

The comparison of sample extraction procedures for the determination of cations in soil by IC and ICP-AES

Research Article

Svetlana M. Stanišić^{1*}, Ljubiša M. Ignjatović¹,
Dragan D. Manojlović², Biljana P. Dojčinović³

¹Faculty of Physical Chemistry, University of Belgrade,
11 000 Belgrade, Serbia

²Faculty of Chemistry, University of Belgrade, P.O. Box 158,
11 000 Belgrade, Serbia,

³Institute of Chemistry, Technology and Metallurgy,
Center of Chemistry, 11 000 Belgrade, Serbia

Received 7 November 2010; Accepted 16 February 2011

Abstract: This paper presents the extraction of cations from a soil sample, type ranker on serpentinite, in deionized water, by use of three different extraction techniques. The first extraction technique included the use of a rotary mixer, the second technique involved the use of a microwave digestion system with different extraction temperatures, and the third technique employed an ultrasonic bath with different extraction times. Ion chromatography was used for determining the concentration of Li, Na, K, Ca, Mg and ammonium ions in soil extracts with subsequent determination of concentrations for all cations, except for ammonium ion extraction, conducted by Inductively Coupled Plasma-Atomic Emission Spectrometry. The results of cation extractions showed that microwave assisted extraction was most efficient for the Li, Na, K, Ca, Mg, Co, Mn, Ni, Pb and ammonium ions. Use of a rotary mixer for extraction was most efficient for Cd and Zn ions, while use of ultrasound bath was most efficient for Cr, Cu, Fe and Al ions. Several times higher amount of cations extracted by the most efficient, compared to the second best technique, under optimal conditions, were noticed in the case of: Ca, Mg, Co, Mn, Fe, Al, and Zn ions.

Keywords: Soil sample extraction • Cation extraction • Sequential extraction procedure • Ion chromatography • ICP-AES.

© Versita Sp. z o.o.

1. Introduction

Alkali and alkaline earth metals, and transition and post-transition metals are found in soil as solid phase bound, exchangeable and soluble, either in the role of constituents or pollutants [1]. The percentage of total element content in soil that presents the mobile, and therefore bioavailable, fraction depends on physico-chemical properties such as: redox potential, pH, organic matter content and other parameters [2]. Element concentration in the soil solution is in balance with the amount adsorbed on clay mineral particles, organic matter and iron, and manganese and aluminum hydroxides [3]. The chemical kinetic balance of elements in soil and their exchange between solid phase and soil solution is very complex and needs further investigation.

The determination of the total content of the above elements and their fractions in soil, especially

the bioavailable fraction, is important due to their positive or negative influences on crop growth, and potential subterranean and drainage water pollution, as it relates to the role of these elements in physico-chemical and biological processes occurring in soil. Determination of cation concentrations can be done in soil solution or soil extract which is obtained by single or sequential procedures of cation extractions. The extraction agents used for single extraction are acids in a wide range of concentrations (HNO₃, aqua regia, HCl, Mehlich 1), chelating agents (EDTA, DTPA, Mehlich 3), buffered salt solutions (ammonium acetate, acetic acid, pH=4.8 or 7) or unbuffered salt solutions (CaCl₂, NaNO₃, NH₄NO₃, NH₄Cl); out of these, low concentration agents are considered as soft extractants [4]. The sequential extraction procedure is conducted for determining element contents in following fractions: water-exchangeable, weakly adsorbed, carbonates and

* E-mail: sstanisic@singidunum.ac.rs

Fe, Al and Mn hydroxides bound, organic matter bound and residual fraction [5,6]. Unlike sequential extraction, the single extraction procedure is conducted in order to estimate the elements' mobility and bioavailability, as well as their migration within the soil profile. The sequential extraction procedure is conducted in accordance with different extraction schemes [7] (BCR, Tessier, Gálan, Maiz, Ure, Krishnamurti, Sahuquillo *etc.*), using specific extraction agents for each of the procedural steps: ammonium acetate, hydroxylamine hydrochloride, hydrogen peroxide and aqua regia [8]. Previous studies show that an exact determination of each soil phase's element content using sequential extraction, as well as single extraction procedure often gives unreliable results, because the selected extraction agent is not selective for both the phase and phase-bound cations simultaneously [9]. For example, NH_4Cl solution has proved to be more advantageous compared to an NH_4NO_3 solution for determining the content of exchangeable cations and the effective cation-exchange capacity (CEC_e), although the latter is used as a standard extractant for the mobile fraction of heavy metals [10]. In addition to this, some extraction agents are not equally efficient for cation extractions from all types of soil, while soft extractants cannot be used for trace element extractions, since the extracted concentrations are beyond the detection threshold. Tlusoš *et al.* [11] reported that determination of the element quantity bound to specific soil phase is strongly dependent on the extracting agents and/or the applied extraction procedure, which is greatly influenced by extraction temperature, time, soil/solvent ratio and extract separation technique – centrifugation or filtration.

