A comparison of sample extraction procedures for the
determination of inorganic anions in soil by ion chromatography

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Abstract: Three different extraction techniques were used for aqueous extraction of anions from soil of the type Ranker that was sampled from a serpentine site. The first technique involved the use of a rotary mixer (rotary mixer assisted extraction), the second, a microwave digestion system (microwave assisted extraction), with different extraction temperatures for every cycle during the procedure as follows: 50, 100 and 150 °C. An ultrasonic bath (ultrasonic assisted extraction) was used for the last technique in which the durations of the extraction process were: 10, 20, 30, 40 and 50 min. The concentrations of inorganic anions in the soil extracts after filtration were determined by ion chromatography. The results showed that the microwave-assisted extraction was highly efficient, giving, at a temperature of 150 °C, several times higher amounts of extracted anions in water than the other two techniques. Moreover, the extracted amounts of anions obtained by means of an ultrasonic bath with an extraction time ranging from 10 to 50 min were similar to those obtained by means of the rotary mixer with an extraction time of 22 h. However, extraction using the rotary mixer was more reliable, since the extracted amounts of anions obtained by means of an ultrasonic bath do not correlate with prolongation of the extraction time.

Keywords: soil sample extraction; inorganic anions extraction; ion chromatography.

INTRODUCTION

The contents of inorganic anions and the mineral composition of soil are the results of different biological, physicochemical, chemical and physical processes, which are themselves the results of the influence of pedogenetic factors.1 Bonma-
rito et al.\textsuperscript{2} demonstrated, by analyzing 120 samples of soil from rural, suburban and urban areas, via HPLC and IC, that different concentration of inorganic anions in soil, which vary in their spatial and temporal parameters, was the consequence not only the chemical composition of the soil, but also of anthropogenic and natural influences.

The more important inorganic anions in soil, NO\textsubscript{3}\textsuperscript{−}, NO\textsubscript{2}\textsuperscript{−}, Cl\textsuperscript{−}, HCO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, H\textsubscript{2}PO\textsubscript{4}−, HPO\textsubscript{4}\textsuperscript{2−}, PO\textsubscript{4}\textsuperscript{3−} and F\textsuperscript{−}, are found as soil constituents. In this role, they are a matter of interest in environmental science. Additionally, they can act as pollutants, as in the case of the increased concentration of sulphates due to atmospheric deposition in developed industrial areas. It should be pointed out that anions as soil constituents and their concentrations are especially significant for agriculture, not only as components in plant nutrition, but also as a restrictive factor in vegetable production in the case of increased concentrations, \textit{i.e.}, carbonates, sulphates and chlorides in naturally saline soils, such as solonchaks.\textsuperscript{3}

All the above mentioned indicates the considerable importance of the determination of the concentrations of anions in soil. This is equally important for a large number of scientific and practical fields, such as water-use management, registration and monitoring of the concentration of chemical species in soil, the monitoring of industrial and mining areas, environmental protection, agricultural crop improvement, preservation of forest ecosystems and the development of ecology.

The determination of the concentrations of inorganic anions can be realized by the analysis of soil solutions \textit{in situ}\textsuperscript{4} (by using porous cups, porous plates, capillary wicks, resin boxes and lysimeters), the analysis of solutions extracted from soil using the techniques of drainage, centrifugation or liquid–liquid substitution\textsuperscript{5} or, as is the case with the method used in this study, by analyzing soil extract obtained through applying different techniques for the extraction of anions from mixtures of soil and water or some other extraction solvent.

The quantity of anions extracted from soil depends, among other factors, on the type of solvent used for the extraction, the extraction time, temperature and pressure, soil/solvent ratio and composition and characteristics of the soil from which the sample was taken.

