

Tungsten Permanent Chemical Modifier for Fast Estimation of Se Contents in Soil by Graphite Furnace Atomic Absorption Spectrometry

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A tungsten carbide coating on the integrated platform of a transversely heated graphite atomizer was used as a modifier for the direct determination of Se in soil extracts by graphite furnace atomic absorption spectrometry. Diethylenetriaminepentaacetic acid ($0.0050 \text{ mol L}^{-1}$) plus ammonium hydrogencarbonate (1.0 mol L^{-1}) extracted predominantly available inorganic selenate from soil. The formation of a large amount of carbonaceous residue inside the atomizer was avoided with a first pyrolysis step at $600 \text{ }^\circ\text{C}$ assisted by air during 30 s. For $20 \mu\text{L}$ of soil extracts delivered to the atomizer and calibration by matrix matching, an analytical curve ($10.0\text{--}100 \mu\text{g of L}^{-1}$) with good linear correlation ($r = 0.999$) between integrated absorbance and analyte concentration was established. The characteristic mass was $\sim 63 \text{ pg of Se}$, and the lifetime of the tube was ~ 750 firings. The limit of detection was $1.6 \mu\text{g L}^{-1}$, and the relative standard deviations ($n = 12$) were typically $< 4\%$ for a soil extract containing $50 \mu\text{g of L}^{-1}$. The accuracy of the determination of Se was checked for soil samples by means of addition/recovery tests. Recovery data of Se added to four enriched soil samples varied from 80 to 90% and indicated an accurate method.

KEYWORDS: Selenium; soil; diethylenetriaminepentaacetic acid; tungsten permanent modifier; GFAAS

INTRODUCTION

The great interest in plant Se is due to the importance of this element in nutrition (1, 2). Selenium may be classified either as essential or toxic to human and animals depending on the ingested amount of its compounds (3). Because the range between essential and toxic levels of Se in human and animal nutrition is narrow (1), the accurate determination of selenium in samples of agricultural interest is important. Among conditions that may influence the translocation of Se from soil to plants are pH, redox potential, soil composition, plant species, microbial intervention, humidity, concentration and form of Se in soil, etc. (2, 4). According to the literature, it seems that selenate (SeO_4^{2-}) is the most mobile and soluble and least sorbed form of the inorganic Se species in aerated soils (4).

The determination of Se in plants may be used to classify a growing soil as Se-deficient or having high levels of Se. The soluble fractions of soil Se is then considered to be the fraction that is available to plants. A close positive linear correlation between Se in plant issues and selenate concentration in the soil solution has also been reported (5). Selenium availability to plants can be assessed by soil extraction tests using diethylenetriaminepentaacetic acid (DTPA) with ammonium hydrogencarbonate (5).

Hydride generation coupled to atomic absorption spectrometry, inductively coupled plasma mass spectrometry, and inductively coupled plasma optical emission spectrometry (5, 6) has often been used to determine Se in soil extracts. On the other hand, graphite furnace atomic absorption spectrometry (GFAAS) is a suitable and widely used technique for the determination of Se at trace levels due to its selectivity, high sensitivity, and capability for direct determination in various matrices (7–9). The latter characteristic is attractive for routine use in laboratories.

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Table 1. Heating Program of THGA for Determination of Se in Soil Extract

step	temperature (°C)	time (ramp, hold) (s)	gas flow (mL/min)
1	110	10, 30	250 (Ar)
2	130	15, 30	250 (Ar)
3	600	10, 20	250 (air)
4	40	5, 35	250 (Ar)
5	1800	10, 10	250 (Ar)
6	2300	0, 5	0 (reading)
7	2500	1, 3	250 (Ar)

There are several papers related to Se determination by GFAAS in a great variety of matrices such as fruit juice (10), serum (11), coconut and coconut milk (12), plant and animal tissues (13), sediments (14), water (15), and coal fly ashes (16). However, procedures involving direct determination of Se in soil extracts by GFAAS using DTPA and thermal stabilization of Se by W-treated platform are not described in the literature. This study reports a simple and fast method for the direct determination of Se in soil extracts by using GFAAS with a transversely heated graphite atomizer (THGA) and longitudinal Zeeman-effect background correction. Tungsten was proposed here as a permanent chemical modifier to improve THGA lifetime.

