Comparison of chemical modifiers for selenium determination in soil aqua regia extracts by ZETAAS

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Abstract

The effect of various chemical modifiers $0.5\,g\,l^{-1}$ Pd, 1% (w/v) Ni, $0.5\,g\,l^{-1}$ Pd + 1% (w/v) Ni and $1.0\,g\,l^{-1}$ Pd on the measurement of selenium in soil aqua regia extracts, by ZETAAS, is described. Two Certified Reference Materials (CRMs) RTC-CRM 023-050 and RTC-CRM 025-050 were used for this study. Pyrolysis and atomization curves were obtained for each chemical modifier and their optimal values were assessed. By using standard addition as calibration method, accurate results were obtained for all the chemical modifiers studied. The precision was similar for both CRMs, with a maximum value of 7.5% R.S.D. The limits of detection and quantification for selenium in the soil extracts ($n = 10$) were 3.0 and $6.0\,\mu g\,l^{-1}$, respectively. The characteristic mass of selenium is assessed as 10 pg. The use of aqua regia as extractant gave quantitative results for selenium in the CRMs assayed.
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1. Introduction

Selenium is a naturally occurring element in soils, and weathering of rocks and atmospheric deposition are its most frequent sources. Selenium in soils is mainly associated with the clay fraction in sedimentary rocks [1]. The atmospheric deposition is mainly attributed to anthropogenic sources, a fact which must be highlighted, since the combustion of coal and, more recently, petroleum-based fuels, contributes to Se emissions [2], in spite of the fact that these contributions have decreased in the last few decades. Several types of industries, among them glass manufacturing, electronic devices, plastics, smelting of some ores and paints can be considered anthropogenic sources of selenium as well. Moreover, selenium is also present in soils as a result of the application of sewage sludges, although its concentration is lower if compared with other elements [1,3]. Selenium levels in soils vary according to soil types and according to countries, within a wide range of concentrations. Thus, the selenium levels in soils reported in the literature show concentration ranges varying from a few $mg\,kg^{-1}$ to some hundreds [1].

Selenium presents a dual character since it is considered an essential nutrient for plants and animals and, on the other hand, can be considered toxic at high concentration levels [4–7]. Due to this toxic character selenium releases are covered by several international agreements such as that of the United Nations Environmental Programme (UNEP) [8] in which selenium, among others, is considered an element that can cause serious pollution of all environmental media and is thus considered in the guidelines on landfill practices. This element is included in several USEPA lists and regulations such as PBT [9] and EPCRA [10] and in the IPPC Directive of the European Union [11]. At present, efforts for developing soil guideline values for selenium, on the basis of soil uses, are in course [12].

Among the analytical techniques for selenium determination, the graphite furnace appears as one of the most adequate for determining this element in a great variety of matrices [13], and the conventional solution sample introduction is the most widely used method for the vast majority of samples [14].

Extraction by hot aqua regia according to ISO Norm [15] to obtain information about pseudo-total element concentration in soils is strongly recommended and should be carried out in such a way that allows the results obtained by using this extraction system to be used for comparison purposes [16]. Very few studies deal with aqua regia extraction, and they are mainly focused on

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the comparison of recovery levels [17,18], and no optimization methods for selenium measurement after extraction by using the above mentioned ISO Norm are reported.

As far as graphite furnace measurement is concerned, the difficulties in determination of selenium and the proposals for metal modifiers recommended is a subject of permanent discussion [19–23]. From the literature, it is also evident that the data reported on the analytical performance of metal modifiers for selenium determination are controversial [24–26]. In general, some parameters, such as quantification method, are not discussed or, in some instances, only information obtained from aqueous standards is reported. Among such studies pure solutions, biological fluids and some environmental matrices of aquatic origin are considered; nevertheless, the studies dealing with the optimization conditions for selenium determination in soils are very scarce and some of them are devoted to extractable Se by using mild extractants [4]. On the other hand, the use of acidic extractants can affect the efficiency of the chemical modifier. For instance, it has been reported the poor performance of palladium nitrate modifier for the determination of selenium in the presence of hydrochloric acid [27].