Previous studies dealt, largely, with the possibility of extracting separate anions from soil samples using different extraction solvents. Fluoride extraction was realized using aqueous CaCl\textsubscript{2}, KCl or AlCl\textsubscript{3} solutions, within the concentration values from 1.0×10\textsuperscript{−3} to 1.0×10\textsuperscript{−1} mol l\textsuperscript{−1}. The studies showed that the highest amount of fluorides was extracted by the use of AlCl\textsubscript{3}, while the results obtained from the employment of the other two extraction solvents depended on the pH value of the soil sample.\textsuperscript{6} Several studies\textsuperscript{7} showed that the use of an exchange resin resulted in 6 to 20 times more fluorides being extracted than the use of water or an aqueous CaCl\textsubscript{2} solution regardless of the soil type from which the
SOIL SAMPLE EXTRACTION FOR IC

A soil sample was taken. Soft extraction solvents that were used include 0.01 mol l\(^{-1}\) HCl, 1.0 mol l\(^{-1}\) and 0.02 mol l\(^{-1}\) NH\(_4\)Cl and 1.0 mol l\(^{-1}\) CaCl\(_2\), giving varying results depending on the soil type, while 5 mol l\(^{-1}\) NaOH, 70 \% HClO\(_4\), concentrated HCl and H\(_3\)PO\(_4\), were used as concentrated extraction solvents. The conclusion was that two times more fluorides were extracted when NaOH and H\(_3\)PO\(_4\) were used than with the other mentioned solvents. The extraction of sulphates was realized using aqueous solutions of LiCl, CaCl\(_2\), Ca(H\(_2\)PO\(_4\))\(_2\), with no significant difference in the obtained extraction results, while an analysis of extractions from a gypsum-free soil sample using water, 0.1 mol l\(^{-1}\) NaCl, 0.016 mol l\(^{-1}\) KH\(_2\)PO\(_4\) and 0.5 mol l\(^{-1}\) NaHCO\(_3\) showed that water was the most efficient extraction solvent for soils with pH < 6. Nitrites were extracted from soil using saturated (0.35 \%) CaSO\(_4\) \(\cdot\) 2H\(_2\)O in solution with 0.03 mol l\(^{-1}\) NH\(_4\)F and 0.015 mol l\(^{-1}\) H\(_2\)SO\(_4\), 0.01 mol l\(^{-1}\) CaCl\(_2\), 0.5 mol l\(^{-1}\) NaHCO\(_3\) and 2.0 mol l\(^{-1}\) KCl, of these KCl, at different molarities was used for nitrate extraction more often than the others.

In relation to the simultaneous extraction of several anions from soil sample, studies were performed using soft extraction solvents, 0.01 mol l\(^{-1}\) H\(_3\)PO\(_4\), deionised water and 0.01 mol l\(^{-1}\) NaOH, with the conclusion that NaOH was the most efficient system for fluoride, bromide and sulphate extraction, while chloride extraction gave varying results depending on the soil type.

In addition to the comparison of the efficiency of different extraction solvents, the influence of extraction time on the achieved results was investigated. However, no study has hitherto involved the use of a rotary mixer, microwave digestion system or ultrasonic bath for soil sample preparation with aim of increasing the efficiency of inorganic anions extraction.

Deionised water that was used as a soft extraction solvent has hydrolytic and dissolving effect on salts contained in soil samples. This dissolving effect is present to a greater extent when simple inorganic salts that are highly soluble (nitrates, nitrites, chlorides and sulphates of sodium and magnesium and sodium carbonate), fairly soluble (gypsum) and sparingly soluble (Ca and Mg carbonates and Ca, Fe and Al phosphates), and to a lesser extent with complex salts (aluminosilicates) and organic compounds.

In this study, different extraction techniques were employed to extract the anions from soil using water as the extractant. The efficiencies of the techniques were investigated by ion chromatographic determination of the extracted anions.

**EXPERIMENTAL**

**Chemicals and procedures**

The soil sample was taken from a site covered with natural vegetation that had been exposed to minimal influences of anthropogenic pollution at the location Bubanj Potok near Belgrade, Serbia. The soil sample, weighing 1.0 kg in total, was obtained by combining samples taken from the surface horizon, rich in humus, from 30 different sites, at a depth of 20 cm.
The depth of the total soil profile at this location is 50 cm. The sample was air dried for 72 h. Then, large fractions were removed, crushed in a mortar and sieved through a 1.0 mm pore diameter sieve. The basic pedological analysis included: the potentiometric determination of the pH in H₂O and 1.0 mol l⁻¹ KCl, the humus content after the Turin method, the adsorptive complex of the soil (H, T, S) after Kappen, determination of the soil texture by the pipette method, the hydrolytic acidity after Kappen, the hygroscopic moisture by drying at 105 °C, the moisture loss after heating at 700 °C for 30 min and the soil conductivity by the conductometric method.

