Determination of Selenium Content in Soil and Parent Material by HG-AAS

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HG-AAS (Hydride generation coupled with atomic absorption spectrometry) was applied to assess selenium concentrations in some soil and parental material samples from South-Eastern Romanian Plain and Central-South Dobrogea. Selenium analysis by HG-AAS requires digestion of solid samples to release selenium into a solution, and extraction of mobile selenium content with a common extraction solution, namely EDTA with Ammonium Acetate. Traditionally, wet acid digestion has been used which involves digestion/heating with strong acids to destroy the organic matter and dissolve the metal ions. The proposed procedure involves microwave sample preparation by using a mixture of H_2O_2/HNO_3/HCl. Parameters for the reduction of Se (VI) to Se (IV) in HCl medium by heating in a microwave oven have been optimized. These contents were determined by atomic absorption spectrometry coupled with hydride generation (HG-AAS). The concentrations of selenium are within the allowed limits, even lower. Certain parameters of the method were validated for selenium content determination from soil and plant samples by atomic absorption spectrometry coupled with hydride generator: the working concentrations, linearity, detection limit, quantification limit. Data obtained regarding selenium content confirms its deficiency in the studied area.

Key words: selenium, soil, microwave digestion, deficiency, reduction

Selenium is a naturally occurring mineral element that is widely distributed in nature in most rocks and soils. In humans, selenium is a trace element nutrient which acts as cofactor for the reduction of antioxidant enzymes such as glutathione peroxidase and certain forms of thioredoxin reductase found in animals and some plants (this enzyme occurs in all living organisms, but not all of its forms in plants require selenium) [1]. Selenium is widely spread in relatively small concentrations in rocks, plants, coal, and other fossil fuels. The occurrence of selenium in the lithosphere is 9 - 10^{-6}%. Selenium compounds have been extensively used in paints, glasses, dyes, rubber, photocells, insecticides and other industries. Selenium is a toxic element as well as a trace element for animals and humans. Its deficiency causes the Keshan and Kaschin-Beckdisease in humans, which have frequently been reported in China [2].

Many spectrophotometric methods for the determination of selenium have been reported with some chromogenic reagents, such as 3,3-diaminobenzidine tetrahydrochloride, 2,3-diaminonaphthalene, 2-mercapto benzothiazole, o-phenylenediamine, dithizone, 8-hydroxyquinoline, leuco crystal violet, variamine blue and methylene blue. Some of these reagents have been reported to be carcinogenic, while few others are less selective and some reagents require heating for the development of color [2].

Rapid, highly sensitive and selective spectrophotometry methods for the determination of selenium(IV) traces are studied. The methods are based on either the oxidation of 2,4-dinitrophenyl hydrazine hydrochloride (2,4-DNPH) by selenium in hydrochloric acid medium and coupling with N-(1-naphthyl) ethylene diamine dihydrochloride (NEDA) to give a pink colored product or the oxidation of 4-aminoresorcinol hydrochloride (4-ARCH) by selenium in sulphuric acid medium and coupling with 4-amino-resorcinol hydro chlorine to yield an orange red colored product [3]. It has been reported that the increased acid concentration (up to 6 mol/L HCl) effectively reduces or even eliminates interferences. However, interferences present in higher concentrations can not be eliminated by acidification only. In such cases various techniques were applied, such as ion-exchange resins, addition of EDTA, the use of $NaBH_3CN$ instead of $NaBH_4$, various masking agents, addition of Fe (III) for delaying the reduction of interfering metal ions to metal [6]. This hydride generation-atomic absorption spectrophotometry method (HG-AAS) is useful for the determination of Se, in a variety of geochemical samples [3-5].