This paper presents new techniques for simultaneous extraction of cations by use of a rotary mixer, microwave digestion system, and ultrasonic bath, in order to obtain soil extract for further cation determinations by means of IC and ICP-AES. The agent used for all extractions was deionized water. The interaction of microwave energy (2450 MHz, 12.2 cm, typically used) with sample and reagents causes both ionic migration and dipole rotation, resulting in fast heating of the suspension with consequent chemical reaction acceleration [12]. The use of microwave energy for soil sample preparation and extraction of herbicides, organophosphorus, and organochlorine pesticides from soil has increased in recent years mainly due to the heating mechanism, resulting in the shortening of extraction and digestion time and the consumption of less extraction agent [13]. Furthermore, ultrasonic cavitation phenomenon, caused by implosion of cavitation bubbles and subsequent local pressure increases and elastic shock waves, has been used until now for soil aggregates dispersion [14] or

sewage sludge disintegration [15]. Cavitation, together with turbulent flow of the soil water suspension and acoustic streaming, leads to friction, stressing and dispersion of soil aggregates. Besides the ultrasonic energy, other factors are influencing the fraction of dispersed material, *e.g.* concentration, temperature and volume of suspension, gas content, position of vessel with soil water suspension in ultrasonic bath *etc.* [16]. Microwave energy produces localized high temperature and pressure in solution, as well as ultrasound energy, which creates extreme conditions for further chemical reactions to occur. The combination of microwave or ultrasonic energy with different extraction agents can be used for cation and anion extractions from soil sample, which would improve the soil sample extraction technique for the purpose of IC and ICP-AES analyses. The application of IC and ICP-AES for the purpose of environmental sample analysis has often been described in literature [17-21].

The sample of serpentine soil, type ranker, was used in the described research as a substrate. Due to the significant influence the soil properties have on the efficiency of a certain extraction agent and thus on the extraction itself, as all previous studies have demonstrated, the sample was subjected to pedological analysis prior to extractions.

2. Experimental Procedure

The soil sample was taken from a site covered with natural vegetation, in a location - Bujan Potok, in the vicinity of Belgrade, Serbia, exposed to minimal influences of anthropogenic pollution. The soil sample, weighing 1 kilogram in total, was obtained by combining samples taken from the surface horizon, rich in humus, from 30 different sites, at a depth of 20 centimeters. The depth of the total soil profile at this location was 50 centimeters. The sample was air dried for 72 hours. After that, large fractions were removed, crushed in a mortar and then sieved through a 1 mm pore diameter sieve. The basic pedological analysis included: determining pH in H_2O and 1.0 KCl - potentiometrically, humus – after Turin's method, adsorptive complex of soil (H, T, S) - after Kappen, determining soil texture by pipette method, determining hydrolytic acidity - after Kappen, determining hygroscopic moisture by drying process, $T=105^\circ\text{C}$, determining moisture loss during heating at $T=700^\circ\text{C}$ for 30 minutes and determining soil conductivity by conductometric method.

Deionized water (18.2 $\text{M}\Omega$ cm) produced by Milli-Q Reagent Grade system (Phenomenex, USA) was used for the extraction and preparation of all suspensions. The substances used for analyses were of high

analytical purity. Eluent was made by dissolving tartaric acid (600 mg) and dipicolinic acid (125 mg) in one litre of degassed and deionized water. The eluent was made on a daily basis, and then filtered through 0.2 µm pore size membrane filter (Phenomenex, USA).

For IC calibration, the standard solution of cations, Li⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺, Primary Multiion Standard Solution, Fluka Switzerland (Cat. No 89316) with addition of Ammonium Ion Chromatography Standard Solution, Fluka, Switzerland (Cat. No 95023) was used for preparing standard solutions with 0.5, 2.5, 10 and 20 mg L⁻¹ concentration. For ICP-AES calibration, Multi-Element Plasma Standard Solution 4, Specpure, Alfa Aesar, Germany (Cat. No 42885) was used for preparation of two series of standard solutions; for alkali and alkaline earth metal elements of 0.01, 0.05, 1, 10 and 50 mg L⁻¹ concentration and for transition elements 0.1, 1, 10, 100 and 500 µg L⁻¹ concentration.

The rotary mixer used was Overhead Mixer Reax 20/8 (Carl Roth, Germany). The type of ultrasonic bath was Transsonic T 760 DH (Elma, Germany) with ultrasonic frequency of 40 kHz and effective ultrasound power of 170 W. The type of microwave digestion system used for soil sample preparation was ETHOS 1, Advanced Microwave Digestion System (Milestone, Italy), equipped with 10 PTFE containers for microwave digestion. The capacity of the containers was 100 mL each, and the maximum pressure and temperature that could be achieved were 100 bar and 240°C.

The used ion chromatography system used was a Metrohm, Switzerland, type 761 Compact IC, with a detector of conductometric type. The separation column used was Metrosep C 2-150. The eluent was 4 mmol L⁻¹ tartaric and 0.75 mmol L⁻¹ dipicolinic acid solution, with flow rate of 1 mL min⁻¹. Full scale range was 50 µS and the injected sample volume was 20 µL for each test.

The ICP-AES measurements were performed by simultaneous ICP-AES using a Thermo Scientific iCAP-6500 DUO ICP (Thermo Fisher Scientific, UK) spectrometer, with continuous wavelength coverage ranging from 166 to 847 nm, equipped with a RACID86 Charge Injector Device (CID) detector, a pneumatic cross-flow type nebulizer, a quartz torch and a quartz detector. Instrumental conditions were set: input power of 1150 W, auxiliary gas flow-0.5 L min⁻¹, coolant gas flow-12 L min⁻¹ and nebulizer flow-0.7 L min⁻¹.

The extraction suspension was prepared in normal flasks, 50 mL volume, by mixing soil sample with deionized water in ratio 1:10, *i.e.*, 2 g/20 mL. Two series of three extractions each were done by using a rotary mixer (Rotary Mixer Assisted Extraction, RAE in further text) in which the suspension was processed for 22 hours by mixing at 10 rpm at room temperature

(20°C). Second technique involved the use of the ultrasonic bath (Ultrasonic Assisted Extraction, UAE in further text) with the suspension positioned at the same place in the bath and the same initial water temperature, 17°C. Two extractions were made for each of the following extraction times: 10, 20, 30, 40 and 50 minutes. The third technique used a microwave digestion system (Microwave Assisted Extraction, MAE in further text) for five extractions at each of the following temperatures: 50, 100 and 150°C. The given temperature was achieved in 15 minutes for each cycle of extraction, while the extraction itself lasted for 15 minutes. After that, the samples were cooled to room temperature. The blank extraction was done for each of the extraction techniques used, with deionized water instead of soil suspension.

