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Direct determination of Ge in hot spring waters and coal fly ash samples by hydride generation-ETAAS

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Abstract

A method for Ge determination in hot spring water and acid extracts from coal fly ash samples involving hydride generation, trapping and atomisation of the hydride generated from Ir-treated graphite tubes (GTs) has been developed. Hydride was generated from hydrochloric acid medium using sodium tetrahydroborate. Several factors affecting the hydride generation, transport, trapping and atomisation efficiency were studied by using a Plackett-Burman design. Results obtained from Plackett-Burman designs suggest that trapping and atomisation temperatures are the significant factors involved on the procedure. The accuracy was studied using NIST-1633a (coal fly ash) reference material. The detection limit of the proposed method was 2.4 $\mu g\,l^{-1}$ and the characteristic mass of 233 pg was achieved. The Ge concentrations in fly ash and hot spring samples were between 6.25–132 $\mu g\,g^{-1}$ and 12.84–36.2 $\mu g\,l^{-1}$.

Keywords: Ge; Hot spring water; Coal fly ash; HG-ETAAS

1. Introduction

The major entering sources of germanium in the environmental are zinc sulphide and lead–zinc–copper sulphide ores. Germanium can also be released from the ash of coal and other lignite, which constitute approximately 0.0007% of the Earth's crust. Various inorganic germanium compounds have been used in the development of semiconductors, catalysts and medical imaging devices. Ge are present in fresh, estuarine, and sea water at extremely low concentrations 0.016, 0.029, 0.009 $\mu g\,l^{-1}$, respectively [1]. These levels are increase up for hot spring water samples.

The determination of hydride elements forming in several samples by hydride generation atomic absorption spectrometry (HG-AAS) has been extensively documented [2–4]. In the same way, the hydride-generation coupled to electrothermal atomic absorption spectrometry (HG-ETAAS) which involve the use of a hot treated graphite furnace to concentrate and atomise the hydride, has been recognised as the most sensible atomic absorption spectrometric detection system [5]. Determination of Ge by HG-ETAAS has been reported in the literature [6–12].

The use of a chemically modified graphite surface with metals such as Pd or Ir and carbide-forming elements such as Zr and W offers an increase in the hydride sequestration efficiency. Owing to its excellent sequestrating properties, [5] palladium has been proposed as the best coating reagent for the "in situ" hydride pre-concentration onto graphite tubes (GTs). Thus, characteristic masses, m_0, of 25.9, 12, 26, 49 and 40 pg have been reported [7,8,10–12]. In addition, a characteristic mass of 38 pg for Pd/Mg-treated graphite tubes [10] and 55 pg for Pd/Mg-treated GTs [6] have been reported. Otherwise, the use of palladium-treated GT presents several disadvantages. Most importantly, due to the high volatility of palladium (boiling point 2970 °C), an injection of palladium into the furnace is necessary after each cycle. The use of different refractory elements to coat graphite tubes overcome this problem. Thus, several carbide-forming elements (Zr, Nb, Ta, W) and noble metals (Ir) were investigated by Haug and Yiping [6] for Ge hydride trapping onto graphite tubes.

Several methods used for metal determination in solid samples require the sample to be in solution. Microwave-

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assisted extraction methods with PTFE bombs, using different acid mixtures, have been proposed for metals extraction for several kinds of samples. In this study a microwave acid extraction procedure using aqua regia was used for Ge determination in fly ash samples. The sample is not ashed, therefore, by using this procedure, metal loss is avoided [13,14].

The purpose of this paper is the optimisation of hydride generation-ETAAS procedure by using Ir-treated GT for Ge determination in waters with relatively high concentrations of Ge (hot spring water) and in products from coal fire power plant (coal fly ash). Although the high germane trapping efficiency was obtained by using Zr-treated GT (133 pg), Ir-treated graphite tubes were selected in this study, due to the use of this permanently-coating offers adequate trapping efficiencies for other hydride elements forming (233 pg). Thus, these elements could be determined at compromise trapping and atomisation temperatures with a minimum sacrifice in sensitivity. Such uniform conditions for as many elements as possible are of vital importance in simultaneous furnace technique, such as the SIMAAC or the FANES system [15,16]. Due to several variables involved throughout the procedure such as hydrochloric acid and sodium tetrahydroborate concentrations, hydrochloric acid and sodium tetrahydroborate flow rates and reaction coil length, affecting the GeH_4 generation efficiency; trapping and atomisation temperatures and trapping time affecting the GeH_4 trapping and atomisation efficiency, and the Ar flow rate affecting the GeH_4 transport efficiency, experimental designs, such as Plackett-Burman and central composite designs, have been used throughout the optimisation. The developed method has been applied to hot-spring waters and coal fly ash samples obtained from coal fire power plants.

