



A simple sample preparation procedure for the fast screening of selenium species in soil samples using alkaline extraction and hydride-generation graphite furnace atomic absorption spectrometry

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ABSTRACT

This work proposes a simple procedure for the determination of selenium species in soil samples using an ultrasound-assisted alkaline extraction and hydride generation atomic absorption spectrometry (HG AAS), which is known to be specific for the determination of Se(IV) only. The hydride was trapped and atomized in a graphite tube furnace (GF) coated with iridium as a permanent chemical modifier. The limits of detection and quantification for the developed method were $6 \mu\text{g L}^{-1}$ and $20 \mu\text{g L}^{-1}$ Se(IV), respectively, with a linear range between 20 and $100 \mu\text{g L}^{-1}$, and a linear coefficient of $R = 0.999$. The total Se content in the samples was determined in the alkaline extract using high-resolution continuum source GF AAS (HR-CS GF AAS), and the content of Se(VI) was determined by difference between the total Se and the content of Se(IV). The extraction efficiency was verified by comparing the results obtained by the alkaline extraction and by direct solid sample analysis using HR-CS GF AAS. The accuracy of the method for total Se determination was ascertained using microwave-assisted acid digestion as well as direct solid sample analysis by HR-CS GF AAS of the certified reference materials MURST-ISS-A1 (Antarctic marine sediment) and BCR 142R (light sandy soil), and soil samples from different regions of Brazil.

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1. Introduction

Selenium is an essential micronutrient for all kinds of life and it is distributed throughout the Earth's crust [1]. It is found in cereals, eggs, and meat and is a constituent of more than 30 selenoproteins [2]. It is known that plants growing on Se-rich soil can absorb and accumulate it in their structures. Soils with low concentration of Se can be fertilized before sowing to generate plants with a higher Se-content [3]. On the other hand, soils with excessive Se content, leaching caused by irrigation might lead to contamination of groundwater and surface water [4].

The bioavailability of Se is strongly dependent on the oxidation state. Selenate (Se VI), the species present in oxidant media, is mobile and accessible to plants; this tetravalent ion is more labile than Selenite (Se IV), which makes compounds with inner-sphere mechanism more stable and less available to plants [3]. The enrichment in soil is ten times more effective when selenate is applied instead of selenite [1]. These facts show the importance not only for the quantification of Se in soil, but also to know its oxidation state.

Several techniques have been reported for the determination of Se, such as spectrophotometric techniques (UV-VIS) [4], neutron activation analysis (NAA) [5], optical emission spectrometry with inductively coupled plasma (ICP OES), and mass spectrometry with inductively coupled plasma (ICP-MS) [6]. Conventional line source atomic absorption spectrometry often has problems to quantify Se, since it is an element with absorption lines in the same spectral region of the PO and NO molecules, and also in the vicinity of some secondary iron lines, which are commonly present in the matrix. Deuterium lamp background correction cannot handle this kind of spectral interference and even Zeeman-effect background corrections has difficulties [7]. The use of high-resolution continuum source atomic absorption spectrometry (HR-CS AAS), however, makes possible to correct for these interferences by subtracting a reference spectrum from the sample spectra using a least-squares algorithm. This feature of HR-CS AAS makes possible the determination of Se using graphite furnace AAS (GF AAS) without separating the analyte from the matrix [8].

Hydride generation (HG) is a different approach, which allows the quantification of Se using line source AAS even without background correction, once it uses a chemical reaction to generate a volatile hydride of the element of interest and separate it from the matrix using a gas-liquid separator [9]. HG linked to AAS with pre-concentration and

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atomization in a GF offers a fast and accurate analysis as this technique shows results without spectral interferences because only the hydride vapor reaches the atomizer for quantification [10,11]. The use of a GF supports the use of a permanent chemical modifier, trapping the analyte in situ, which allows pre-concentration; thus the method can be applied even for samples where the analyte is at low concentration [12].

However, only Se(IV) forms a hydride, whereas inorganic Se(VI) and any selenium species strongly bound to organic matter cannot react with the reductant to form a hydride. Hence, sample preparation is a fundamental part of the determination of Se using HG-GF AAS, since it can change the oxidation state of Se in the sample. Shaltout et al. [9] used a microwave-assisted acid digestion, followed by a reduction step, to convert all organic Se and Se(VI) to inorganic Se(IV), showing reliable results for soil samples. Ribeiro et al. [10] prepared samples of sediment slurries using acid solution of *aqua regia* and 50% HCl, obtaining good results when compared with the certified values of environmental and geological certified reference materials (CRM). Both methods are able to convert all Se to Se(IV), and their results are presented as total Se.

In the present work we have taken a different approach, trying to conserve the original oxidation state present in the soil sample and determine these oxidation states separately. As Se(-II) and Se(0) are poorly soluble and are present in negligible concentration in soil, it can be assumed that only Se(IV) and Se(VI) are present in the supernatant of the alkaline extract. Once the alkaline extraction can release Se from organic complexes (humic and fulvic acids), the content of Se(IV) can be determined in the supernatant by HG-GF AAS. The total content of Se can then be determined as well by HG-GF AAS after microwave-assisted digestion, and the content of Se(VI) can be calculated by difference.