MATERIALS AND METHODS

Instrumentation. A Perkin-Elmer SIMAA 6000 simultaneous multielement atomic absorption spectrometer with longitudinal Zeeman-effect background correction, a THGA, and an AS-72 autosampler were used. A Perkin-Elmer electrodeless discharge lamp (EDL) was used for the determination of Se at the analytical wavelength recommended by the manufacturer (196.0 nm; slit = 0.7 nm) and lamp current of 12 mA. Argon (White Martins) of 99.999% purity and synthetic air (White Martins) with 20.0 ± 0.5% (v/v) oxygen and 80.0 ± 0.5% (v/v) nitrogen were used as auxiliary gases during the pyrolysis step. The experiments were carried out under STPF conditions (17). The heating program of the THGA atomizer used for the determination of Se in soil extract is shown in **Table 1**.

Reagents, Reference Solutions, and Samples. High-purity deionized water obtained by using a Milli-Q water purification system (Millipore) was used throughout. To prepare the W-treated platform, a 1.0 g L⁻¹ W solution was used by dissolving 0.1794 g of Na₂WO₄·2H₂O (Merck) in 100 mL of water. The coating and thermal treatment of the tube were performed according to Lima and co-workers (18). Experiments involving thermal stabilization of Se in the presence of palladium nitrate and magnesium nitrate as chemical modifiers were also carried out. Solutions containing 1 g of Pd L⁻¹ and 1 g L⁻¹ Mg solutions were prepared by appropriate dilution of 10 g L⁻¹ Pd (Perkin-Elmer part no. BO19-0635) and 10 g L⁻¹ Mg (Perkin-Elmer part no. BO19-0634) stock solutions.

The DTPA solution (0.0050 mol L⁻¹) was weekly prepared by appropriate dilution of the reagent (Acros Organics) in 1.0 mol L⁻¹ ammonium hydrogencarbonate (Merck). The pH was adjusted to 7.6 with ammonium hydroxide (Merck). This solution was used for Se extraction studies from soils.

Stock standard solutions (1000 mg of Se L⁻¹) were prepared by dissolving 0.2190 g of Na₂SeO₃ (Synth) or 0.2392 g of Na₂SeO₄ (Carlo Erba) in 100 mL of water. All reference solutions (10, 25, 50, 75, and 100 µg of Se L⁻¹) were daily prepared by diluting the sodium selenate stock solutions in 0.028 mol L⁻¹ Suprapur grade nitric acid (Merck) and DTPA solution. For each measurement, 20 µL of soil extracts or reference solution was directly delivered to the atomizer platform. For thermal stabilization studies involving Pd/Mg, 20 µL of sample or reference solution was injected into the atomizer followed by 5 µL of 1 g L⁻¹ palladium solution plus 3 µL of a 1 g L⁻¹ magnesium chemical modifier solution. All measurements of integrated absorbance were made at least in triplicates.

Table 2. Optimized Pyrolysis/Atomization Temperatures and Characteristic Masses (*m*₀) for Se in 0.028 mol L⁻¹ HNO₃, DTPA, and Soil Extracts

modifier	HNO ₃	DTPA	soil
W-treated tube	1800/2300 °C <i>m</i> ₀ = 72 pg	1800/2300 °C <i>m</i> ₀ = 71 pg	1800/2300 °C <i>m</i> ₀ = 72 pg
W-treated tube + Pd/Mg(NO ₃) ₂	1800/2200 °C <i>m</i> ₀ = 61 pg	1800/2200 °C <i>m</i> ₀ = 56 pg	1800/2300 °C <i>m</i> ₀ = 63 pg

The thermal behavior of Se during pyrolysis and atomization stages was investigated in diluted nitric acid and soil extract solutions using W-treated platform and W-treated platform plus co-injection of Pd(NO₃)₂ + Mg(NO₃)₂. This study was made using the following solutions containing 1.0 ng of Se: (a) 0.028 mol L⁻¹ HNO₃; (b) DTPA solution; (c) soil extracts.

Different growing soil samples were collected at farms located around Araraquara, São Paulo State, Brazil. Extraction was similar to that recommended by the literature (19): ~10 g of dried powdered and sieved (no. 20 sieve, 0.84 mm openings) soil was accurately weighed and mixed with 20 mL of DTPA solution in 125 mL flasks. After 5 min of extraction in a mechanical shaker, the extract was filtered through Framex filter paper (1500 s). A volume of 20 µL of this final solution was directly injected into the graphite tube.

