

ORIGINAL RESEARCH PAPER

AN ANALYTICAL METHOD FOR CHEMICAL SPECIATION OF SELENIUM IN SOIL[♦]

Mihaela M. Aldea^{1*}, Constantin Luca²

¹ *National Research-Development Institute for Soil Science,
Agrochemistry and Environmental Protection,
61 Mărăști Blvd., 011464, Bucharest, Romania*

² *“Politehnica” University of Bucharest, Department of Analytical
Chemistry and Instrumental Analysis, 1-5 Polizu St., Bucharest, Romania*

*Corresponding author: monica.aldea80@gmail.com

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Abstract: Selenium is an essential microelement, sometimes redoubtable, through its beneficial role - risk depending on its concentration in the food chain, at low dose is an important nutrient in the life of humans and animals, contrary at high doses, it becomes toxic. Selenium may be found in the environment (soil, sediment, water) in many forms (oxidized, reduced, organometallic) which determine their mobility and toxicity. Determination of chemical speciation (identification of different chemical forms) provides much more complete information for a better understanding of the behavior and the potential impact on the environment. In this work we present the results of methodological research on the extraction of sequential forms of selenium in the soil and the coupling of analytical methods capable of identifying very small amounts of selenium in soils. An efficient scheme of sequential extractions forms of selenium (SES) consisting in atomic absorption spectrometry coupled with hydride generation (HGAAS) has been developed into five experimental steps, detailed in the paper. This operational scheme has been applied to the analysis of chemical speciation in the following areas: the Bărăgan Plain and Central Dobrogea of Romania.

Keywords: *selenium, sequential extraction, soil, speciation, equilibrium diagrams*

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INTRODUCTION

Selenium is a trace mineral essential for animal and human nutrition, being involved in many metabolic processes, including the antioxidant, thanks to its presence in the composition of the enzyme glutathione peroxidase, seems most important. The form of selenocysteine gets into the composition of more than 40 selenoproteins. In addition to the antioxidant role, selenium is involved in thyroid hormones homeostasis, immunity and fertility processes, etc. Also, antiviral and anticarcinogenic effects have been observed at selenium [1 – 4].

Deficient selenium soil areas are: Sweden, Norway, Finland and Denmark; Canada (eastern part); USA (eastern and western coast); Australia (northern and western area); China (south-eastern part); East of Europe. Abundant selenium soil areas are: small surfaces in Wales and Ireland; local surfaces in central part of USA; more extensive areas in Central Asia (especially China).

The link between the amount of estimated selenium intake and blood levels of selenium can be made based on data shown in Table 1. It shows a direct connection between those two parameters [5].

Table 1. *Estimated amount of selenium ingested in different countries and blood selenium level [5]*

Country	Ingested amount [µg/day]	Blood selenium level [µg/L]
Belgium	55	123
Canada	98-224	182
China		
- in selenifereous areas	4990	3180
- in deficient areas	11	8
New Zealand	56	83
USA	62-216	157-265
Venezuela	218	355

In soil, selenium is distributed among all its components. Thus, it is present in soil solution, is related to organic matter, adsorbed to the surface oxides and hydroxides, falling sometimes in the crystalline mineral soil network. Depending on the physicochemical characteristics of the soil, selenium can be present in various oxidation states, namely: selenides (-2), elemental selenium (0), selenites (4) and selenates (6) in inorganic compounds and -2 in organic compounds. Selenites predominate in acid medium to neutral and selenates predominate in alkaline medium. This diversity of chemical species has been outlined in our work with equilibrium diagrams potential – pH of Pourbaix type [6], simultaneously used for developing sequential extraction method for forms of selenium in soil, but also for interpretation of analytical results.

Soil samples analyzed for studying of selenium contents were collected from the upper horizon (0 – 20 cm) from two areas of Romania: the *Bărăgan Plain* (**P2** and **P3**) and *Central Dobrogea* (**P1**), the analytical determination of these samples being made by atomic absorption spectrometry coupled with hydride generator (HGAAS), having previously been made a series of sequential extractions with different extractants.