This work presents a simple method to determine the two most important selenium species in soil samples using an alkaline extraction and hydride-generation graphite furnace atomic absorption spectrometry. The main parameters, such as temperature program, concentration of alkaline extraction solution, chemical vapor generation, stirring and ultrasonic agitation time have been investigated and optimized. As there are no CRM of soil or a comparable matrix available with a certified value for Se(IV) and Se(VI), we called this a 'screening method', which means that for an exact determination it might be necessary to choose a more sophisticated analytical technique.

2. Experimental

2.1. Instrumentation

Most of the measurements were performed using an atomic absorption spectrometer AAS 5EA (Analytik Jena, Jena, Germany) with transversely heated graphite tube atomizer and tubes without platform, but with a dosing hole (Analytik Jena, Part No. 407-A81.011). The tubes were coated with 200 µg of iridium in five injections of 40 µL of a 1000 mg L⁻¹ Ir standard solution, each injection followed by the temperature program shown in Table 1.

A Se hollow cathode lamp operating at 13 mA was used, monitoring the primary emission line at 196.0 nm and the spectral slit was 0.8 nm. Argon with a purity of >99.98% (White Martins, Brazil) was used as a purge gas. For the chemical vapor generation, a HYDREA 5 system in

continuous-flow mode was adopted, with a gas flow of 12 L h⁻¹, and argon with a purity of >99.98% (White Martins) as carrier gas. An ultrasonic bath Model Ultracleaner 1450 (Unique, Brazil) was used for the extraction of Se from the soil samples.

All comparative measurements were carried out using a high-resolution continuum source atomic absorption spectrometer, Model contrAA 600 (Analytik Jena AG, Jena, Germany), equipped with a transversely heated graphite tube atomizer, which is essentially identical with that used in the AAS 5EA. This spectrometer consists of a high-intensity xenon short-arc lamp operating in a hot-spot mode as a continuum radiation source that covers a range between 189 and 900 nm, a high resolution double monochromator and a CCD array detector with 588 pixels, 200 of which are used for analytical purposes. The double monochromator consists of a pre-dispersing prism monochromator and a high-resolution echelle grating monochromator, both in Littrow mounting.

The same analytical line at 196.026 nm was used for Se determination. The peak volume selected absorbance (PVSA) has been used for signal evaluation, i.e., the integrated absorbance summated over three pixels around the line core (center pixel plus the adjacent ones, CP ± 1), corresponding to a spectral interval of about 4.5 pm.

The experiments with alkaline extracts were carried out using PIN platform tubes (Analytik Jena Part No. 407-A81.025), while solid sampling (SS) graphite tubes (Analytik Jena, Part No. 407-A81.303) and SS graphite platforms (Analytik Jena, Part No. 407-152.023) were used for direct solid sample analysis; all graphite parts were coated with pyrolytic graphite. An M2P microbalance (Sartorius, Göttingen, Germany) was used for weighing the samples directly onto the SS platforms. The sample mass was automatically transmitted to the computer of the instrument after each measurement, to calculate the normalized integrated absorbance, i.e., the integrated absorbance was calculated for an adequate fixed mass, which varied for each sample. This is necessary as it is impossible to always introduce exactly the same sample mass onto the SS platform in direct SS analysis. A pre-adjusted pair of tweezers, which is part of the SSA 6 manual solid sampling accessory (Analytik Jena), was used to transfer the SS platforms to the atomizer.

2.2. Reagents and reference materials

Ultrapure water with a resistivity of 18 MΩ cm was obtained from a Model Mega ROUP (Equisul, Pelotas, Brazil) purification system, and it was used in the dilution and preparation of standard solutions and samples. A stock standard solution of 1000 mg L⁻¹ Se (Sigma-Aldrich, Germany) was used to prepare the calibration curve and aqueous standard solutions. For the microwave-assisted digestion of the samples, 67% HNO₃ (Fluka, Germany) and 37% HCl (Fluka) were further purified using sub-boiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). NaBH₄ (Sigma-Aldrich), NaOH (Merck) and HCl (Fluka), all of analytical reagent or superior grade, were used for hydride generation. For the samples, which produced foam during hydride generation, a few droplets of Anti-Foam A (Sigma-Aldrich) were added. All samples have been prepared and homogenized in 50-mL polypropylene flasks and transferred to the HYDREA 5 system flask.

The CRM MURST-ISS-A1—Antarctic marine sediment (Programma Nazionale di Ricerche in Antartide, Italy) was used for all optimizations of the method. The developed method was applied to reference material BCR 142R—Light sandy soil (Institute for Reference Materials and Measurements, Belgium) and also applied to soil samples from different regions of Brazil, such as: Minas Gerais, Santa Catarina, Mato Grosso do Sul, Amazônia and Rio Grande do Sul, after previous drying in an oven.

2.3. Sample preparation

2.3.1. Collection and preparation of the samples

Different soil samples were collected in four states of Brazil (Amazonas, Santa Catarina, Mato Grosso do Sul, and Minas Gerais). The samples

Table 1
Temperature program for iridium coating of graphite tubes for HG-GF AAS.

Step	T/°C	Ramp/°C s ⁻¹	Time/s
1	90	5	40
2	110	1	40
3	130	1	40
4	1200	300	25
5	2100	500	10
6	2100	0	5

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