2. Experimental

2.1. Apparatus

Measurements were performed using a AAnalyst 800^{TM} atomic absorption spectrometer (Perkin-Elmer Instruments, Shelton, CT, USA) equipped with a THGA^{TM} (transversely heated graphite atomiser) furnace and an autosampler AS-800. Electrodeless discharge lamp operated at 310 mA, which provided a 265.1 nm line were used. The spectral bandwidth was 0.2 nm. A FIAS^{TM}-400 system (Perkin-Elmer) with a 5-port flow injection (FI) valve was used for germane generation. A PC computer program automatically controls the rotation speed of the two multichannel peristaltic pumps. A PTFE-membrane gas liquid separator (Perkin-Elmer) was used. The FIAS-furnace sample transfer tube was supplied by Perkin-Elmer. This transfer tube consists of quartz capillary (2 cm long × 1.3 mm o.d. × 0.5 mm i.d.). The tube is attached to a metal mount with a short piece of silicone rubber tubing, which in turn is attached to a PTFE tube. The metal mount of the FIAS furnace sample transfer tube was loaded into the spring clip at the end of the autosampler arm.

A Milestone MLS 1200 microwave oven (Sorisole, Italy), programmable for time and microwave power, was used for the metal extraction from the samples.

2.2. Reagents

Ge stock standard solution, 995 $\mu g\,ml^{-1}$ was obtained from Aldrich (Milwaukee, USA). Nitric acid 69–70% (Baker, Phillipburg, PA USA) and hydrochloric acid 36.5–38% (Baker) were used for sample digestion. Sodium tetrahydroborate (Merck, Darmstad, Germany) dissolved in 0.5% (w/v) of sodium hydroxide (Panreac, Barcelona, Spain) was used as the reducing solution. This solution was prepared daily and filtered before use. Hydrochloric acid solution was prepared from hydrochloric acid 37% (Panreac). Iridium standard solution 2.5 $g\,l^{-1}$ prepared from IrCl 99.9% (Aldrich), was used as coating for the graphite tubes. NIST-1633a (Trace Elements in Coal Fly Ash) from US Department of Commerce National Institute of Standard and Technology (Gaitersburg, MD, USA) reference material was used to study the accuracy. Argon N-50 purity (99.999%) was used as sheath gas for the atomiser and to purge internally, this was obtained from Carburos Metálicos (Barcelona, Spain).

2.3. Sample collection

Hot-spring water samples, collected from sources of Ourense and Lugo (Galicia, Northwest, Spain) in 100 ml polyethylene bottles were acidified with 100 μl of concentrated nitric acid to achieve $pH < 1.6$ and kept at 4 °C before measurement.

2.4. Microwave acid extraction procedure

A microwave acid extraction procedure was achieved for coal fly ash samples. 0.4000 g of sample was placed into the PTFE bombs, 6 and 2 ml of concentrated HCl and HNO_3, respectively were added, and the mixture subjected to microwave energy (Table 1). After microwave extraction, the acid liquid phase was filtered (Watman No. 40 paper filter) and the solutions were made up to 25 ml with ultrapure water and kept in polyethylene bottles at 4 °C before measurement.