The present study deals with the optimization of the selenium measurement by electrothermal atomization atomic absorption spectrometry in soil extracts obtained by using aqua regia extraction [15]. Two Certified Reference Materials RTC-CRM 023-050 and RTC-CRM 025-050 were used for the overall study. As palladium and nickel have been successfully used for the analysis of biological and environmental matrices [22,28], the behaviour of four chemical modifier solutions containing this elements, $0.5\,\mathrm{g\,l^{-1}}$ Pd, 1% (w/v) Ni, $0.5\,\mathrm{g\,l^{-1}}$ Pd + 1% (w/v) Ni and $1.0\,\mathrm{g\,l^{-1}}$ Pd, is studied. The characteristic mass values for Se under all the studied conditions are determined. Performance parameters: precision, accuracy, detection and quantification limits are also established. Quantification by using both external curve and standard addition methods is reported and discussed.

2. Experimental

2.1. Instrumentation and apparatus

A single beam atomic absorption spectrometer (Unicam 939 AA Spectrometer) equipped with a Zeeman background correction (Unicam GF90 furnace) and an FS-90 plus furnace autosampler was used. All measurements were performed using a hollow cathode selenium lamp running at 15.0 mA, at 196.0 nm wavelength and a bandpass of 0.5 nm. Pyrolytically coated graphite tubes were used with L'vov platform built-in (Unicam 9423 393 95041 ELC cuvettes). Argon was used as the purge gas at a flow rate of $250\,\mathrm{ml\,min^{-1}}$.

A Salter analytical balance was used to weigh the soil samples.

A digestor system (P/Selecta Bloc Digest 12) was used to digest the Certified Reference Materials analysed. Sample pre-reduction was performed in a sand-bath.

2.2. Standards solutions and reagents

All solutions were prepared in de-ionized water from a Milli-Q system (USF Purelab Plus) with a resistivity of $18.2\,\mathrm{M\Omega\,cm^{-1}}$. A stock solution of $1000\,\mathrm{mg\,l^{-1}}$ of Na_2SeO_3 (Aldrich; >99%, MW 172.94) was used to prepare appropriate concentrations of working selenium standard solutions on a daily basis. Solutions and concentrations tested as chemical modifiers were as follows: 0.5 and $1.0\,\mathrm{g\,l^{-1}}$ of aqueous Palladium solutions were prepared from $10.0 \pm 0.2\,\mathrm{g\,l^{-1}}$ of $Pd(NO_3)_2$ in 15% HNO_3 (Merck); 1.0% (w/v) aqueous Nickel solutions were prepared from standard Nickel (Nickel wire, Alfa Puretronic) following NIST recommendation [29]; a mixture of Pd/Ni ($0.5\,\mathrm{g\,l^{-1}}$/1.0%, w/v) from the same reagents described above.

For aqua regia extraction concentrated nitric acid (J.T. Baker Instra®, 37%, $12\,\mathrm{mol\,l^{-1}}$) and concentrated hydrochloric acid (J.T. Baker Instra®, 70%, $15.8\,\mathrm{mol\,l^{-1}}$) were used.

2.3. Certified Reference Materials

Two Certified Reference Materials (CRMs) with suitable values for selenium were selected for the study: RTC-CRM 023-050 and RTC-CRM 025-050 soils from the Resource Technology Corporation, WY, USA, with 116.72 and $518\,\mathrm{mg\,kg^{-1}}$ Se, respectively. These soils are from a moderately contaminated site located in the western USA.

2.4. Procedures

2.4.1. Sample digestion

CRMs were digested by following the ISO Norm [15] with a modification (air-cooler connection following water cooler, in order to prevent any selenium losses during the digestion process). 1.5 g of soil was placed into a 250 ml Pyrex reaction tube, 0.5 ml de-ionized H_2O, 3.5 ml concentrated HNO_3 and 10.5 ml concentrated HCl were added slowly. The mixture was left for 16 h at room temperature, and then refluxed for 2 h at 130 °C.