The soil samples were subjected to the three-step extraction scheme, suggested by the Standards, Measurements and Testing Programme (BCR, formerly) of the European Commission [4]. Aqua regia was used for the fourth stage of the extraction, according to EPA 3050B digest extract method, for determining the total metal content of the analytes. In order to make a distinction between the easily reducible fraction, bound to manganese oxides, and the moderately and poorly reducible fraction, bound to amorphous and crystalline iron oxides, we modified the procedure, by adding the third extraction step, according to the Förstner extraction scheme [22]. The extracting reagents for the sequential extraction procedure were prepared by dissolving substances, of analytical-reagent grade or higher purity, in deionized water. The sequential extraction was performed in triplicate. Aliquots of 1 g of dry soil sample were weighed into 50-mL polystyrene flasks, and after adding extraction reagents, the flasks were shaken on a horizontal shaker at 150 rpm. The residue was washed with 25 mL of deionized water, and centrifuged at 3000 rpm, prior to the next extraction step. A brief summary of the procedure is shown in Table 1.

When the extraction processes were finished, each of the extraction suspensions was first centrifuged, then filtered through medium pore sized filter paper and finally through 0.2 µm pore size syringe membrane filter (Phenomenex, USA). The soil extracts, thus obtained, with exception of the EDTA extracts, were acidified by adding 1 µL mL⁻¹ of perchloric acid solution and preserved at 4°C in the laboratory refrigerator for further analysis. After accuracy evaluation the conclusion was that IC analyses presented a RSDs as follows: Li⁺ -1.14%, Na⁺ -3.11%, NH₄⁺ -0.98, K⁺ -2.98%, Ca²⁺ -0.34% and Mg²⁺ -0.11%. In addition to this, ICP-AES analyses presented a RSDs as follows: Li⁺ -1.12%, Na⁺ -0.82%, K⁺ -2.68%, Ca²⁺ -0.21% and Mg²⁺ -0.79%, and for total

Table 1. Experimental conditions for sequential extraction procedure.

Elements fraction	Extraction time (hours)	Agitation method	Extraction agent amount (mL)	Extracting agent
Water-exchangeable, weakly adsorbed	16	Shaking, room temp.	40	0.11 mol L ⁻¹ acetic acid (HOAc)
Easily reducible	16	Shaking, room temp.	40	0.1 mol L ⁻¹ NH ₂ OH•HCl / HNO ₃ , pH=2
Moderately reducible	10	Shaking, room temp.	40	0.2 mol L ⁻¹ ammonium oxalate/ 0.2 mol L ⁻¹ oxalic acid
Oxidisable	3	Occasional agitation, +85°C	2x10	30% (8.8 mol L ⁻¹) H ₂ O ₂ / HNO ₃ , pH=2
	16	Shaking, room temp.	40	1 mol L ⁻¹ NH ₄ OAc, pH=5
Residual	0.5	Water bath, +95°C	10	Aqua regia, HNO ₃ /HCl (1:3)

ion content, as follows: Al -1.06%, Cd -8.69%, Co -6.91%, Cr -7.17%, Cu -6.21%, Fe -0.63%, Mn -4.86%, Ni -8.42%, Pb -7.62% and Zn -8.67%.

3. Results and Discussion

The measured pH value in KCl (5 g soil: 10 mL KCl) was 6.0, and in deionized water pH value was (5 g soil: 10 mL water) 6.9. The results of other pedological analyses are shown (Table 1).

The lithium ion extraction using a rotary mixer (Table 2) gave the same results as the microwave extraction at T=150°C. The extracted quantities obtained at T=50°C and T=100°C by microwave extraction and those obtained by use of the ultrasonic bath (Table 3) were in the range between 0.001 and 0.004 mg/100 g soil measured by ICP-AES, but beyond the detection threshold for IC.

The quantity of extracted sodium ion using the ultrasonic bath shows tendency for a mild increase with increased extraction time; thus, 50 minutes UAE gives the same quantity as the MAE at the highest temperature. It can be concluded, also, that the quantity of Na ions extracted by means of rotary mixer is equal to the quantity extracted by means of ultrasonic bath with 30 minutes of extraction time, while the quantity extracted by MAE at T=100°C was lower (Table 4).

The highest ammonium ion concentration was extracted by means of UAE, with an extraction time of 10 minutes. With the extraction time increased to 30 minutes, the quantity of extracted ammonium ion gradually decreases to a value that remains constant regardless of further increases in the extraction time (Fig. 1), but still two times higher than the one extracted by RAE. Microwave extraction at T=150°C resulted in half the amount of the extracted ammonium ion

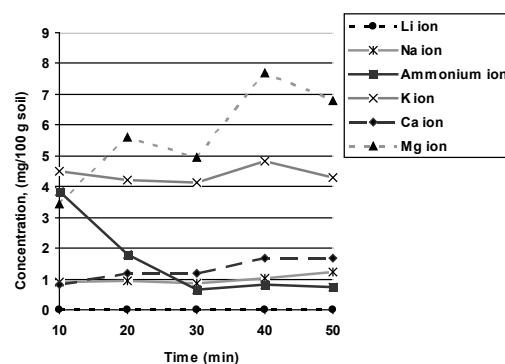


Figure 1. The change of extracted amounts of Li, Na, NH₄, K, Ca and Mg ions, obtained by means of UAE, with different extraction times (mg/100 g soil).

compared to 10 minute UAE, but still 4 times higher than the one extracted by RAE.