Deionised water from a Milli-Q Gradient system (Millipore, USA) was used for the extraction and preparation of all mixtures. The resistivity of the deionised water used was 18.2 MΩ·cm (at 25 °C). The substances used for analysis were of high analytical purity grade. The eluent was prepared by dissolving 3 mmol of Na₂CO₃ (Fluka, Switzerland), previously dried for 2 h at 105 °C) in a litre of deionised and degassed water. The eluent was made on a daily bases and then filtered through a 0.20-µm pore size membrane filter (Phenomenex, USA). A primary multi-anion standard solution, produced by Fluka, Switzerland, (Cat. No. 89886, Lot 1265008) was used for calibration.

The extraction mixtures were prepared in normal flasks, 50 ml volume, by mixing soil sample with deionised water in the ratio 1:10, i.e., 2 g / 20 ml. Two series, four extractions each, were performed using a rotary mixer (rotary mixer assisted extraction, RAE in the further text) in which the mixture was processed for 22 h at 10 rpm at 20 °C.

The second technique involved the use of an ultrasonic bath (ultrasonic assisted extraction, UAE in the further text) with the mixture positioned at the same place in the bath and at same initial water temperature, 17 °C. Two extractions were made for each of the following extraction times: 10, 20, 30, 40 and 50 min.

The third technique involved the use of a microwave digestion system (microwave assisted extraction, MAE in the further text). Five extractions at each of the following temperatures: 50, 100 and 150 °C, were performed. The given temperature was achieved in 15 min for each extraction cycle, while the extraction itself lasted 15 min. Subsequently, the samples were cooled to room temperature.

In addition, two further extractions were performed on soil that had been dried at 700 °C for 30 min using the ultrasonic bath for a duration of 15 min.

A blank extraction was performed for each of the employed extraction techniques.

When the extraction processes were finished, each of the extraction mixtures was first centrifuged, then filtered through a medium wide pore sized filter paper and finally through a 0.20-µm pore-sized membrane syringe filter (Phenomenex, USA). The soil extracts were preserved at 4 °C in a laboratory refrigerator for the further analyses.

**Equipment**

An overhead mixer Reax 20/8 (Carl Roth, Germany) rotary mixer and a Transsonic T 760 DH (Elma, Germany) ultrasonic bath with an ultrasonic frequency of 40 kHz and an effective ultrasound power of 170 W were employed for the extractions. The type of the microwave digestion system consisted of an ETHOS 1, Advanced Microwave Digestion Labstation (Milestone, Sorisole, Italy), equipped with 10 Teflon containers. The capacity of the containers was 75 ml each, and the maximum pressure and temperature that could be achieved were 10 MPa and 300 °C. The extraction mixtures were centrifuged using Sigma 2-5 centrifuge (Sigma, Germany) at 2500 rpm.
The employed ion chromatography system was a Metrohm, type 761 Compact IC (Switzerland) with a conductometric detector. The conductometric detection was realized after suppression of the conductivity of the eluent, for which the packed-bed Metrohm Suppressor Module (MSM) was used. The principle of the conductivity suppression is the exchange of Na\(^+\) from the eluent with H\(^+\) from the suppressor module. The result of this is that low conductive species, H\(_2\)O and CO\(_2\), are formed in the eluent instead of primary present high conductive Na\(^+\). The separation column used was Metrosep A Supp1-250, with carrier material polystyrene–divinylbenzene copolymer (particle size 7 \(\mu\)m, column dimensions 4.6 mm\(\times\)250 mm), and with guard column (Metrosep A Supp 1 Guard). The eluent was 3 mM Na\(_2\)CO\(_3\) at a flow rate of 1.0 mL min\(^{-1}\). The full-scale range was 50 \(\mu\)S and the injected sample volume was 20 \(\mu\)L for each probe.