Table 1

Operating conditions for selenium determination in *aqua regia* soil extracts by ZETAAS

Wavelength	196 nm
Lamp type	EDL
Lamp current	80%
Bandpass	0.5 nm
Signal type	Transient (area)
Measurement time	3.0 s
Background correction	Zeeman effect
Injection temperature	Room temperature
Cuvette type	Extended life

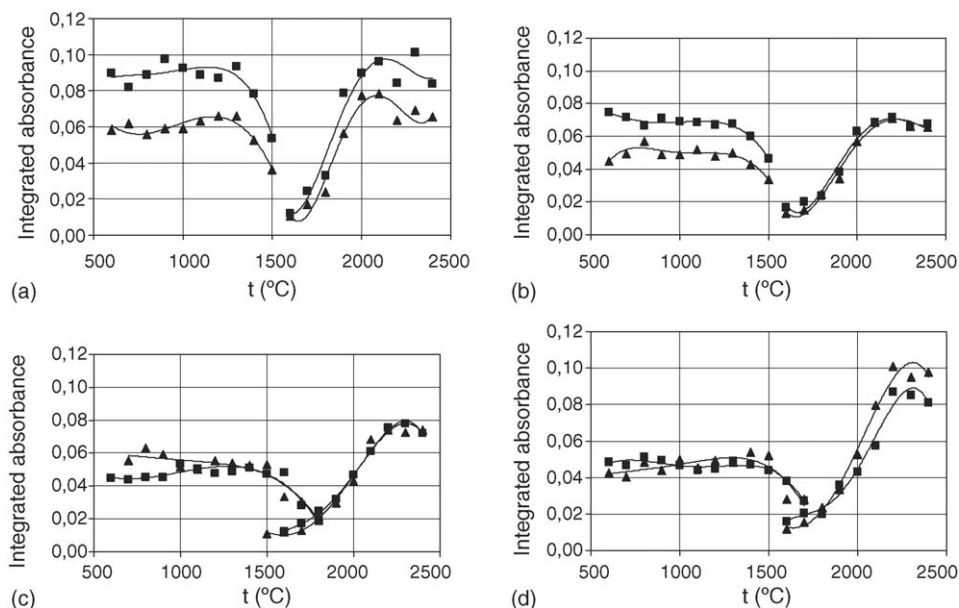| Stage	t (°C)	Ramp time (s)	Hold time (s)	Ar flow (ml min^{-1})
Temperature programme				
Drying	90	3	20	250
	120	5	10	250
Pyrolysis	$t_{optimal}$	50	20	250
Atomization	$t_{optimal}$	0	3	0
Cleaning	2500	0	3	250

