and 240.7 nm for Co, and the spectral bandpass was 0.2 nm for both elements. Longitudinally-heated graphite tubes with integrated L'vov platform were used throughout the work. A 200 W, 24 KHz ultrasonic reactor UTR 200® (Dr. Hielscher Company, Germany) was employed for ultrasound-assisted extraction. With this system ultrasound are not transmitted into the liquid via the tip of a sonotrode but via the oscillating bottom of a compact chamber. The oscillating bottom of the sonoreactor, screwed to the transducer, is made of extremely durable titanium alloy. An MC5 Sartorius microbalance (Goettingen, Germany) with 1 μg of sensitivity was used to

Table 1. Temperature programmes for determination of Sb and Co by electrothermal-atomic absorption spectrometry following ultrasound-assisted extraction.

Stage	Temperature (°C)	Hold time (s)	Ramp (°C s ⁻¹)	Gas flow-rate Ar (L min ⁻¹)
Drying 1	120	20	20	0.2
Drying 2	225	15	15	0.2
Drying 3	300	12	25	0.2
Pyrolysis	1200 ^a 1400 ^b	30	100	0.2
Atomisation	2200 ^a 2400 ^b	6	0	0 ^c
Cleaning	2800	2	300	0.2

Notes: ^aSb; ^bCo; ^cRead stage.

Pd (5 µL, 1300 mg L⁻¹) as modifier, added at the same time as the sample solution.

weigh the sample. A Denver instrument Force 7 microcentrifuge (Norfolk, UK) was used for rapid separation of liquid and solid phases.

Atomisation conditions were established using both sonicated extracts from several matrices and calibration solutions prepared in 3% volume/volume HNO₃ solution. Sb required a matrix or chemical modifier to reduce its volatility. The matrix modifier allows the use of a higher pyrolysis temperature (from 900°C to 1200°C) to vaporise more matrix components and minimise molecule formation during the atomisation step. Palladium nitrate (5 µL, 1300 mg L⁻¹) was chosen as the appropriate modifier. The determination of Co does not require a chemical modifier; however, nitric acid at low concentration can act as a modifier [22,23]. Optimised temperature programmes for Sb and Co are shown in Table 1.

2.4 UAE procedure

A portion (3–25 mg) of sample was weighed into an Eppendorf vial (1.5 mL capacity) and 1 mL of extractant solution (20% v/v HF + 20% v/v HNO₃) was added. Then, the sample was sonicated for 20 min at fixed ultrasound amplitude. After sonication, the supernatant liquid was separated from the solid phase by centrifugation for 2 min at 5000 rpm. Determination of Sb and Co was carried out in the supernatant. Blanks were treated in the same way. A quantity of 15 µL of standard or sample + 5 µL of matrix modifier (only for Sb) was deposited onto the L'vov platform. When the concentration of the element of interest was found to be too high, a suitable dilution with nitric acid (3% v/v) was performed before injection into the graphite furnace.

3. Results and discussion

3.1 Optimisation of UAE of Sb and Co from Marine Sediment (SRM 2702)

Inorganic matrixes are troublesome in UAE applications because the crystal lattice of silicates cannot be normally destroyed unless HF is added to the extractant medium. Therefore, incomplete metal extractions are usually expected without this acid. HF destroys the silicate matrix, through the formation of the volatile silicon fluoride (SiF₄, b.p. -86°C), and hence, the metals trapped in the silicate matrix are released into

Table 2. Operating conditions for Sb and Co.

Variables	Level (-) of variables	Level (+) of variables	Optimal conditions	
			Sb	Co
A (nitric acid, % v/v)	0.1	20	20	20
B (hydrofluoric acid, % v/v)	0.1	20	20	20
C (sonication time, min)	1	20	20	20
D (sonication amplitude, %)	20	60	20	20

the extractant solution. Consequently, the presence of HF could reduce the deterioration of the graphite surface, since it reduces the formation of silicon carbide that is formed at a temperature higher than 1650°C. The removal of the silica matrix using HF has previously been demonstrated by scanning electron microscopy images of the L'vov platforms [24]. In addition, HF could act as a chemical modifier when applying slurry sample introduction [25].

Preliminary experiments were aimed at establishing suitable intervals for the different variables influencing the extraction of Co and Sb by using the cup-horn sonoreactor. A full factorial design at two levels was carried out for screening optimisation of the extraction process.

SRM 2702 (Marine Sediment) was used as the target matrix for multivariate optimisation purposes. Extractions were performed with 5 mg amounts of this material following the experimental conditions of the factorial design.