The amount of potassium ion extracted by UAE was constant regardless of the extension of extraction time, while in the case of MAE the amount of extracted ion showed tendency to increase with an increase in the extraction temperature (Fig. 2). Thus, microwave extraction at T=150°C resulted in higher potassium ion quantity than that obtained by means of the ultrasonic bath. The RAE of potassium ion with extraction time of 22 hours was least efficient, giving half the amount of the one extracted by UAE.

When it comes to calcium ion extraction, the MAE was the most efficient, giving, at T=100°C, an extracted amount that was 1.7 times higher, and at T=150°C even 5.2 times higher, than the one obtained by RAE. The quantity of calcium ion extracted by UAE showed an increase with increased extraction time (Table 3), and the average obtained amount by means of ultrasonic bath was equal to the amount extracted by MAE at 50°C. Considering magnesium ion, the higher amounts that were extracted correspond to the properties of the

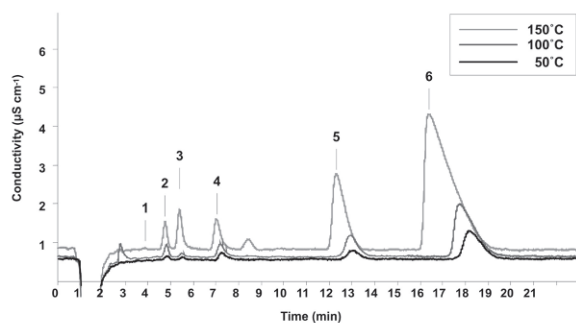


Figure 2. The comparison of chromatograms of the soil extracts provided by MAE at different temperatures. Cation No: lithium, peak 1; sodium, peak 2; ammonium, peak 3; potassium, peak 4; calcium, peak 5; magnesium, peak 6.

soil itself, since ranker over serpentine type of soil has the ratio Ca: Mg < 1, unlike other soil types. An interesting fact was that the ratio of the extracted magnesium ion amount and calcium ion amount was 2.1 for all extractions that involved MAE technique, 2.9 in the case of RAE, and 4.3 for all extractions that involved UAE technique (Fig. 3). Therefore, it can be concluded that, within each of the extraction techniques, Mg/Ca extracted ion amount ratio remained constant regardless of the extraction parameters variations.

The amount of cadmium ion extracted by RAE was 1.5 times higher than the average amount obtained by UAE for all extraction times (Table 5). Microwave extraction at T=50°C and 100°C resulted in 10 a times lower extraction amount compared to the amount extracted by RAE. The temperature increase to T=150°C gave significantly higher amount of extracted cadmium ion, but that was still half of the amount obtained by RAE.

The highest amount of zinc ion was extracted by use of rotary mixer and was 3.6 times higher than amount obtained by use of microwaves at the highest temperature (Tab. 6). The quantity extracted by means of UAE did not show any increase with the extension of the extraction time, with the average quantity equal to the one obtained by microwave extraction at T=150°C.

The amount of extracted cobalt ion obtained by UAE and RAE was quite low, close to or even below the detection threshold (Table 5). The quantity of cobalt ion extracted by use of microwaves increases 5.8 times with the rise of extraction temperature: From 5.06 that was extracted at T=100°C, to 29.49 µg/100 g of soil, extracted at T=150°C.

The MAE at T=150°C resulted in the highest amount of manganese, nickel and lead extracted ions compared to any other extraction techniques used (Table 6). Ranker over serpentine soil type is characterized by high concentrations of Ni, Cr and Mn ions, and a

lack of essential nutrients such as available nitrogen, potassium, and phosphorus necessary for the growth of agricultural species [23].

When it comes to manganese ion, the amount extracted by MAE at the highest temperature was 25 times higher than the average amount obtained by use of ultrasonic bath for all extraction times, and even 190 times higher than the amount extracted by use of rotary mixer.

In the case of nickel ion, the ratio between the amount extracted by MAE at T=150°C and the average amount extracted by UAE was 3.1, which was lower than in the case of manganese.

The lowest ratio between amount extracted by MAE at T=150°C and the average amount extracted by UAE was 1.7 in the case of lead ion. The ratio between the amount extracted by means of a microwave digestion system at T=150°C and the amount extracted by use of rotary mixer was 4.7 for the nickel ion and 2.7 for the lead ion. This leads to the conclusion that, in the case of these three metal ions, the most effective was the extraction by use of the microwave digestion system at the highest temperature, with the use of ultrasonic bath as second best (Fig. 3).

The UAE was, on average, giving 1.6 times higher amount of chromium ion compared to MAE at the highest extraction temperature, and even up to 3 times higher than the amount obtained by the use of a rotary mixer.

The highest quantity of copper ion was extracted by UAE with the extraction time of 50 minutes (Table 5). This quantity amounted to 457 µg/100 g of soil. The copper ion amount extracted by use of ultrasound bath varied with the increase of extraction time. The average amount extracted by use of this technique, taking into consideration all extraction times, was equal to the one obtained by use of rotary mixer, that is, 5 times higher than the highest amount extracted by use of microwaves.

The amount of the extracted iron ion was 29-35% higher than the amount of aluminium ion that was obtained, which indicates that these two cations underwent the same variations for each of the applied extraction techniques. The only exception to this was the soil extract obtained by microwave extraction at T=100°C and T=150°C which contained more aluminium than iron. The average extracted amounts of iron and aluminium ions obtained by means of ultrasound bath was several times higher than the amounts extracted by use of a microwave digestion system at T=150°C and rotary mixer.