Fig. 1. Pyrolysis and atomization curves for 0.16 ng of Se in soil extracts from both CRMs ((▲) RTC-023 and (■) RTC-025) using different chemical modifiers: (a) Pd $0.5\,g\,l^{-1}$, (b) Pd $1.0\,g\,l^{-1}$, (c) Ni 1.0% (w/v) and (d) Pd $0.5\,g\,l^{-1}$ + Ni 1.0% (w/v).
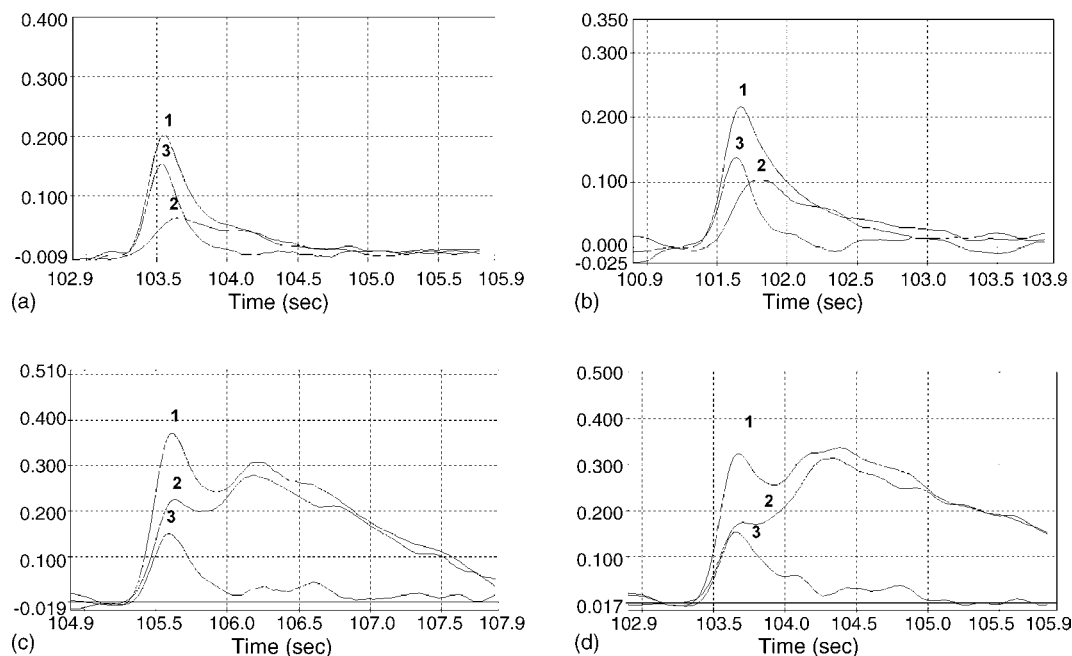

Fig. 2. Total (1), background (2) and corrected (3) absorbance–time profiles for the atomization of 0.36 ng of Se in soil CRM RTC-023 extract in the presence of 5 μl of: (a) Pd $0.5\,g\,l^{-1}$, (b) Pd $1.0\,g\,l^{-1}$, (c) Ni 1.0% (w/v) and (d) Pd $0.5\,g\,l^{-1}$ + Ni 1.0% (w/v) chemical modifiers.

After cooling, the relatively sediment-free supernatant was carefully decanted through a filter paper (Whatman no. 40) collecting the filtrate in a 100.00 ml volumetric flask. Then, the remaining residue was washed onto the filter paper with a minimum amount of $0.5\,mol\,l^{-1}$ HNO$_3$. This filtrate was added to the first solution and diluted in a volumetric flask up to 100 ml with $0.5\,mol\,l^{-1}$ HNO$_3$. Finally, this extract was placed into a 125 ml PE flask and stored at 4 °C until analysis.

Table 2
Characteristic mass (pg of Se giving 0.0044 absorbance units)

Chemical modifier	pg of Se (n)
Pd $0.5\,g\,l^{-1}$	11 ± 1 (17)
Pd $1.0\,g\,l^{-1}$	9 ± 2 (24)
Ni 1.0% (w/v)	10 ± 2 (18)
Pd $0.5\,g\,l^{-1}$ + Ni 1.0% (w/v)	9 ± 3 (24)

Mean values and standard deviations obtained for n replicates.

Table 3
Selenium content (mg kg^{-1}) in the studied CRMs by ZETAAS

Chemical modifier	Concentration	RTC-CRM 023-050		RTC-CRM 025-050	
		External curve	Standard addition	External curve	Standard addition
Pd	0.5 g l^{-1}	99 ± 6 (6.1)	119 ± 2 (1.7)	334 ± 17 (5.1)	509 ± 20 (4.0)
	1.0 g l^{-1}	76 ± 2 (2.6)	124 ± 6 (4.8)	515 ± 22 (4.3)	529 ± 18 (3.4)
Ni	1% (w/v)	116 ± 6 (5.2)	112 ± 8 (7.1)	506 ± 38 (7.5)	497 ± 29 (5.9)
Pd/Ni	0.5 g l^{-1}/1% (w/v)	113 ± 7 (6.2)	123 ± 5 (4.0)	502 ± 34 (6.7)	496 ± 16 (3.2)
Certified value		117 ± 4 (3.4)[a]		518 ± 74 (14.3)	

The results are expressed as the mean value ± standard deviation ($n = 6$). Additionally, R.S.D.% is also given.