MATERIALS AND METHODS

Collection points of studied soil samples belong to different soil zones (Fig. 1).

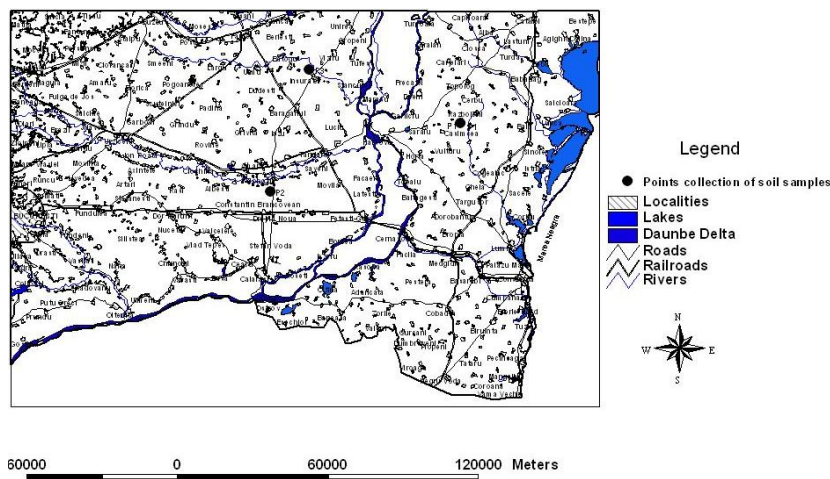


Figure 1. Location of soil points ($n = 3$)

In our laboratory, the fractional and total selenium content of collected soil samples has been determined. For these soil samples a sequential extraction scheme effective for selenium forms (SES) [7], consistent with atomic absorption spectrometry coupled with hydride generator (HGAAS) has been developed:

- ◆ **Step 1.** Extraction of soluble fraction, extraction performed with CaCl_2 ;
- ◆ **Step 2.** Extraction of exchangeable fraction, extraction made with 1N $\text{CH}_3\text{COONH}_4$, pH 7;
- ◆ **Step 3.** Extraction of fraction bounded to organic matter, form extracted with 0.1M $\text{K}_4\text{P}_2\text{O}_7$;
- ◆ **Step 4.** Extraction of fraction bounded to Fe and Mn free oxides, extraction made with $(\text{COOH})_2 + (\text{COONH}_4)_2$, pH 3.25;
- ◆ **Step 5.** Digestion with concentrated acids (HNO_3/HCl) of the residue remaining after each extraction step for determining the elemental selenium.

All five phases are subjected extracts to reduce selenium (by concentrated HCl) to H_2Se and dosed by HGAAS; full scheme of extraction together with reagents and reaction conditions are shown in Figure 2.

For the actual extraction, we used a procedure of balancing successive soil: solution to a specific report and the solid-liquid phase separation was achieved by filtration. Analytical practice has shown that using of a larger number of successive extractions, deals at an increase of passage probability of the chemical element in certain proportions of one part to another.

Because of this "ideal" division of selenium in soils is achieved with a minimum number of extractions, but with increased specificity for the major forms in which it is bound selenium in soils. Before determination of selenium by HGAAS (by dosing with sodium borohydride and NaOH, Se passes from the oxidation state IV to II), each fraction resulting from the extraction is subjected to reduction with 3 mL concentrated HCl [Se (VI) passes into Se (IV)] by heating them to 80 °C for 30 minutes on a sand bath.