Analytical methods for determination of total and mobile selenium content in the analyzed samples are presented in this paper. The digestion method chosen for the extraction of total selenium is based on wet digestion of soil samples under pressure in a microwave oven with a mixture of nitric acid, hydrochloric acid and hydrogen peroxide to convert selenium to selenate (SO_4^{2-}), its reduction with $NaBH_4$ to H_2Se and its determination by HG-AAS (hydride generation of selenium determination by flame atomic absorption spectroscopy) [7]. In this type of samples working with the microwave oven avoids the selenium losses (very volatile compounds) during digestion. This method also minimizes the digestion time. After bringing the samples in solution, it is necessary to separate selenium because of its dosing difficulties induced by the interference of the other elements present in the sample or organic substances occurence. The method for the determination of mobile selenium content in soil has the following steps: extraction of mobile selenium form in

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different extraction solutions, selenium separation, and selenium dosage. This paper is focused on the South-Eastern part of Romania, where a study was done regarding the low selenium level in the parent material. The area is characterized by a natural handicap: the selenium deficiency [8, 9].

Experimental part

Materials and methods

All the chemicals used were of analytical quality (Merck, Germany). High quality water, obtained using a Milli-Q system (Purelab ELGA, England) was used exclusively.

The HG–AAS measurements were performed with a Thermo Electron Corporation SOLAAR S atomic absorption spectrometer equipped with a Thermo Electron Corporation VP 100 hydride generation system and samples were digested by acid assisted microwaves using Microwave Millestone Start MD 12. Parent material and soil samples were air-dried at room temperature, sieved (< 2 mm) and grounded in an agate mortar.

For total selenium content, 1 g portion of each sample was placed into a 100 mL PTFE (polytetrafluorethylene) vessel, and 6 mL HNO_3 65%, 3 mL HCl 37 % and 0.25 mL H_2O_2 were added [10]. After digestion the samples were cooled for 30 min through ventilation; they were kept in the digestion vessels at least 12 h (overnight) and then diluted to 50 mL with ultrapure water in a volumetric flasks.

The phases for the digestion procedure on microwave system for total selenium are showed in table 1.

For extraction of mobile Se, 10 g samples were weighed into a 200-250 mL wide mouthed PE bottle, extracted with a 0.01 m EDTA and 1 n ammonium acetate solution solution at *p*H 7.0 [11]. The mixture was stirred for 2 h at room temperature on a horizontal shaker (160 movements per min).

At the end of the digestion period and after extraction with EDTA – ammonium acetate solution, selenium is reduced from oxidation state +6 to +4 as follows: 3 mL concentrated HCl are added to an extract aliquot which is then heated for 30 min at 80°C. Samples were left to cool at room temperature and then diluted to 25 mL with ultrapure water in a volumetric flasks. Sample solutions were analyzed through HG–AAS.

Table 1
THE OPTIMAL CONDITIONS OF WORKING PARAMETERS

Stage	Time (min)	Power (W)	Temp (°C)
1	15	850	150
2	15	850	210
3	15	850	210

Results and discussions

Selenium content in the investigated soil samples

The data regarding the total and mobile soil and parent material samples selenium contents from the studied area are presented in table 2. If we compare these values to the analytical data of total Se content in similar parent material types [12], it results that in the loess located in the South-Eastern part of the country, including Dobrogea green schist and limestone, the total Se content is much lower. The mobile Se content, soluble in EDTA – ammonium acetate solution at *p*H 7.0, represents about 10% of total Se content. It is noted that mobile Se content in the loess of the South-Eastern Romanian Plain is double as compared to that of the loess or green schist or Jurassic limestone from Dobrogea. If we compare the average values of total Se content in soils of both areas with the 383 ± 5μg/L average value, representing the total selenium content in the upper horizons of many soils in different countries [13], it results that the total selenium in soils of both Romanian areas is only 38% (South-Eastern Romanian Plain), and 62% (Central and Southern Dobrogea) of this value.