The variables studied as well as their values for each (+ representing the maximum and - the minimum levels) are shown in Table 2. Maximum and minimum levels were chosen according to a previous experience with the application of ultrasound for Sb and Co extraction. Sixteen experiments were carried out in duplicate in order to accomplish the factorial design (2^4) for each metal [24]. As can be observed in Table 3, each experiment was randomly made order and at the appropriate levels of the variables.

The following variables were considered for optimisation of ultrasound-assisted extraction method: nitric acid concentration (variable A), hydrofluoric acid concentration (variable B), sonication time (variable C) and sonication amplitude (variable D). Main effects for each variable and the interactions between two, three and four variables were calculated from the recovery results (%) obtained in each experiment.

Particle size could be an interesting variable to optimise; however, grinding certified samples to a small size is a tedious strategy. Moreover, the contamination is very likely because of the low concentration of the analytes in the sample. In previous works, quantitative extraction was obtained with a particle size less than 150 µm. Small particle sizes also facilitate metal extraction because the total area of the solid in contact with the liquid medium is higher [26,27]. In this case, all of the reference materials have a particle size less than 105 µm.

3.2 Main effects and interactions between variables

Recoveries obtained for Sb and Co in each experiment are shown in Tables 4 and 5, respectively. Results for each replicate, average values and estimated variance are also

Table 3. Signs used to calculate the main effects and the interactions between the variables in the two-level full factorial design (2^4).

Exp	Effects				Interactions										Order	Results	
	A	B	C	D	AB	AC	AD	BC	BD	CD	ABC	ABD	ACD	BCD			ABCD
1	-	-	-	-	+	+	+	+	+	+	-	-	-	-	+	8	Y_1, S_1
2	+	-	-	-	-	-	-	+	+	+	+	+	+	-	-	2	Y_2, S_2
3	-	+	-	-	-	+	+	-	-	+	+	+	-	+	-	10	Y_3, S_3
4	+	+	-	-	+	-	-	-	-	+	-	-	+	+	+	4	Y_4, S_4
5	-	-	+	-	+	-	+	-	+	-	+	-	+	+	-	15	Y_5, S_5
6	+	-	+	-	-	+	-	-	+	-	-	+	-	+	+	9	Y_6, S_6
7	-	+	+	-	-	-	+	+	-	-	-	+	+	-	+	1	Y_7, S_7
8	+	+	+	-	+	+	-	+	-	-	+	-	-	-	-	13	Y_8, S_8
9	-	-	-	+	+	+	-	+	-	-	-	+	+	+	-	16	Y_9, S_9
10	+	-	-	+	-	-	+	+	-	-	+	-	-	+	+	5	Y_{10}, S_{10}
11	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+	11	Y_{11}, S_{11}
12	+	+	-	+	+	-	+	-	+	-	-	+	-	-	-	14	Y_{12}, S_{12}
13	-	-	+	+	+	-	-	-	-	+	+	+	-	-	+	3	Y_{13}, S_{13}
14	+	-	+	+	-	+	+	-	-	+	-	-	+	-	-	12	Y_{14}, S_{14}
15	-	+	+	+	-	-	-	+	+	+	-	-	-	+	-	6	Y_{15}, S_{15}
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	7	Y_{16}, S_{16}

Table 4. Extraction efficiency for Sb (%).

Experiment number	Recovery of duplicates		Average (Y_i)	Estimated variance ($s_i^2, n = 2$)
1	33.8	30.7	32.2	4.76
2	39.9	38.9	39.5	0.45
3	84.0	84.3	84.2	0.04
4	85.3	82.8	84.0	3.09
5	51.7	50.5	51.1	0.79
6	84.8	74.5	79.6	53.4
7	92.2	105.0	98.6	80.9
8	98.9	95.3	97.1	6.56
9	34.1	27.2	30.6	23.6
10	68.2	66.8	67.5	0.89
11	94.1	86.1	90.1	31.7
12	87.7	86.4	87.1	0.79
13	40.7	48.9	44.8	33.7
14	94.2	82.0	88.1	74.5
15	91.0	91.3	91.2	0.05
16	98.6	95.5	97.1	4.87

included in Tables 5 and 6. As can be seen, recoveries close to 100% were obtained, i.e. 98.6% in experiment 7 and 97.1% in experiments 8 and 16 for Sb; 93.0% in experiment 4, 92.7% in experiment 8 and 92.4% in experiment 16 for Co. Seemingly, extraction conditions corresponding to those of experiments 8 and 16 are appropriate to obtain total extraction of both elements.