RESULTS AND DISCUSSION

A sample of soil, type Ranker, taken from a serpentine site in Bubanj Potok, a rural area near Belgrade, was used as the substrate. The measured pH value in KCl (5 g soil:10 ml KCl) was 6.0, and in deionised water, the pH value was (5 g soil:10 ml water) 6.9. The results of other pedological analysis are given in Table I. The basic pedological analyses were performed not only to determine the chemical properties of the soil, but also to investigate the possible presence of factors that could influence the adsorption of inorganic anions by positively charged colloid particles in the solution. The investigated soil was characterized as rich in humus, with weakly acidic reaction. As other studies demonstrated, the chemical properties of soil can have, to some extent, an influence on extraction results, which should also be considered.

### TABLE I. The results of the basic pedological analysis of the soil

<table>
<thead>
<tr>
<th>Soil parameter</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Humus, %</td>
<td>5.15</td>
</tr>
<tr>
<td>Total C, %</td>
<td>2.99</td>
</tr>
<tr>
<td>The sum of base cations, meq 100 g(^{-1})</td>
<td>34.6</td>
</tr>
<tr>
<td>Large sand particles, %</td>
<td>4.87</td>
</tr>
<tr>
<td>Small sand particles, %</td>
<td>30.1</td>
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<tr>
<td>Colloid clay, %</td>
<td>45.8</td>
</tr>
<tr>
<td>Silt, %</td>
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<tr>
<td>Hygroscopic moisture, %</td>
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<tr>
<td>Heating loss, %</td>
<td>14.2</td>
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</table>

The results of the determinations of the amounts of fluorides, chlorides, nitrates, phosphates and sulphates present in the extracts obtained using RAE, UAE and MAE are presented in Tables II–IV, respectively.

After accuracy evaluation of the obtained results, it was concluded that the employed analytic method presented an relative standard deviation RSD for fluorides of 4.85 %, for chlorides 1.19 %, for nitrates 2.13 %, for phosphates 1.24 % and for sulphates 1.00 %.
The extraction of fluorides by means of the rotary mixer gave the results presented in Table II, which were, on average, similar to the results of extraction realized using the ultrasonic bath with an extraction time of 10 min. As shown in Table I, prolongation of the UAE time was not in positive correlation with the amount of extracted fluoride. By using MAE (Table IV, Fig. 1), a significant increase in the amount of extracted anions occurred at a temperature of 150 °C, even up to 4.5 times more than the amount extracted at the lower temperatures.

The UAE of chlorides demonstrated (Table III) that prolongation of the extraction time led initially to an increased amount of extracted ions, first by 10 % and finally to an insignificant 1.7 % when the extraction was extended from 40 to...
50 min. Compared to the UAE, the RAE (Table II) was more efficient for the extraction of chloride ions.

TABLE IV. The results of determinations of anions after MAE (mg 100 g⁻¹ soil)