Conditions for Se determination by HG-AAS

Areas	*Parental material type*	*total Se*	*mobile Se*
South-Eastern Romanian Plain	loess	97 ± 22	9.4 ± 2.6
	loess	100 ± 15	4.6 ± 0.5
Central Dobrogea	green schist	22 ± 7	4.6 ± 1.0
	Jurassic limestone	20 ± 3	30 ± 0.8
Southern Dobrogea	loess	84 ± 18	4.8 ± 1.3

Table 2
MEDIUM TOTAL AND MOBILE SELENIUM CONTENT (μg/L) IN SOIL AND PARENTAL MATERIAL

[13]Total Se in clay (400-600 μg/L), sandstone (50-80 μg/L), limestone (30-100 μg/L) in Kabata – Pendias and Pendias, 2001

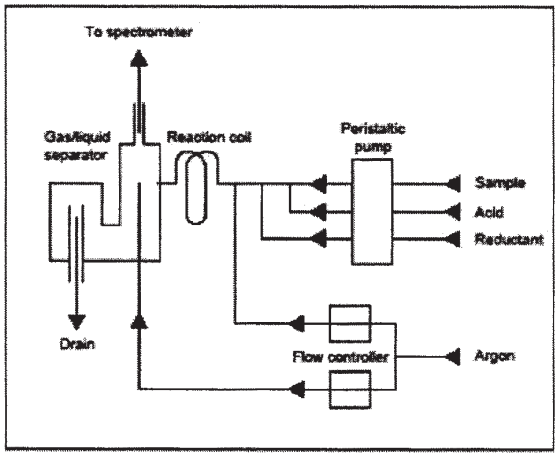

Fig. 1. Scheme of HG–AAS system

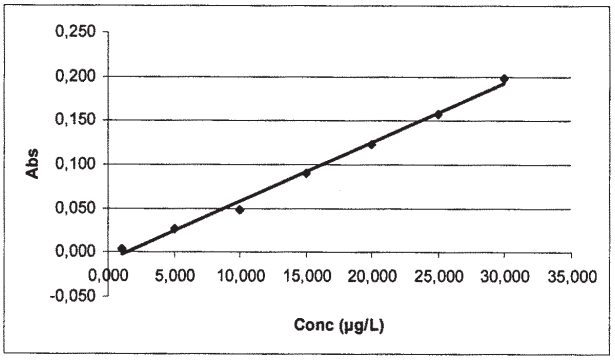

Fig. 2. Calibration curve

i	$x_i = logc_i$	y_i	x_i^2	y_i^2	$x_i y_i$
1	0	0,004	0	0	0
2	0,70	0,027	0,49	0,001	0,02
3	1,00	0,049	1,00	0,002	0,05
4	1,18	0,090	1,39	0,008	0,11
5	1,30	0,123	1,69	0,015	0,16
6	1,40	0,158	1,96	0,025	0,22
7	1,48	0,199	2,19	0,040	0,29
$\sum_{i=1}^{N}$	7,05	0,650	8,72	0,091	0,85

Table 3
THE EXPERIMENTAL DATA OBTAINED TO CALCULATE LINEAR REGRESSION FUNCTION

$y = a + bx$	y=0,007x+0,009
Slope – sensitivity	$b = \frac{\sum_{i=1}^{N}(x_i - \bar{x})(y_i - y)}{\sum_{i=1}^{N}(xi - \bar{x})} = 0,007$
Origin ordinate	$a = \bar{y} - b \cdot \bar{x} = 0,009$
Residual standard deviation	$s_y = \frac{\sum_{i=1}^{N}[y_i - (a + b \cdot x_i)]^2}{N-2} = 0,006$
Standard deviation of the method	$s_{x01} = \frac{s_y}{b} = 0,900$
Coefficient of variation (RSD %)	$V_{01} = \frac{s_{x01}}{\bar{x}} \cdot 100 = 0,059$
Standard deviation of slope	$s_b = \frac{s_y}{\sqrt{\sum_{i=1}^{N}(x_i - \bar{x})^2}} = 0,0025$
Standard deviation of the origin ordinate	$s^a = \sqrt{\frac{\sum_{i=1}^{N} x_i^2}{n\sum_{i=1}^{N}(x_i - \bar{x})^2}} = 0,5098$
Correlation coefficient	$R = \frac{\sum_{i=1}^{N}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{N}(x_i - \bar{x})^2 \cdot \sum_{i=1}^{N}(y_i - \bar{y})^2}} = 0,997$
Detection limit (LOD)	LOD = 3s + $\bar{x}$ = 0,121 µg/L
Quantification limit (LOQ)	LOQ = 10·s + $\bar{x}$ = 0,140 µg/L