Table 5. Extraction efficiency for Co (%).

Experiment number	Recovery of duplicates		Average (Y_i)	Estimated variance (s_i^2), $n = 2$
1	37.6	41.0	39.3	5.82
2	41.3	43.5	42.4	2.57
3	83.2	83.7	83.5	0.12
4	95.1	90.9	93.0	8.96
5	64.1	58.3	61.2	16.4
6	72.8	69.1	71.0	6.80
7	88.2	87.3	87.7	0.43
8	90.1	95.2	92.7	13.2
9	38.9	37.3	38.1	1.40
10	54.7	56.9	55.8	2.43
11	81.0	79.4	80.2	1.21
12	83.2	88.6	85.9	14.2
13	54.0	58.4	56.2	9.32
14	76.9	73.1	75.0	7.05
15	86.8	88.9	87.8	2.28
16	92.3	92.4	92.4	0.00

Table 6. Evaluation of the proposed method using different certified reference materials (CRMs).

Element	CRM	Certified value ($\mu\text{g/g}$)** $\bar{x} \pm t \cdot s\sqrt{n}$	Found value ($\mu\text{g/g}$)** $\bar{x} \pm t \cdot s\sqrt{n}$	Recovery (%)	t_{exp}	RSD (%)
Sb	SRM 2710	38.4 ± 3.0	38.4 ± 2.0	100.0 ^a	0.03	2.1
	SRM 2711	19.4 ± 1.8	19.6 ± 2.7	101.0 ^a	0.38	5.5
	SRM 2702	5.60 ± 0.24	5.1 ± 3.3	91.1 ^a	3.82	4.3
	SRM 2782	2*	1.5 ± 0.8	75.0 ^a	2.97	21.1
	BCR 176R	850 ± 50	856 ± 30	100.7 ^a	0.88	1.4
	SRM 1633b	6*	3.98 ± 1.14	66.5 ^a	7.58	11.5
Co	SRM 2710	10*	9.23 ± 1.30	92.3 ^a	2.49	5.7
	SRM 2711	10*	9.6 ± 0.5	96.0 ^a	3.77	2.0
	SRM 2702	27.76 ± 0.58	26.4 ± 1.9	95.1 ^a	3.16	2.9
	SRM 2782	66.3 ± 4.8	67.2 ± 15.9	101.4 ^a	0.23	9.6
	BCR 176R	26.7 ± 1.6	21.1 ± 5.9	79.0 ^a	4.06	11.0
	SRM 1633b	50*	36.1 ± 5.5	72.2 ^a	10.83	6.1
			46.2 ± 9.1	92.3 ^b	1.80	7.0

Notes: RSD, relative standard deviation.

*Indicative value.

**The uncertainty was taken as the 95% confidence interval of the mean.

^a20% v/v HNO₃, 20% v/v HF, 20 min sonication time, 20% sonication amplitude.

^b20% v/v HNO₃, 20% v/v HF, 5% v/v H₂O₂, 20 min sonication time, 20% sonication amplitude.

Then, the effects and interactions were calculated. The experimental error ($2\bar{s}$), \bar{s} being the average standard deviation, was 6.7 and 4.2 for Sb and Co, respectively. When the effects and interactions were lower than $-2\bar{s}$ or higher than $+2\bar{s}$, it meant that the extraction of the metals was significantly affected in a negative or positive way, respectively. However, when the effects or interactions were within the interval $\pm 2\bar{s}$, it