<table>
<thead>
<tr>
<th>Extraction temperature, °C</th>
<th>No. of extraction</th>
<th>Fluorides</th>
<th>Chlorides</th>
<th>Nitrates</th>
<th>Phosphates</th>
<th>Sulphates</th>
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<td>50</td>
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<td>2.10</td>
<td>12.7</td>
<td>0.43</td>
<td>1.38</td>
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<td></td>
<td>2</td>
<td>0.18</td>
<td>1.71</td>
<td>34.4</td>
<td>0.45</td>
<td>2.69</td>
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<td></td>
<td>3</td>
<td>0.18</td>
<td>2.65</td>
<td>13.0</td>
<td>0.38</td>
<td>5.14</td>
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<tr>
<td></td>
<td>4</td>
<td>0.18</td>
<td>2.43</td>
<td>18.6</td>
<td>0.41</td>
<td>3.65</td>
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<tr>
<td></td>
<td>5</td>
<td>0.18</td>
<td>1.87</td>
<td>21.6</td>
<td>0.43</td>
<td>2.45</td>
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<tr>
<td>Mean</td>
<td></td>
<td>0.18±0.03</td>
<td>2.15±0.17</td>
<td>20.1±0.4</td>
<td>0.42±0.21</td>
<td>3.05±0.06</td>
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<tr>
<td>100</td>
<td>1</td>
<td>0.18</td>
<td>8.25</td>
<td>69.1</td>
<td>0.49</td>
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<td></td>
<td>2</td>
<td>0.13</td>
<td>5.81</td>
<td>320</td>
<td>0.71</td>
<td>7.66</td>
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<td></td>
<td>3</td>
<td>0.14</td>
<td>9.47</td>
<td>272</td>
<td>1.46</td>
<td>8.16</td>
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<tr>
<td></td>
<td>4</td>
<td>0.14</td>
<td>8.52</td>
<td>212</td>
<td>0.97</td>
<td>5.36</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.16</td>
<td>7.16</td>
<td>229</td>
<td>0.81</td>
<td>7.82</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>0.15±0.02</td>
<td>7.84±0.15</td>
<td>221±4</td>
<td>0.89±0.44</td>
<td>6.59±0.13</td>
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<td>150</td>
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<td>0.71</td>
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<td>415</td>
<td>1.69</td>
<td>18.5</td>
</tr>
<tr>
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<td>45.7</td>
<td>606</td>
<td>1.97</td>
<td>15.3</td>
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<tr>
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<td>32.7</td>
<td>523</td>
<td>2.03</td>
<td>13.9</td>
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<tr>
<td></td>
<td>4</td>
<td>0.73</td>
<td>35.7</td>
<td>483</td>
<td>1.83</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.79</td>
<td>41.6</td>
<td>546</td>
<td>1.97</td>
<td>15.2</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>0.76±0.13</td>
<td>38.6±1.5</td>
<td>515±10</td>
<td>1.90±0.95</td>
<td>15.9±0.3</td>
</tr>
</tbody>
</table>

Fig. 1. A comparison of the chromatograms of the soil extracts provided by each of the three extraction techniques.

The average value from the two RAEs was higher than the value obtained by UAE after the longest extraction time, 50 min, which gave the highest extracted
amount. The concentration of extracted chloride ions by MAE at 100 °C was about two times higher than the highest concentrations obtained by the other two techniques. On increasing the temperature to 150 °C, the obtained concentration was about 12 times higher than the highest concentrations resulting from the use of RAE and UAE.

The UAE of nitrates (Table III) showed the extracted amount of these anions did not vary with changing extraction time. The obtained amount was less than the one obtained by RAE (Table II). Given the fact that nitrates are highly soluble, their concentration determined in the soil solution obtained by centrifugation was almost equal to the amount obtained by extraction with water. The amounts of nitrates obtained by MAE were 10 times higher at a temperature of 50 °C, and even up to 100 times higher at 100 °C, than the amounts obtained using the other two techniques. MAE at a temperature at 150 °C gave concentrations of nitrate ions that were beyond the given measurement range for all probes obtained. After dilution of the extracts, the IC results showed that the extracted amount of nitrate ions obtained at 150 °C was 2.4 times higher than that obtained by extraction at 100 °C (Table IV, Fig. 1).

The UAE of sulphate ions (Table III) gave results demonstrating that the extracted ion amount did not depend on the extraction time. At the same time, the amount of sulphate ions extracted by RAE was almost equal to the average amount of sulphate ions extracted by UAE with extraction times of 10, 20, 30, 40 and 50 min. The MAE results demonstrated (Table IV) also in the case of sulphate ions that significantly increased amounts of extracted ions occurred with increasing extraction temperature. Although there were some variations in the results of each of extractions as the extraction temperature was changed, the average amount of the extracted sulphates at 150 °C was 7 times higher than the highest amount of sulphates extracted by the other two extraction techniques (Fig. 2).

The UAE of phosphates demonstrated that with prolongation of the extraction time to 20 or more minutes, the previously low concentrations of extracted phosphates went beyond the detection threshold. The average concentration of the extracted phosphates obtained by RAE was higher than the concentration extracted by UAE for 10 min. The use of MAE at a temperature of 150 °C gave an almost five times higher amount of phosphate ions than the average amount obtained by RAE. The extracted amount of phosphate ions was low, since the investigated soil was formed on a substrate (serpentine) with a low level of P2O5. Generally, the average concentration of phosphates in this type of soil ranges from 1–3 mg 100 g⁻¹ of soil.