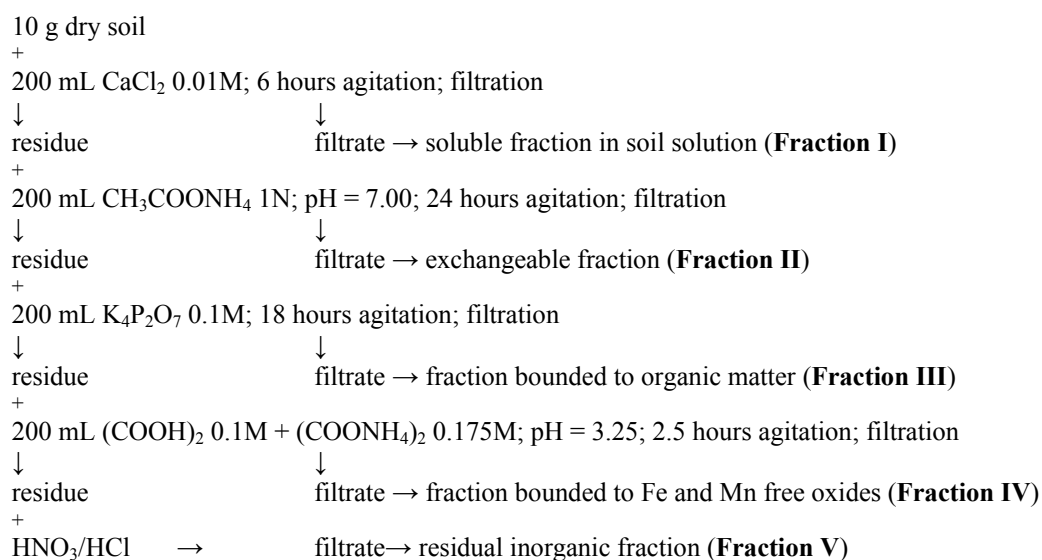


Figure 2. Analytical scheme for the fractional extraction of soil selenium

Separately of these steps of extraction, it is made an analysis for determination of total soil selenium content [which consists of Se (VI), Se (IV), Se (II)]. Soil samples taken for analysis were carried out in three repetitions, finally making the arithmetic means of their content.

RESULTS AND DISCUSSION

Results of sequential extraction procedures used for the studied soil samples are presented in Table 2.

Table 2. Extraction of selenium fraction in soil samples collected from the upper horizon (0 – 20 cm)

Sample	Fraction					Sum of Se fractions I ÷ V	Total Se in sample
	I	II	III	IV	V		
	[mg/kg]						
P1	0.048	0.052	0.074	0.062	0.277	0.513	0.432
P2	0.038	0.048	0.089	0.081	0.316	0.572	0.461
P3	0.046	0.087	0.092	0.077	0.354	0.656	0.490

The three soil samples belong to different soils. **P1** sample located in the *Central Dobrogea* belongs to the class of chernozem soils. Point **P2** is located in the *Bărăgan Plain* in cernisols class with cambic chernozem soil type, and point **P3**, also located in the *Bărăgan Plain*, belongs to the class of soils, namely salsodisols, mollic soils rich in carbonates and salts. Generally these soils have a neutral - slightly alkaline reaction, and a moderate organic matter and total nitrogen content.

Three soil samples were analyzed containing fractional average 0.044 mg/kg in soluble form extracted with 0.05M CaCl_2 solution. Analytical results have shown that between 8 and 12% of average total selenium content was soluble in 0.05M CaCl_2 solution, the

mean percentage being 11.1% for samples **P1**, 8.24% for **P2** and 10.65% for **P3** (Table 3).

Table 3. The percentage distribution of the three samples from fractions: soluble in soil solution (**Fraction I**), exchangeable (**Fraction II**), bounded to organic matter (**Fraction III**), bounded to Fe and Mn free oxides (**Fraction IV**) and inorganic residue (**Fraction V**)

Sample	Selenium in fraction [%]				
	I	II	III	IV	V
P1	11.11	12.03	17.13	14.35	64.12
P2	8.24	10.41	19.30	17.57	68.54
P3	10.65	17.55	18.77	15.71	72.24