Table 1
Microwave-acid extraction program

Step	Time (min)	Power (W)
1	5	300
2	3	650
3	3	450
4	3	0

Table 2
Optimum conditions for germane generation and germane trapping and atomisation from Ir-treated GTs

Hydride generation conditions

Variable	Value	*b* coefficients
HCl concentration (M)	3.0	0.019
$NaBH_4$ concentration (%) (m/v)	2.0	0.015
HCl flow rate (ml min^{-1})	9.0	0.017
$NaBH_4$ flow rate (ml min^{-1})	5.0	−0.017
Reduction coil length (cm)	100	0.022
Ar flow rate (ml min^{-1})	50	0.027
Sample volume (μl)	500	−0.021

Trapping and atomisation conditions

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml min^{-1})
Collection	1000	1	10	250
Atomisation	2500	0	5	0 (read)
Cleaning	2500	1	3	250

2.5. *Germane generation and in situ pre-concentration*

Germanium hydride was generated from a 500 μl sample. The tip of the quartz capillary tube was inserted from the outlet of the gas liquid separator at the centre of the graphite tube. The hydrochloric acid (3.0 M) and sodium tetrahydroborate (2%, m/v) solutions were pumped into the generator for 10 s at a rate of 9 and 5 ml min^{-1}, respectively. The evolved hydride was transported (using argon flow rate of 50 ml min^{-1}) and sequestered onto Ir-GTs (at 1000 °C) for 10 s and then atomised at 2500 °C for 5 s using maximum power heating and internal gas stop. The optimum hydride generation conditions and the graphite furnace programmes are listed in Table 2.

2.6. *Coating graphite tubes*

The coating methods used [17], involved the injection of five 100 μl aliquots of Ir solutions (2.5 g l^{-1}). Each injection was dried slowly by heating the atomiser at 150 °C with 30 and 40 s of ramp rate and hold times, respectively. Then a second dried step at 200 °C with 20 and 30 s of ramp rate and hold time was used. Following this, a reduction step at 2000 °C was applied during 5 s. The tube treated in this manner can be cycled through about 300–400 firings.

2.7. *Statistical treatment of data*

For experimental design modelling, programs from Statgraphics Plus 4.0 (Statgraphics Graphics Corporation, ST.SC, USA) were used.

3. Results and discussion

3.1. *Optimisation of Ge hydride procedure using experimental design*

Different variables affecting the Ge hydride generation efficiency (hydrochloric acid and sodium tetrahydroborate concentrations, hydrochloric acid and sodium tetrahydroborate flow rates and reaction coil length); germane transport efficiency (argon flow rate) and germane trapping and atomisation efficiency (trapping and atomisation temperatures and trapping time) from Ir-treated GT have been studied using factorial design experiments namely, Plackett-Burman and orthogonal central composite designs. The Plackett-Burman factorial design allows the main effects of a greater number of variables to be known with relatively few experiments. The significant parameters obtained (trapping and atomisation temperature) have been optimised by using a 2^n + star central composite design. The optimisation has been developed by using standard aqueous solutions of 10 μg l^{-1} of germanium. Table 3 lists the upper and lower values given to each factor. Hydrochloric acid and sodium tetrahydroborate levels and trapping and atomisation temperature levels were chosen according to literature values.

3.2. *Plackett-Burman designs*

A two level Plackett-Burman 2^9*3/128 with two degrees of freedom and twelve runs was carried out to find the main factors affecting HG-ETAAS procedure. The experimental design matrix and the response (integrated absorbance, mean of three determinations) obtained for each run are shown in

Table 3
Experimental field definition for the Plackett-Burman and central composite designs involves on germane generation and germane trapping and atomisation

Factor	Key	Low (−)	High (+)
HCl concentration (M)	A	0.1	3.0
$NaBH_4$ concentration (%, m/v)	B	0.2	2.0
HCl flow rate (ml min^{-1})	C	5.0	9.0
$NaBH_4$ flow rate (ml min^{-1})	D	5.0	9.0
Trapping temperature (°C)	E	20	1000
Atomisation temperature (°C)	F	1500	2500
Trapping time (s)	G	10	30
Reaction coil length (cm)	H	11	100
Ar flow rate (ml min^{-1})	I	50	100

Table 4
Plackett-Burman design for the determination of significant variables involves on the procedure for germane generation and trapping and atomisation from Ir-treated GTs

Run no.	A	B	C	D	E	F	G	H	I	Integrated absorbance[a]/A.s.
1	+	−	+	−	−	−	+	+	+	0.001
2	+	+	−	+	−	−	−	+	+	0
3	−	+	+	−	+	−	−	−	+	0
4	+	−	+	+	−	+	−	−	−	0.008
5	+	+	−	+	+	−	+	−	−	0.001
6	+	+	+	−	+	+	−	+	−	0.123
7	−	+	+	+	−	+	+	−	+	0.008
8	−	−	+	+	+	−	+	+	−	0
9	−	−	−	+	+	+	−	+	+	0.018
10	+	−	−	−	+	+	+	−	+	0.013
11	−	+	−	−	−	+	+	+	−	0.001
12	−	−	−	−	−	−	−	−	−	0.001

[a] Mean of three determinations.