The results of extracted anions from soil sample using the MAE technique showed (Table IV, Fig. 2) that the extracted amounts were higher with increasing extraction temperature.
Ranker found on serpentine sites is characterized by a low ratio of Ca:Mg of less than one, high concentrations of Ni, Cr and Mn, and a lack of the essential nutrients, such as available nitrogen, potassium and phosphorus, necessary for the growth of agricultural crops. Compared to other soil types, Ranker on serpentine sites has increased concentrations of magnesium that influences the generation of simple inorganic salts which are more soluble, containing a high percentage of crystallized water.

A significant amount of Ni in a soil sample, which gives insoluble Ni$_3$(PO$_4$)$_2$·7H$_2$O, can be one of the limiting factors for the extraction of phosphates. Unlike phosphates, the fluorides, chlorides and sulphates of Ni demonstrate relatively high solubilities in water. In addition to this, an investigation of the colloid fraction of the soil (particles ≤ 0.2 µm) evidenced that a certain amount of positively charged colloid particles was present in the soil. These particles have the ability to adsorb anions. The adsorption of anions in soil, that can have negative influence on their extraction, is also influenced by the properties of anions (in accordance with their increasing ability to be adsorbed Cl$^-$ = NO$_3$$^-$ < SO$_4^{2-}$ < PO$_4^{3-}$ < OH$^-$), the presence of sesquioxides to a greater extent and the acidic reaction of the soil.

The extraction of anions from a soil sample previously heated at 700 °C for 30 min was realized by means of the ultrasonic bath, with an extraction time of 15 min (Fig. 3). The results showed that the extracted amount of nitrate was 5 times less than the amount extracted under the same conditions from a soil sample that had not been heated. The reason for this can be the conversion of nitrates.
of heavy and alkaline earth metals, by heating, into metal oxide, nitrogen dioxide and oxygen. The chromatograms of heated soil samples showed a significant increase of sulphates peak due to sulphur conversion during the combustion of organic matter into sulphate, but also to the possibility that dissolution of sulphate salts occurred.

![Chromatogram of heated soil sample](image)

**Fig. 3.** The chromatogram of the extract of the previously heated soil. Anions concentrations (mg 100 g⁻¹ soil; peak number): F⁻ (0.33; peak 1), Cl⁻ (3.13; peak 2), NO₃⁻ (0.31; peak 3), PO₄³⁻ (4.58; peak 4) and SO₄²⁻ (77.0; peak 5).

**CONCLUSIONS**

The conclusions that can be drawn from the obtained results are that the extraction technique involving the use of an ultrasonic bath was less reliable and less efficient for the simultaneous extraction of inorganic anions from soil than the extraction technique that uses a rotary mixer. In addition, the results of the ultrasonic bath assisted extractions showed that prolongation of the extraction time did not influence the amount of extracted anions, except in case of chloride ions. On the other hand, the ultrasonic assisted extraction is less time consuming and minimizes the expenditure of extraction solvent.

Unlike these two extraction techniques, the microwave-assisted extraction of inorganic anions for later chromatographic determination was efficient, reliable and less time consuming. The amount of anions obtained by microwave-assisted extraction correlated with the increasing extraction temperature and was significantly higher compared to the amounts obtained by conventional techniques for soil sample preparation.

The techniques employed in this study for the preparation of soil samples for analysis can also be applied to other types of soil, and are significant for esti-
mating the concentration of inorganic anions in soil, originating from highly soluble salts. In addition, the results of such preparations of soil samples for ion chromatographic analysis give a certain insight into the concentration of anions in the soil solution, i.e., in the soil liquid phase.

Applying these new techniques of for the extraction of anions from soil samples combined with different extraction solvents, e.g., soft extractants, concentrated acid, base or salt solutions, can be considered and requires further investigation. The aim was to improve the extraction procedures and soil analyses, which is important for many scientific and practical reasons.

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