[a] Uncertainty values estimated from the confidence interval and the certified value reported.

2.5. Selenium measurement in soil extracts by ETAAS

The determination of selenium in soil extracts was carried out by ZETAAS under the measurement conditions shown in Table 1, and pyrolysis and atomization temperatures were optimized for each modifier. Chemical modifier and standard/samples were injected at room temperature. Aqueous selenium standards solutions, from 10 to 40 µg l^{-1} Se, were prepared from a 1000 mg l^{-1} Na$_2$SeO$_3$ stock solution.

When a calibration curve was used, 5 µl of 70 µg l^{-1} Se or 8–20 µl selenium standard solution, 5 µl of chemical modifier and diluent (1% HNO$_3$) to 25 µl total volume was injected into the graphite furnace. For standard addition, 5 µl of 70 µg l^{-1} Se, 5 µl chemical modifier, 5–11 µl of diluent and 4–10 µl of selenium standard solution (80 µg l^{-1}), respectively, were injected up to a volume of 25 µl.

3. Results and discussion

3.1. Establishment of measurement conditions

For the overall study solutions from both Certified Reference Soils after aqua regia digestion were used. The corresponding pyrolysis and atomization curves were established as follows: 8 µl soil extract (20 µg l^{-1} Se), 5 µl of chemical modifier and 2 µl of diluent were injected as wet injected mode. First, a pyrolysis curve was analysed for each modifier. After selection of the optimal pyrolysis temperature for each modifier, the atomization curve was obtained and the atomization temperature was selected. The optimal temperatures were chosen, based on curve shapes, absorbance values and background signals. Fig. 1 shows pyrolysis and atomization curves for each chemical modifier and for both soil extracts. Optimal pyrolysis temperatures selected ranged from 1300 to 1500 °C and from 2000 to 2200 °C for atomization.

The influence of the aforementioned chemical modifiers on selenium absorption signal was also studied. Fig. 2 shows some examples of signals (total, background and corrected) obtained for each chemical modifier in the CRM 023-050 soil extracts. From the figure, it can be observed that for Ni-based modifiers (c and d) the corrected signals were broader and less symmetric than those obtained by using only Pd (a and b). All the corrected signals show similar maximum absorbance values. The curve corresponding to Pd 0.5 g l^{-1} (a) shows the best corrected signal shape for the soil extracts studied.

The characteristic masses were also determined in the soil extracts for each chemical modifier and using data from both external calibration curves and standard additions, obtained in different non-consecutive days. Table 2 summarizes the results obtained (expressed as mean value and standard deviation), and shows that similar sensitivity can be obtained with the four chemical modifiers studied.

3.2. Performance quality parameters

The detection and quantification limits (LOD and LOQ) were established. For this, 10 blank extracts were performed by following the overall procedure. The values obtained were 3.0 µg l^{-1} for LOD and 6 µg l^{-1} for LOQ (by considering 3 and 10 times the standard deviation, respectively).

The accuracy and the precision of the method were assessed by determining the selenium content in both soils CRMs. For selenium quantification the results obtained by using both external curve and standard addition were compared. For this six independent determinations were performed in two non-consecutive days and the results are summarized in Table 3. From the table, it can be concluded that standard addition leads to accurate results irrespective of the chemical modifier used, whereas when external curve is applied low results are obtained in some cases. Precision of the method was evaluated simultaneously from all the values used for assessing the accuracy. Precision was better than 7.5% (as R.S.D.%) in all cases.

4. Conclusions

A detailed study on the determination of selenium in *aqua regia* soil extracts leads to a reliable proposal of the optimal measurement conditions by ZETAAS. When standard addition is used for calibration, all the chemical modifiers tested led to accurate results and good sensitivity. The characteristic mass value established under the proposed conditions is estimated as 10 pg Se. The aqua regia extraction of the selenium content in the studied CRMs is quantitative.

Acknowledgement

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