Table 5
Central 2^2 + star orthogonal composite design for the set trapping temperature/atomisation temperature for Ge determination from Ir-treated GTs

Run no.	Trapping temperature (°C)	Atomisation temperature (°C)	Integrated absorbance[a]/A.s.
1	K_0[b]	K_0[c]	0
2	−	−	0
3	+	−	0.001
4	−	+	0.030
5	+	+	0.089
6	$-\alpha$[d]	K_0[c]	0
7	$+\alpha$[e]	K_0[c]	0.006
8	K_0[b]	$-\alpha$[f]	0
9	K_0[b]	$+\alpha$[g]	0.071
10	K_0[b]	K_0[c]	0.002

[a] Mean of three determinations.
[b] $K_0 = 510\,^\circ$C.
[c] $K_0 = 2000\,^\circ$C.
[d] $-\alpha = 0$.
[e] $+\alpha = 1200\,^\circ$C.
[f] $-\alpha = 1300\,^\circ$C.
[g] $+\alpha = 2600\,^\circ$C.

Table 4. Table 4 was provide from Statgraphics Plus 4.0 routine. The analysis of the results are visualised (Fig. 1) using a standardised ($P = 95.0\%$) main effect Pareto chart and two-factor interactions Pareto charts ($P = 95.0\%$). In these charts, bar length are proportional to the absolute value of the estimated effects. A black line show the minimum t values (at the 95% CI) 4.3 and 2.6 corresponding to the main and two-factor interaction Pareto charts, respectively. We consider a factor as a significant when its value was higher than $\pm t$. After the study of results, trapping temperature (E) and atomisation temperature (F) were statistically significant. All the other considered variables were not significant in the ranges studied.

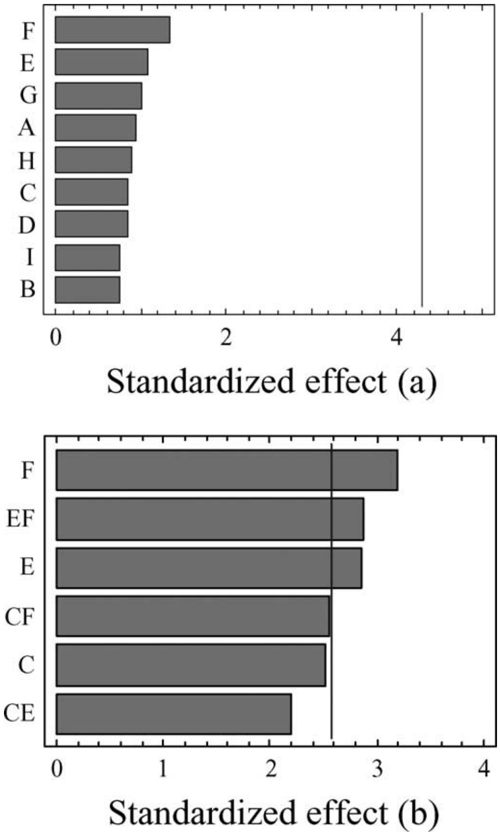

Fig. 1. Standardised ($P = 95\%$) main effects Pareto charts (a) and two-factor interactions Pareto charts (b) from the Plackett-Burman design for Ge hydride. (A) Hydrochloric acid concentration; (B) sodium tetrahydroborate concentration; (C) hydrochloric acid flow rate; (D) sodium tetrahydroborate flow rate; (E) trapping temperature; (F) atomisation temperature; (G) trapping time; (H) reaction coil length; (I) Ar flow rate.