Considering the UAE technique, the extracted amount of cations varied directly with the length of the extraction time, which can be explained by the effect

of ultrasonic energy on the soil suspension which is, alternately, influencing the processes of ion adsorption and desorption (Fig. 1). Ultrasonic energy can cause soil particle fragmentation and soil aggregate disintegration, thus increasing the surface area available for reactions with the extraction agent. Hwang *et al.* [24] reported that UAE efficiency increased with the sonication time and was highest at 12 minutes; Väisänen *et al.* [25] reported the optimal extraction time was 9 minutes. Besides the ion adsorption and desorption processes, this can be explained with the formation of new chemical species with longer sonication time due to the recombination of reactive groups under the extreme conditions in the suspension [26]. Still, the main advantages resulting from UAE, but also MAE, comprise the reduction of the procedural time and reagent consumption [27].

Considering the MAE technique, as expected, there was an obvious positive correlation between the amount of extracted ions and extraction temperature (Fig. 2). The variations in the extracted ion amount, due to the use of different extraction techniques, were minimized in the case of alkali ions, Li, Na, K, and ammonium ion. For these cations, the MAE technique was almost equally efficient as either of two other techniques, UAE or RAE.

In the case of K ion, the extracted amounts obtained by UAEs were almost constant for all extraction times. The extension of the extraction time in the case of the UAE technique, as well as the extraction temperature rise in the case of the MAE technique, had a negative influence on the amount of extracted ammonium ion. In the case of Ca and Mg ions, the use of MAE technique at the highest temperature was most efficient. In contrast to alkali ions extraction, the extractions of Ca and Mg ions at T=150°C gave a significantly higher amount of extracted ions than the extractions using two other techniques.

Comparing to two other techniques, UAE was the most efficient in the case of Fe, Al, Cr and Cu ions, giving significantly higher extracted amounts (Fig. 3). Also, significantly higher extracted amounts are noticed in the case of Co and Mn ions, by use of microwaves and Zn ion by use of a rotary mixer.

Several studies have been carried out in order to decrease the long treatment time of sequential extractions [28-30]. The results of these studies, obtained upon application of ultrasound for the sample preparation, indicate that ultrasound-assisted conventional sequential extractions can be accomplished within 20-30 minutes. Therefore, good agreement between the results obtained by conventional and the results obtained by ultrasound-assisted extractions was attained, particularly in the case of BCR extraction schemes. The use of microwaves for speeding up the conventional extractions, according to some researches, showed, in general, worse performance, compared to the use of ultrasound, with exception in case of sewage sludge extractions [31-33]. As indicated above, in our study conducted on serpentinite soil samples, the influence of microwave and ultrasonic energies on the soil sample preparation has been found to be significant, however, not only because of a possible decrease in the extraction time. It is significant due to exhibited selectivity for metal species, observed through big differences in amounts of extracted cations, by use of microwaves and ultrasound. Therefore, it can be concluded that microwaves and ultrasound cannot simply replace conventional treatments like conductive heating, in each of extraction steps of sequential procedure, as was attempted in previous studies, but it can be used in other ways for sequential extraction improvement.

The results of the sequential extraction procedure, obtained for Cd, Co, Cr, Cu, Ni, Pb, Zn, Fe, Al and Mn, are shown in Table 2. For extracting water soluble and exchangeable metal fractions, as well as for carbonate bound metal fractions, 0.11 mol L⁻¹ acetic acid (HOAc) was used. Due to the formation of metal acetate complexes, readsorption of the cations was prevented. For extracting metal fractions bound to iron and manganese oxyhydroxides, 0.1 mol L⁻¹ NH₂OH·HCl / HNO₃, pH 2 was used. The organically bound metal fraction was released by oxidation of the organic material using 30% (8.8 mol L⁻¹) H₂O₂ / HNO₃, pH=2. Considering the fact that we used deionized water as the extracting agent, the extracted amounts of the cations are significantly lower, compared to the amounts extracted by means of

Table 2. The results obtained by sequential extraction procedure. Participation of different metals fractions in total metal content (%).

↓Fraction / Cation→	Cd	Co	Cr	Cu	Ni	Pb	Zn	Fe	Al	Mn
Water-exchangeable	-	0.05	-	-	1.42	0.01	-	-	-	1.42
Easily Reducible	90.28	49.86	0.93	1.25	17.09	18.91	15.44	1.20	1.58	73.50
Moderately reducible	9.71	14.67	17.78	22.72	7.09	1.27	6.52	13.17	6.16	10.30
Oxidisable	-	3.90	16.32	0.05	15.85	5.87	5.12	0.13	0.30	1.58
Residual	-	31.52	64.96	75.98	58.55	73.94	72.92	85.50	91.96	13.20