Table 4
STATISTICAL PARAMETERS OF THE EXPERIMENTAL DATA

Hydride generation – atomic absorbtion spectrometry (HG-AAS) offers good accuracy and is reliable, rapid, and relatively inexpensive. During HG-AAS analysis, selenite (the only reactive selenium species) in an aqueous sample reacts with a reducing agent, sodium borohydride ($NaBH_4$), in the presence of hydrochloric acid to generate gaseous selenium hydride (H_2Se) (eq. 1). To minimize interferences with transition metals at selenium dosage, optimal concentrations of the reagents have been established:

-sodium borohydride 0.5% m/v in sodium hydroxide 0.5% m/v

-hydrochloric acid 50 % v/v.

$$4H_2SeO_3 + 3BH_4^- + 3H^+ \Leftrightarrow 4H_2Se + 3H_3BO_3 + 3H_2O \quad (1)$$

Selenium dosage by AAS involves drawing H_2Se in the system with inert gas (argon) and its decomposition in air-acetylene flame. Selenium dosage in flame is made using a quartz cell with open ends, placed over the burner and connected to the VP100 through a rubber tube. Selenium determination is based on the injection flow, when the peristaltic pumps are used simultaneously for transporting the reducing agent and the sample, and for waste removal; when the fill valve is opened, the exact volume of sample is loaded; when the valve is on the injection position, the sample is introduced into the carrier phase and transported to the reaction section with sodium borohydride, the reaction mixture is then transported to a gas-liquid separator where selenium is separated and, after passing through the filter of tetra-fluorine-ethylene, is transported in the flame to the absorption cell (located on a metal support mounted above the atomic absorption spectrophotometer burner) by carrier gas argon which absorbs radiation from a selenium hollow cathode lamp of the spectrophotometer. The scheme of HG-AAS system is presented in figure 1.

The spectrophotometer ''Thermo Elemental'' is controlled by computer, and after adding the reducing agent to analyzed solution the absorbance measurement begins. On the computer screen, the adequate selenium vapor absorbance is recorded as peaks whose height is proportional to the element concentration in the analysed sample.

To demonstrate if the analytical response is linear or not in the working concentrations domain, it is necessary to perform a calibration with several points. Setting the range of working concentrations is done by calibration [14], by choosing a preliminary domain work. Selenium calibration curve for atomic absorption spectrometry coupled with hydride generation is made from seven points standard (1-30 µg/L) (fig. 2).

Appropriate statistical calculations are recommended in addition to visual evaluation of the analytical signal value function of concentration. Thus, the statistical parameters are computed, such as the calibration curve slope and the origin ordinate, the sum of squares residual values and the correlation coefficient based on the data from table 3 with the aid of the data from table 4 [15].

Conclusions

The HG-AAS technique was applied for the determination of selenium in actual soil samples. The microwave sample dissolution has some advantages as comapred to the procedures for the sample preparation published in the past. The risk of contamination is lower since smaller amounts of reagents are used for the sample dissolution. An aliquot of hydrochloric acid added to the soil sample extract serves in the first place for a satisfactory elimination of interferences and in the second place for the reduction of Se (VI) to Se (IV) by heating the acidified sample solution in the flask. This method of soil sample preparation is very fast and easy. Based on the results obtained in the present study it is concluded that the present technique is adequate for the routine determination of selenium concentration in soil samples.

Selenium mobile content soluble in EDTA – ammonium acetate solution at *p*H 7.00 is about 10% of the total selenium content. It is observed that the mobile selenium content in loess from the South-Eastern part of the Romanian Plain is double as comapred to the one in the loess or green schists and Jurassic limestone from Dobrogea, and the total content of selenium in the soils is only 38% (South-Eastern Romanian Plain) and 62% (Central and South Dobrogea) of this value.

The investigated parameters in the validation study were: the working concentrations, linearity, detection limit, quantification limit.

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