3.3. Orthogonal central composite design

Screened out the variables that did not have a significant effect on the response, the remaining factors trapping temperature (E) and atomisation temperature (F) have been optimised. A central 2^2 + star orthogonal composite design with four degrees of freedom and involving 10 experiments was performed. Table 5 shows the central composite design together with the response obtained. The trapping/atomisation temperature estimated response surface (Fig. 2) showed that the maximum values for the factors studied have not been included in the experimental region. A new factorial design

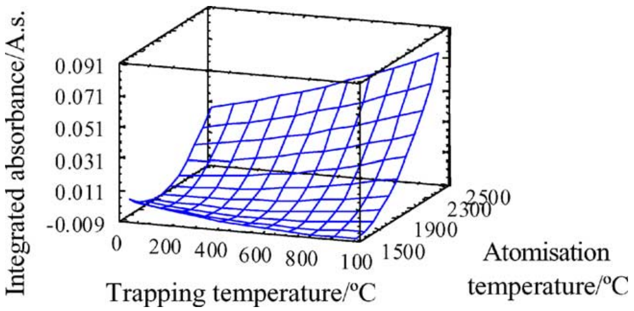

Fig. 2. Estimated response surface from the central composite design obtained for the pair trapping temperature/atomisation temperature for Ge determination.

Table 6
Ge concentrations in several environmental samples

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Coal fly ash (μg g^{-1})	99 ± 1	6.25 ± 0.1	7.5 ± 0.1	125 ± 1	117 ± 1	132 ± 1
Hot spring water (μg l^{-1})	15.6 ± 0.1	12.8 ± 0.1	14.3 ± 0.1	36.2 ± 0.1	–	–

shifted in the direction of the maximum gradient would reach practical limitations. The highest trapping and atomisation temperatures, which could be used, are 1000 and 2600 °C. Thus, we selected these temperatures as adequate values for the studied. The fixed values for the insignificant factors (results from Plackett-Burman design) are also given in Table 2.

3.4. Figures of merit

The slopes of the calibration and addition equations obtained for aqueous standard solutions, hot-spring water sample and coal fly ash samples, spiked with 5.0, 10.0 and 20.0 μg l^{-1} of Ge were 0.009, 0.01 and 0.008 respectively. A *t*-test (for a confidence level of 95.0%) was applied to compare the calibration and standard additions slopes. Results show that, the slopes of the calibration and standard additions graphs are identical. Therefore, matrix effect is not important. The characteristic mass, m_0 (i.e. the mass of analyte which provides a peak absorbance of 0.0044 A.s.) was 233 pg. The blank values obtained were low. The detection and quantification limits, LOD and LOQ (defined as 3 and 10 s/m, where S.D. is the standard deviation of 11 measurements of a blank and m is the slopes of the calibration graphs) are 2.4 and 7.1 μg l^{-1} and 1.4 and 7.5 μg g^{-1} for hot spring waters and coal fly ash, respectively. The precision obtained, R.S.D. (%), is lower than 10% for all concentrations tried. Aqueous reference materials with germanium certified or information values are not available. Thus, the method was validated by analysing the NIST-1633a (coal fly ash) reference material. NIST-1633a offers an information value for Ge (6.0 μg g^{-1}). The result obtained (5.0 ± 0.1 μg g^{-1}) was close to the information value. In addition, several authors [18,19] have been reported germanium levels from the NIST-1633a of 5.6 ± 0.1 and 5.0 ± 0.1 μg g^{-1}, respectively. An ANOVA test was performed to compared the information value, the published data and the value found. This test showed that there is not statistically significant differences among the means at the 95% confidence level when concentration means were compared.

3.5. Application

The optimised procedure was applied to several hot spring waters samples, as well as, acid extracts from coal fly ash samples. The solid samples were subjected twice to the microwave-assisted acid digestion. Six samples of coal fly ash and four samples of hot-spring water were analysed. The results are shown in Table 6, where the concentration of each metal ($N = 3$) is given together with the standard deviation. The germanium concentration in coal fly ash samples was between 6.25 and 132 μg g^{-1}. For hot-spring water was between 12.84 and 36.16 μg l^{-1}.

4. Conclusions

The use of Plackett-Burman designs, as factor screening, show that the trapping temperature and the atomisation temperature are the most significant variable in the germanium determination by HG-ETAAS. By using Ir-treated graphite tubes, and adequate accuracy and sensitivity is obtained for Ge determination in coal fly ash and hot-spring waters. Moreover, for the determination of germanium, the method of hydride generation combined with electrothermal atomisation is freedom from interferences that are present when the graphite furnace atomic absorption spectrometry is used [10,18].

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