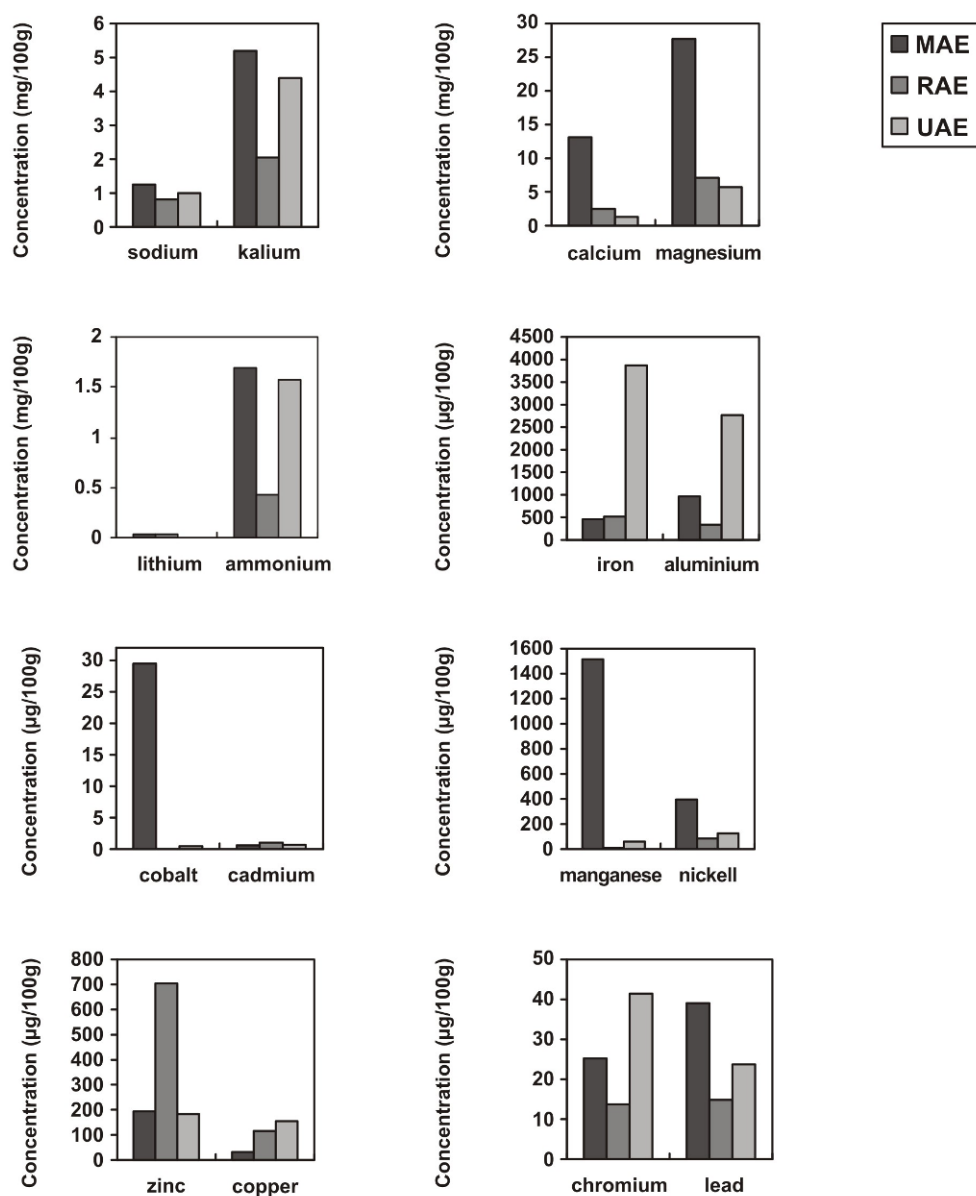


Figure 3. The comparison of the amounts of cations extracted by each of the three extraction techniques, MAE (150°C), RAE and UAE (average amount taking all extraction times in consideration).

Table 3. The results of basic pedological analysis.

Soil parameter	Meas. 1	Meas. 2	Meas. 3	Mean value
Humus, %	5.15	5.23	5.12	5.16
Total C, %	2.99	3.03	2.97	2.99
The sum of base cations, mEq/100 g	34.60	33.50	39.60	35.90
Large sand particles, %	4.87	6.22	6.83	5.97
Small sand particles, %	30.10	30.80	31.58	30.85
Colloid clay, %	45.75	43.61	40.99	43.45
Silt, %	19.28	19.28	20.60	19.72
Hygroscopic moisture, %	3.10	3.10	3.10	3.10
Heating loss, %	14.20	14.60	14.40	14.40

Table 4. The results of determinations of Li⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺ ions obtained by IC and ICP-AES after RAE (mg/100 g soil).

Determin. method	Sample series No.	No. of extraction	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺
IC	1	1	0.025	1.08	0.538	2.31	2.78	6.36
		2	0.036	0.602	0.327	1.73	2.33	6.63
		3	0.039	0.644	0.542	2.15	3.02	7.04
	2	1	0.048	0.617	0.311	2.53	2.26	7.32
		2	0.054	0.789	0.458	2.71	2.03	6.93
		3	0.059	0.673	0.422	1.14	2.39	7.28
ICP-AES	1	1	0.022	1.03	-	2.23	2.82	6.45
		2	0.028	0.850	-	1.56	2.06	6.99
		3	0.023	0.923	-	2.13	3.02	7.24
	2	1	0.031	0.835	-	2.13	2.45	7.94
		2	0.051	0.935	-	2.50	2.17	7.29
		3	0.028	0.699	-	1.47	2.60	7.51

Table 5. The results of determinations of Li⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺ ions obtained by IC and ICP-AES after UAE (mg/100 g soil).

Extraction time	Determination method	No. of extraction	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺
10	IC	1	-	0.845	4.01	4.32	0.712	3.25
		2	-	0.968	3.71	4.71	0.877	3.44
	ICP-AES	1	0.003	0.829	-	4.21	0.700	3.53
		2	0.003	1.04	-	4.82	1.05	3.50
20	IC	1	-	0.893	1.95	4.59	1.29	6.47
		2	-	0.922	1.66	4.06	1.04	4.89
	ICP-AES	1	0.003	0.863	-	4.12	1.14	6.53
		2	0.003	1.05	-	4.08	1.27	4.61
30	IC	1	-	0.722	0.72	4.03	1.10	4.82
		2	-	0.961	0.56	4.14	1.26	5.06
	ICP-AES	1	0.003	0.758	-	4.08	1.02	4.92
		2	0.003	1.06	-	4.31	1.29	5.03
40	IC	1	-	0.926	0.799	4.88	1.81	7.04
		2	-	1.15	0.813	4.66	1.52	8.21
	ICP-AES	1	0.003	1.00	-	5.00	1.76	7.20
		2	0.003	1.18	-	4.70	1.63	8.36
50	IC	1	-	1.13	0.698	4.12	1.80	6.92
		2	-	1.24	0.800	4.11	1.64	6.52
	ICP-AES	1	0.003	1.21	-	4.42	1.75	7.02
		2	0.003	1.27	-	4.54	1.59	6.73

extracting agents, according to the proposed sequential extraction procedure. This is due to the influence of deionized water, which exhibits dissolving and hydrolytic effects on simple salts, depending on their solubility level, and also, to a much lesser extent, on Al and Fe complex salts and elements bound to Al, Fe and