RESULTS AND DISCUSSION

Electrothermal Behavior of Selenium. All measurements were initially carried out according to the conditions recommended by the manufacturer. Although GFAAS with Zeeman-effect background correction presents a potential to direct determine Se at trace levels in soil extract, a large amount of carbonaceous residue was generated after a few firings, impairing the performance of the atomic absorption spectrometer. This drawback was circumvented by using an air-assisted pyrolysis step at 600 °C for 30 s (step 3 of the heating program described in **Table 1**) in order to determine Se in soil extracts without previous dilution. Pyrolysis and atomization curves were employed to determine the optimum pyrolysis and atomization temperatures for Se in diluted nitric acid, DTPA, and soil extract solutions using a W-treated platform with and without co-injection of Pd(NO₃)₂ + Mg(NO₃)₂. All results were based on peak area measurements and are summarized in **Table 2**. For this study, all media were spiked with 1.0 ng of Se. The positive effects of chemical modifier on both sensitivity and stabilization of analyte in the presence of soil extract were relevant. For comparison purposes, the recommended Pd + Mg(NO₃)₂ mixture was employed as a conventional chemical modifier.

For Se determination in soil extracts, the optimized heating program of the atomizer with two pyrolysis steps is summarized in **Table 1**. It should be mentioned that measurements of atomic signals injecting the mixture Pd(NO₃)₂ + Mg(NO₃)₂ onto the W-treated platform of the THGA atomizer lead to integrated absorbance 30% higher than those obtained without Pd/Mg co-injection. Although W-treated platform with or without Pd/Mg co-injection stabilized Se up to 1800 °C, only the W-treated platform permanent modifier was selected in this work for further experiments because it gave similar characteristic masses (*m*₀, **Table 2**) and lower background signals. The atomization temperature obtained with permanent modifier plus Pd + Mg(NO₃)₂ co-injected was 2300 °C for Se in soil extract.

Matrix Effects. Matrix effects were evaluated by comparing the slopes of analytical curves built up from different media: 0.2% (v/v) HNO₃, DTPA solution, and soil extracts. These media were spiked with Se to produce a calibration curve in the 10–100 µg L⁻¹ concentration range. Despite good linear

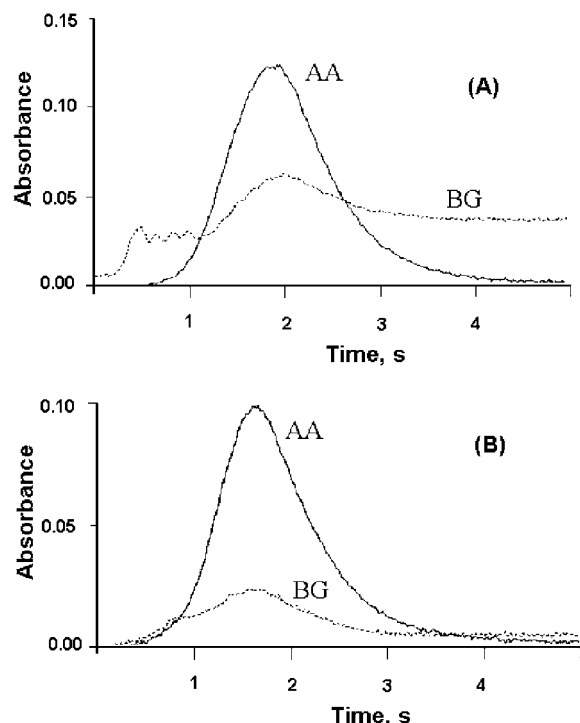


Figure 1. Absorbance–time profiles for Se determination. AA and BG represent atomic absorption and background signals, respectively. Signals correspond to 20 μL of soil extract containing 50 μg of Se L^{-1} using W-treated THGA atomizer with (A) and without (B) 5 μg of Pd plus 3 μg of $\text{Mg}(\text{NO}_3)_2$ co-injected.