The mean value of exchangeable fraction for the two areas of interest is located around the concentration of 0.062 mg/kg at pH 7 with 1N ammonium acetate solution, because the solution is often used to determine exchangeable cations. Concentration of fractions in 1N ammonium acetate solution was between 10 and 18% of average total selenium content and the mean percentage of the three samples was: 12.03% (**P1**), 10.41% (**P2**) and 17.55% (**P3**). The third step of sequential extraction, extraction performed using 0.1M potassium pyrophosphate, is represented by the fraction bounded to organic matter with its average content of 0.085 mg/kg. Average analytical values obtained are between 17 and 20% of average total selenium content of the average of 17.13%, 19.3% and 18.7% typical samples **P1**, **P2** and **P3**. At a pH of 3.25, a fraction of soil samples have linked Fe and Mn free oxides, fraction extracted with oxalic acid and ammonium oxalate, with a mean concentration of 0.073 mg/kg. The concentration of this fraction varies between 14 and 18%, with averages of 14.35%, 17.57% and 15.71% for **P1**, **P2**, **P3** respectively. Residual inorganic fraction resulting from the four steps of extraction, then treated with strong acids (HNO_3/HCl), indicates an average concentration of 0.315 mg/kg. Content ranges of average concentrations of residual inorganic fraction are situated between 60 and 75%, the percentage averages being of 64.12%, 68.54% and 72.24% for the three soil samples.

Average value of the sum selenium fractions from these five steps of extraction of soil samples from both *Bărăgan Plain* and *Central Dobrogea* (0.580 mg/kg) is around the average total content of selenium (0.461 mg/kg) obtained after digestion (wet digestion with concentrated mineral acids, HNO_3/HCl) of soil samples separately of extraction, directly from the original sample, collected, dried and fine grinded. There is also a good linearity with the sum of selenium fractions and selenium total content as shown in Figure 3 ($R^2 = 0.9899$).

Chemical species resulting from the sequential extraction can be created in several formulas of stable and less stable balance of selenium. Based on these formulas representing equilibrium reactions of chemical species of selenium, Pourbaix equilibrium diagram potential – pH of system selenium – water at 25 °C is shown in Figure 4. According to this equilibrium diagram, selenium can be easily reduced to hydrogen selenide H_2Se or selenides; HSe^- and Se^{2-} , are oxidized in selenous acid or selenites H_2SeO_3 , HSeO_3^- and SeO_3^{2-} , but in selenic acid H_2SeO_4 or selenates HSeO_4^- and SeO_4^{2-} . Aqueous solutions of H_2Se are actually unstable in air; this is quite fast decomposed with separation of selenium. Selenous acid H_2SeO_3 and selenites HSeO_3^- , SeO_3^{2-} are stable compounds in the presence of water and aqueous solutions without

reducing and oxidizing. Because of this, these species can act as oxidizing and reducing. Predominant character of selenic acid H_2SeO_4 and selenates HSeO_4^- , SeO_4^{2-} is found throughout the upper part of equilibrium diagram.

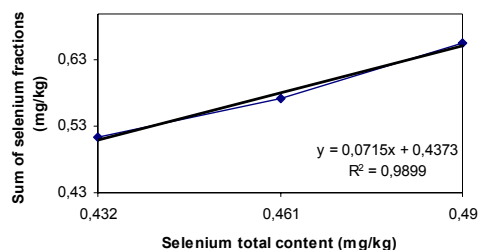


Figure 3. Linearity of the sum of selenium fractions

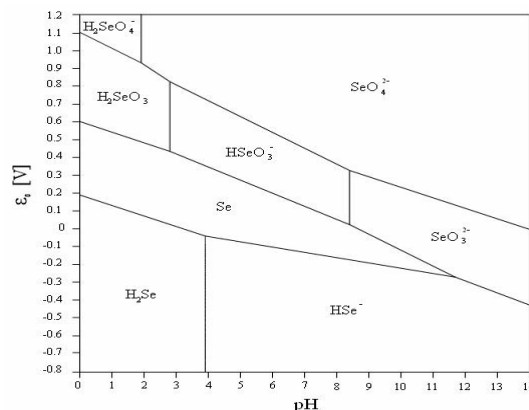


Figure 4. Equilibrium diagram potential – pH of the system selenium – water at 25 °C

CONCLUSIONS

The paper presented a sequential extraction scheme performed with various inorganic and organic extractants of different concentrations.

The average amount of all fractions of selenium concentrations obtained in the five-step sequential extraction approaches the value of total selenium concentrations resulting from the initial soil sample digested with concentrated strong acids.

The three analyzed soil samples belong to different soils which have a neutral - slightly alkaline pH, being collected from different areas of Romania.

ACKNOWLEDGMENTS

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