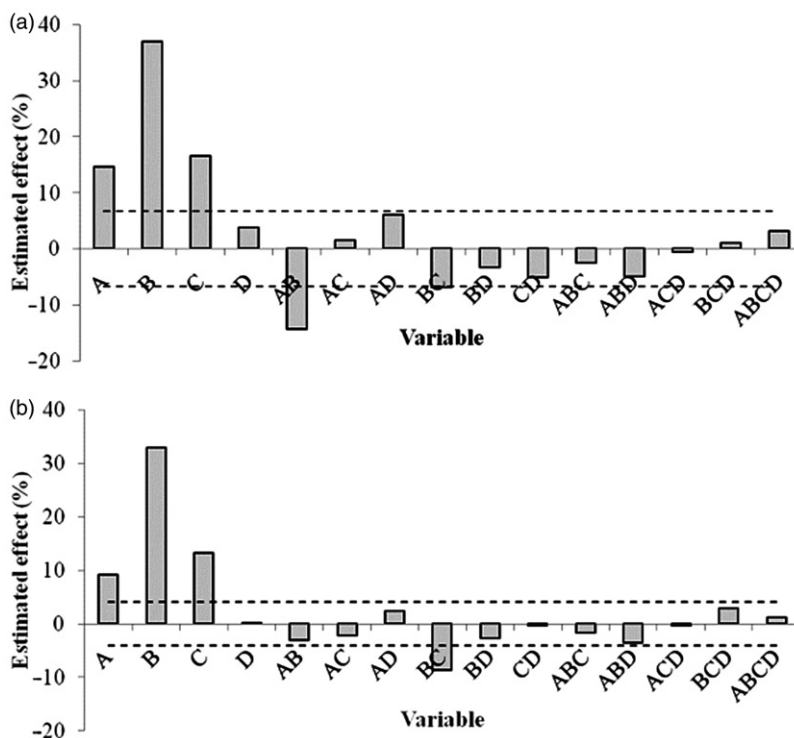


Figure 1. Estimated effects obtained in the application of the two full factorial design for Sb (A) and Co (B) ultrasound-assisted extraction. Variable A = nitric acid concentration (% v/v); variable B = hydrofluoric acid concentration (% v/v); variable C = sonication time (min); variable D = sonication amplitude (% of 200 W). The dashed lines represent the experimental error ($\pm 2\sigma$).

meant that extraction was not affected, so in principle, any level of the variable could be chosen in the studied interval.

As can be seen in Figures 1A and 1B, HNO_3 concentration (variable A), HF concentration (variable B) and sonication time (variable C) have a significant positive effect over the extraction of Sb and Co. A change in the HNO_3 concentration from the (–) to the (+) level led to an increase in the recovery of 15 and 9% for Sb and Co, respectively. When the HF concentration was changed from the (–) to the (+) level, an increase in the recovery of 37 and 33% for Sb and Co occurred, respectively. Likewise increases in the recovery of 16 and 13% for Sb and Co occurred when the sonication time was varied from the (–) to the (+) level, respectively. The sonication amplitude did not cause any significant effect over the Sb and Co extraction.

A relevant interaction between two variables was observed for Sb, i.e. variables A and B (Figure 1A). On the contrary, there is an interaction between the variables B and C for Co (Figure 1B). However, interactions are smaller than the main effects of variables A, B and C for both elements.

Schematic diagrams were prepared in order to explain the interactions between variables (Figure 2). The first interaction arises from the dependence of the HNO_3

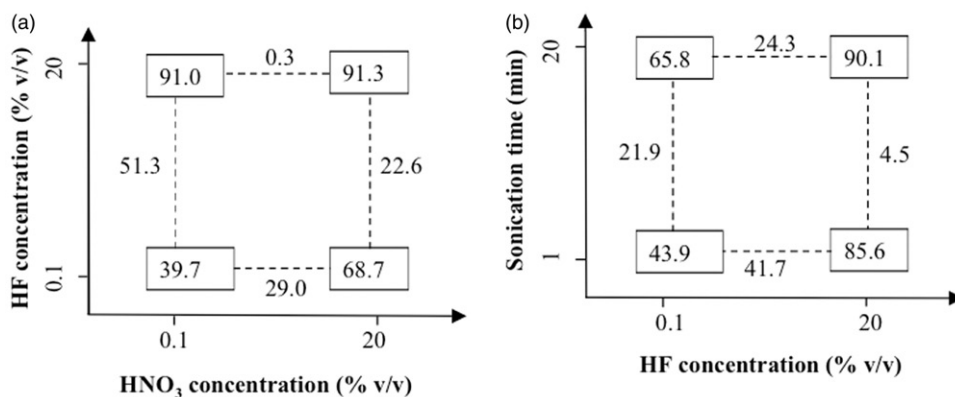


Figure 2. Schematic diagrams showing the significant interactions between two factors. The extraction recovery was included inside each square. (A) Nitric acid concentration and hydrofluoric acid concentration for Sb extraction. (B) Hydrofluoric acid concentration and sonication time for Co extraction.

concentration on the HF concentration (Figure 2A). When the HF concentration is at the low level, there is a positive effect of the HNO₃, although poor recovery is observed; but when the HF concentration is at the high level, there is no effect of the HNO₃ concentration, and the extraction recovery is around 91%. Therefore, the higher level of HF concentration should be employed.