Mn hydroxides, or organic matter phase. The results (Table 2) represent the percentage of the total elements' content contained in water-exchangeable, easily and moderately reducible, oxidisable, and residual fractions. Residual fractions, although containing the biggest amount of elements, cannot be indicators of elements'

Table 6. The results of determinations of Li⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺ ions obtained by IC and ICP-AES, after MAE (mg/100 g soil).

Extraction temperature	Determination method	No. of extraction	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺
50°C	IC	1	-	0.320	0.030	1.00	1.12	3.19
		2	-	0.212	0.072	1.30	1.36	3.05
		3	-	0.225	0.065	0.81	1.20	2.57
	ICP-AES	1	0.001	0.399	-	1.16	1.24	3.38
		2	0.001	0.233	-	1.23	1.61	3.29
		3	0.001	0.231	-	0.973	1.38	2.60
100°C	IC	1	-	0.502	0.078	2.20	4.09	8.76
		2	-	0.552	0.201	2.73	4.52	7.96
		3	-	0.728	0.308	2.39	4.21	9.76
	ICP-AES	1	0.004	0.592	-	2.26	3.61	9.15
		2	0.004	0.678	-	3.00	5.07	8.47
		3	0.004	0.914	-	2.23	4.28	9.62
150°C	IC	1	0.052	0.941	2.00	5.16	11.7	29.6
		2	0.043	1.34	1.29	5.10	12.6	25.6
		3	0.038	1.39	1.78	5.19	15.0	28.7
	ICP-AES	1	0.031	1.00	-	5.41	11.7	29.0
		2	0.022	1.42	-	5.25	13.0	26.2
		3	0.033	1.38	-	5.08	14.7	27.3

Table 7. The results of determinations of total ion content of Cd, Co, Cr, Cu and Fe obtained by ICP-AES, after three extraction techniques (μg/100 g soil).

Extraction procedure	Sample series No.	Cd ion	Co ion	Cr ion	Cu ion	Fe ion
RAE	1	1.15	0.101	14.00	154	468
	2	0.921	-	13.50	157	563
Average concentration		1.03	0.050	13.70	155	516
UAE	Extraction time					
	10	0.945	0.150	49.20	119	4875
	20	0.386	0.969	22.50	121	1633
	30	0.612	0.802	33.40	57.1	3188
	40	0.963	0.240	61.90	16.4	6013
	50	0.644	0.203	40.20	457	3650
Average concentration		0.710	0.482	41.40	154	3871
MAE	Extraction temperature					
	50°C	0.110	0.260	3.79	10.5	144
	100°C	0.120	5.060	9.45	24.0	159
	150°C	0.590	29.500	25.20	31.4	455

mobility due to the fact that they can be extracted only by use of concentrated acids. Concerning the other fractions, the biggest amounts of Cr, Cu, Fe, and Al ions are contained within a moderately reducible fraction, associated with amorphous and crystalline iron oxides. For the same elements, the most efficient extracting

technique was the UAE. Furthermore, the biggest amount of Cd, Co, Ni, Pb, Zn, and Mn ions are contained within the easily reducible fraction of these elements that are associated with manganese oxides. For these metals, MAE and RAE were more efficient extraction techniques, comparing to UAE.

Table 8. The results of determinations of total ion content of Al, Mn, Ni, Pb and Zn obtained by ICP-AES, after three extraction techniques ($\mu\text{g}/100\text{ g soil}$).

Extraction procedure	Sample series No.	Al ion	Mn ion	Ni ion	Pb ion	Zn ion
RAE	1	356	9.17	84.2	15.2	823
	2	319	8.46	83.9	14.4	585
Average concentration		337	8.81	84.1	14.8	704
UAE	Extraction time					
	10	3589	59.40	122	21.7	308
	20	733	64.00	135	27.9	110
	30	2271	39.20	101	22.2	44.2
	40	4612	87.10	154	26.4	271
	50	2622	51.10	116	20.5	180
Average concentration		2765	60.20	126	23.7	182
MAE	Extraction temperature					
	50°C	126	13.60	36.8	10.9	170
	100°C	190	194	164	29.4	187
	150°C	965	1515	395	39.1	193

Most of the sequential extractions include 3-7 extraction steps, and, during each step, the applied chemical agent should extract a certain portion of metal species bound to the specific soil phase. However, because of the lack of selectivity or/and efficiency of the extracting agents, the extraction procedures are not harmonized. The introduction of microwaves and ultrasound requires further investigations; first of all, in order to determine whether they have the same effect on different soil samples, and second, to explore whether they can contribute to the efficiency of chemical extractants. Under some conditions they could be used in certain particular extraction steps, in combination with chemical extractants for efficiency enhancement and for improvement of the time-consuming sequential extractions.