correlation coefficients (r^2) between integrated absorbance and analyte concentrations (0.9987, 0.9974, and 0.9999), the slopes of analytical curves for these media were 2.35×10^{-3} , 2.00×10^{-3} , and 1.89×10^{-3} . The data show appreciable matrix effects mainly for soil extracts. Errors associated with absorbance measurements of Se in soil extract using the end part of the calibration curve from aqueous reference or DTPA solutions were around 22 and 10%, respectively. Therefore, it was decided to investigate the possibility of using the matrix matching method for calibration using soil extract. The influence of different soil matrices on sensitivity was also investigated by building up four curves from different soils. Each soil extract was spiked with Se to produce a calibration curve in the 10–100 μg of L^{-1} range. Good linear correlation coefficients between integrated absorbance and analyte concentration were obtained. Slightly multiplicative matrix effects were observed as it was found that all soil extracts behaved similarly, or else the curves presented similar slopes. However, the errors using any calibration curve generated by matrix matching are $<3\%$, which are reasonable and admissible for soil analysis for Se. **Figure 1** shows typical absorbance and background signals profiles for 1.0 ng of Se in NH_4HCO_3 –DTPA extracts using W-treated platform with or without Pd + $\text{Mg}(\text{NO}_3)_2$ co-injected. As similar atomic signal profiles for Se were obtained, it can be considered that the W coating acted as an effective modifier for Se in the sample matrix.

Extraction of Selenate and Selenite Species from Soil. The effect of the concentration of DTPA on the efficiency of extraction and atomic and background signals were investigated in the concentration range 0.0025–0.010 mol L^{-1} . Different soil samples were artificially contaminated and used as Se-enriched soil samples by adding 10 mL of a 1.0 mg L^{-1} selenate or selenite solution to 50 g soil samples. The efficiency of extraction of selenate increased from 68 to 85% when the DTPA

concentration was varied from 0.0025 to 0.0050 mol L^{-1} , above which the percentage of extraction became constant. The extraction of selenite from soil was too low ($\sim 10\%$). According to the literature, this may occur because SeO_3^{2-} is more strongly adsorbed than SeO_4^{2-} species to clay particles of soil (4). Selenium availability to plants has been assessed by soil extraction tests using DTPA in slightly alkaline medium (5), and the percentage of extraction obtained was similar to those found in this work. In another study a linear correlation between Se in plant issues and selenate concentration in the soil solution was observed (20).

Because integrated absorbance and background signals did not alter significantly with increased DTPA concentration, the extractor concentration selected for further experiments was 0.0050 mol L^{-1} . The influence of shaking time on extraction of Se was investigated in the 5–60 min interval. The percentage of Se extracted increased steeply with time up to 5 min, above which recoveries became constant. Shaking time was then fixed at 5 min, which extracted $\sim 90\%$ of Se. Although it is a semiquantitative analysis, the proposed procedure can be used as a good tool for fast estimation of Se in soil.

Analytical Characteristics. The performance of the developed procedure was assessed by determining Se in four enriched soil samples. With calibration of the method by matrix matching approach, recoveries within 80–90% for spiked samples were found. The limit of detection (LOD) was 1.6 μg L^{-1} (32 pg of Se), and the relative standard deviation was $<4\%$ after 12 consecutive determinations. The long-term stability curves for untreated and W-treated platform were investigated for 1.0 ng of Se in soil extract. Using permanent modifier, the lifetime of the graphite tube was equivalent to ~ 750 firings. This was 3 times higher than the lifetime obtained for untreated platform using only Pd + $\text{Mg}(\text{NO}_3)_2$. A new coat of the platform with W permanent modifier should be made after 200 consecutive firings. However, it is good practice to set an acceptable relative standard deviation threshold before the platform coating is renewed. It should be stressed that small variations in sensitivity during W-treated THGA firing were observed as compared with untreated THGA tubes with Pd/Mg modifiers. In addition to modification properties, the tungsten carbide or oxycarbide coating of the platform presents a high chemical resistance that helps to protect and lengthen the lifetime of the THGA tube.

In conclusion, this work presents a new strategy for the direct determination of Se in soil extract samples by GFAAS. Comparative results and recovery values of spiked samples indicated that the matrix matching and W-treated platform of the THGA atomizer were suitable to determine Se in soil. Recovery data from just four enriched soil samples indicate (but do not prove) an accurate method. The W permanent modifier improved the THGA lifetime, leading to a substantial decrease in analytical costs.

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