A second interaction occurred as a consequence of the different influence of the sonication time on Co extraction depending on the HF concentration (Figure 2B). If the HF concentration is at the low level, there is an increase in extraction efficiency, but recovery reaches only *c.* 66%. On the contrary, if the HF concentration is fixed at the high level, the increase in sonication time only provokes a smaller increase in recovery (i.e. from 86 to 96%). Therefore, the higher level of HF concentration and sonication time should be used for Sb and Co extraction. Moreover, experiments with a 10% v/v HF + 10% v/v HNO₃ mixture along with 20 minutes of sonication showed no complete recoveries in all cases.

Optimal conditions for UAE of Sb and Co are shown in Table 2. Variables A, B and C were fixed at the high levels whereas variable D was fixed at the low level.

3.3 Analytical characteristics

The equations for the linear range of the Sb and Co calibration curves were respectively, $Y = 4.65 \cdot 10^{-3}[\text{Sb}] + 7.23 \cdot 10^{-4}$ ($R^2 = 0.9976$) and $Y = 1.15 \cdot 10^{-2}[\text{Co}] + 1.59 \cdot 10^{-2}$ ($R^2 = 0.9998$), where Y is the integrated absorbance and the element concentration is expressed as $\mu\text{g L}^{-1}$. They were linear up to 50 and 60 $\mu\text{g L}^{-1}$ for Sb and Co, respectively. Characteristic masses were 14.2 and 5.7 μg for Sb and Co, respectively. The method detection limit (MDL) was defined as $3\sigma m^{-1}$, where σ is the standard deviation corresponding to 10 blank injections and m is the slope of the calibration graph. The MDLs in the original samples were calculated as if 10 mg of the solid material were extracted in 1.5 mL volume and 5 μL were injected into the furnace, and they were 0.20 and

0.06 $\mu\text{g g}^{-1}$ for Sb and Co, respectively. Between-batch precision was expressed as relative standard deviation (RSD) for $n=3$ independent extractions. In general, RSDs were less than 5.5 and 9.6% for Sb and Co, respectively.

3.4 Analysis of environmental CRMs

The proposed methodology was evaluated using five CRMs. The results are shown in Table 6. A t -test was applied for testing the accuracy of the results. The condition $t_{\text{exp}} < t_{\text{crit}}$ ($t_{\text{crit}} = 4.303$ for $n - 1 = 2$ df) was fulfilled in most cases, and consequently, non-significant differences were observed ($p = 0.05$) between the certified (or indicative) and found metal contents.

With a few exceptions, acceptable recoveries were observed. The Sb and Co recoveries from NIST SRM 1633b were 66.5 and 72.2%, respectively. Spiking experiments were performed in order to assess the possibility of matrix effects in the determination of Sb and Co in extracts obtained from this material. Recoveries of spikes were 111 ± 4 and 109 ± 3 for Sb and Co, respectively. Therefore, low recovery occurs as a result of incomplete extraction. On the other hand, no certified values were provided for this CRM, but only indicative, and uncertainty was not reported. Addition of H_2O_2 and HCl was attempted to improve the Sb and Co extraction from SRM 1633b. Whilst the Sb recovery was not influenced even using a concentration as high as 20% v/v of those reagents, the Co recovery was improved to reach 92.3% when 5% v/v H_2O_2 was added to the extractant. The addition of hydrogen peroxide, along with nitric acid could facilitate the partial oxidation of organic matter present in the coal fly ash, hence improving the extraction of Co from it.

According to the certificate of the SRM 1633b, it is a bituminous coal fly ash, meaning that it belongs to the class F. In that case, the sum of silica (SiO_2), iron oxide (Fe_2O_3) and alumina (Al_2O_3) is higher than 70%, CaO represents less than 5%, and it also contains a high amount of unburnt carbon [28]. As a consequence of the combustion process, metals are more strongly bound in comparison with other samples, and they have less-reactive properties [29]. The structure is formed by small sphere particles with size around 10 μm , and some large particles between 10 and 100 μm , the structure being sphere-within-sphere (pleospheres) [30].

4. Conclusions

The proposed methodology describes a simple and efficient sample treatment based on ultrasound-assisted extraction from solid materials containing silicates. In most cases, quantitative recoveries are reached for Sb and Co from a variety of environmental CRMs using a cup-horn ultrasonic processor along with a mixture of diluted acids (HF and HNO_3) as extractant medium. This ultrasonic equipment allows high intensity sonication in closed vials, hence combining the advantages of bath and probe ultrasonic processors. The fact that the vials are closed reduces the possibilities of the sample contamination and analyte losses as a consequence of the cavitation phenomenon. Moreover, it allows the use of HF for extraction with no damage of the sonication device. A two-level full factorial design (2^4) is suitable for the optimisation of the most important variables involving relatively few experiments.

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