4. Conclusion

It can be concluded that the extracted amount for each of the cations are obtained by the microwave digestion system and correlate positively with increasing the extraction temperature. In contrast to this, in the case of the extraction by use of the ultrasonic bath, there was no positive correlation between the amount of extracted

cations and extraction times. In addition to this, in the case of Cd and Zn ions, the most efficient extraction technique was RAE; in the case of Na, K, Ca, Mg, Co, Mn, Ni, Pb, and ammonium ions, MAE at the highest temperatures appeared to be the most efficient. For Cr, Cu, Fe, and Al ions, the UAE technique was the most efficient. For Li ions, the RAE and MAE at the highest temperature appears to give the same result. Introduction of new techniques for element extractions from soil can be substantial for the improvement of extraction procedures. However, our observation shows that use of microwaves and/or ultrasound to speed up the conventional sequential extraction procedures cannot be conducted, since both exhibit a certain selectivity for the metal species, regardless of the experimental conditions, like extraction time or temperature. In relation to this, application of microwaves and ultrasound on other soil samples should be further investigated. If the results for other soil types would show that microwaves and ultrasound exhibit certain selectivity for cations dominantly bound to specific soil phase, like in case of serpentinite soil, the combination of the ultrasonic and microwave energies, with different extraction agents for particular steps of sequential extractions, would be substantial for extraction procedure enhancements.

References

- [1] H.L. Bohn, B.L. Mc Neal, G.A. O'Connor, *Soil Chemistry*, 3rd edition (John Willey and Sons, New York, 2001)
- [2] M. Flues et al., *J. Braz. Chem. Soc.* 15, 496 (2004)
- [3] A. Bibak, *Commun. in Soil Sci. Plant Anal.* 25, 3229 (1994)
- [4] G. Rauret, *Talanta* 46, 449 (1998)
- [5] A.V. Filgueiras, I. Lavilla, C. Bendicho, *J. Environ. Monit.* 4, 823 (2002)
- [6] B. Krasnodębska-Ostręga, H. Emons, J. Golimowski, *J. Soils and Sediments* 4, 43 (2004)
- [7] A. Zimmerman, D.C. Weindorf, *Int. J. Anal. Chem.* Art. ID: 387803 (2010)
- [8] C. Gleyzes, S. Tellier, M. Astruc, *Trends Anal. Chem.* 21, 451 (2002)
- [9] O. Schramel, B. Michalke, A. Kettrup, *Sci. Tot. Env.* 263, 11 (2000)
- [10] A. Schöning, G. Brümmer, *J. Plant Nutr. Soil Sci.* 171, 392 (2008)
- [11] P. Tlusoš, J. Száková, A. Stárková, D. Pavliková, *Cent. Eur. J. Chem.* 3, 830 (2005)
- [12] E. De Oliveira, *J. Braz. Chem. Soc.* 14, 174 (2003)
- [13] M.V. Silva, F.W. Costa, V. Visentainer, E.N. Souza, C.C. Oliveira, *J. Braz. Chem. Soc.* 21, 1045 (2010)
- [14] A. Mentler, H. Mayer, P. Strauß, W.E.H. Blum, *Int. Agrophysics*, 18, 39 (2004)
- [15] P. Sorys, E. Zielewicz-Madej, *Mol. Quantum Acoustics* 28, 247 (2007)
- [16] H. Mayer et al., *Int. Agrophysics* 16, 53 (2002)
- [17] P.L. Buldini, D. Tonelli, F. Valentini, *Anal. Lett.* 42, 483 (2009)
- [18] A. Lakhani, R.S. Parmar, G.S. Satsangi et al, *Environ. Monit. Assess.* 133, 435 (2007)
- [19] S.M. Hassan, A.W. Garrison, *Chem. Spec. Bioavail.* 8, 85 (1996)
- [20] T. Umemura, R. Kitaguchi, H. Haraguchi, *Anal. Che.* 70, 936 (1998)
- [21] B. Takano, S.M. Fazlullin, P. Delmelle, *J. Volcanol. Geoth. Res.* 97, 497 (2000)
- [22] W. Salomons, U. Förstner, *Metals in the Hydrocycle* (Springer-Verlag, Berlin, 1984)
- [23] A. R. Đorđević, PhD thesis, University of Belgrade (Belgrade, Serbia, 1997) (in Serbian)
- [24] S.S. Hwang, J.S. Park, W. Namkoong, *Ind. Eng. Chem.* 13, 650 (2007)
- [25] A. Väisänen, A. Ilander, *Anal. Chim. Acta* 570, 93 (2006)
- [26] S.C.C. Arruda, P.M. Rodriguez, M.A.Z. Arruda, *J. Braz. Chem. Soc.* 14, 149 (2003)
- [27] D.S. Júnior, F.J. Krug, M.de G. Pereira, M. Korn, *App. Spectr.* 41, 305 (2006)
- [28] C. Bendicho, I. Lavilla, *Applications of Ultrasound-Assisted Metal Extractions*, *Encyclopedia of Separation Science* (Academic Press, London, 2000)
- [29] B. Pérez-Cid, I. Lavilla, C. Bendicho, *Anal. Chim. Acta* 360, 35 (1998)
- [30] B. Pérez-Cid, I. Lavilla, C. Bendicho, *Int. J. Anal. Chem.* 73, 79 (1999)
- [31] E. Campos, E. Barahona, M. Lachica, M.D. Mingorance, *Anal. Chim. Acta* 369, 235 (1998)
- [32] M. Ginepro, M. Gulmini, G. Ostacoli, V. Zelano, *Int. J. Environ. Anal. Chem.* 63, 147 (1996)
- [33] M. Gulmini, G. Ostacoli, V. Zelano, A. Torazzo, *Analyst* 119, 2075 (1994)