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**JOSIP JURKOVIĆ\*<sup>1</sup>, KEMAL KOVO<sup>1</sup>, LAMIJA DURIĆ<sup>1</sup>,  
MAJDA BOTONJIĆ<sup>1</sup>, JASMINA SULEJMANOVIĆ<sup>2</sup>,  
TEMIMA AJANOVIĆ<sup>2</sup>, MIRZA NUHANOVIĆ<sup>2</sup>, EMINA SIJAHOVIĆ<sup>1</sup>**

## **USE OF GREEN SOLVENTS IN SHAKING AND ULTRASOUND ASSISTED EXTRACTION OF MOBILE AND MOBILIZABLE FRACTIONS OF POTASSIUM FROM SOIL**

### **SUMMARY**

Extraction of potassium from agricultural soil often involves strong acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, HF), whose decomposition results in formation of toxic gases. Green solvents are environmentally friendly and are used in place of conventional solvents that are hazardous to both human and the environment. Also, potassium in agricultural soils is often incorporated in minerals that are highly insoluble, and thus highly unavailable to plants. Usage of strong acids may result in much higher concentrations of potassium, and a wrong insight into potassium bioavailability. This erroneous result for the potassium content could lead to improper usage of fertilizers. The most important fractions of potassium for plant growth are mobile and easily mobilizable fractions. Those fractions are extracted with water and weak acids. Technique for sample preparation that is often used is shaking and ultrasound assisted extraction. In this research, two green extraction solutions with two different extraction mechanisms and two different soil types were used. All results were compared to pseudo-total amounts of metals. pH, EC, moisture content and Al - solution extracted potassium (available to plants), as basic quality parameters were measured. Potassium content was measured by means of flame atomic emission spectroscopy (FAES). Mobile and easily mobilizable fractions correlate to a high extent ( $r < 0.800$ ), but they are negatively correlated to pseudo-total amounts. Pseudo-total amount gives a wrong insight into the content of potassium available to plants. The ultrasound method could be used in case of soils that are low in a clay content.

**Keywords:** mobile, potassium, pseudo-total, shaking, ultrasound

<sup>1</sup> Josip Jurković\* (corresponding author: j.jurkovic@ppf.unsa.ba), Kemal Kovo, Lamija Durić, Majda Botonjić, Emina Sijahović, Applied Chemistry, Faculty of Agriculture and Food Sciences, Sarajevo, Zmaja od Bosne 8, BOSNIA AND HERZEGOVINA;

<sup>2</sup> Jasmina Sulejmanović, Temima Ajanović, Mirza Nuhanović, Chemistry, Faculty of Science, Sarajevo, Zmaja od Bosne 33-35, BOSNIA AND HERZEGOVINA.

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## INTRODUCTION

Solvents are often used in chemical industry and chemical analysis. The chemical industry of today uses solvents in large quantities. Therefore, solvents define a major part of the environmental performance of a process and have impact on cost, safety and health issues. The extraction of metals from soil samples is a step without which it is impossible to measure metals by most analytical methods. Strong acids are mainly used for extraction of metals from soil. Hydrochloric, hydrofluoric, nitric, and sulfuric, are some of the strong acids. These acids and their products ( $\text{Cl}_2$ ,  $\text{F}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ) are very corrosive and toxic for people, animals and plants. Mixtures of strong acids (*aqua regia*) are frequently used. The idea of “green” solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production (Capello *et al.*, 2007). The use of green solvents in chemical industry could lead to a healthier future. Healthier future involves reduced use of strong acids as reagents and solvents. Soils are dynamic systems in which a very delicate equilibrium exists between the pseudo-total content (inactive and inert), the mobile fraction (effective soluble, very active, bioavailable) and the mobilizable fraction (potentially bioavailable, leachable and partly active). However, between these three fractions there is an equilibrium attained as a result of complex physico-chemical and biochemical processes (Gupta *et al.*, 1996). The mechanisms of metals affecting their solubility can have crucial impacts on ecosystems. Most metals are essential nutrients for normal growth of plants, hence their practical relevance for productivity of agricultural and forest ecosystems. High concentrations of some metals may give rise to ecotoxicological concerns (McBride, 1994).

Potassium is a macro element (the average value of total potassium in agricultural soils ranges from 10-20 g/kg), and is highly important for plant growth. Average soil potassium content is relatively large, but it is mostly unavailable for plant intake. This is why it is important to introduce soluble potassium salts as fertilizers. Current soil analysis methods for K are insufficient for some common soils posing the risk of imbalanced fertilization (Zörb *et al.*, 2014). Adequate content measurement is thus highly important in order to face the problems of potassium presence in agricultural soil.

*Aqua regia*, which is a mixture of hydrochloric and nitric acid in 1:3 ratio, is used today for the assessment of metal concentration in soil. The *aqua regia* extraction gives the “pseudo-total” (meaning almost total) concentrations of metals. Since *aqua regia* is a strong extraction solution, it gives higher results of potassium content in agricultural soil - the amounts that are not available for plant growth. This may result in false information about potassium content in soils and wrong amounts of fertilizer used. The most important fractions in the nutritive and ecotoxicological terms are mobile and easily mobilizable fractions of metals. Mobile and easily mobilizable fractions are those fractions which are more soluble than others. Distilled water is often used to extract mobile fraction of metals. Easily mobilizable fraction, also known as acid-extractable one, is gained

by hydrochloric acid extraction method. Water is a green solvent, but hydrochloric acid is not. This is why acetic acid as a green solvent (Byrne *et al.*, 2016), will be used. Acetic acid is used as solvent of extraction of mobile fraction of macronutrients (Neugschwandtner *et al.*, 2022). The shaking procedure is very often used for extraction of metals from soil with water, weak acids or complexing agents (DTPA, EDTA) (Néel *et al.*, 2006; Soumaré *et al.*, 2007). Instead of shaking, it is also possible to extract metals by use of ultrasounds, which is a green method (Yebra, 2012) (Câmara *et al.*, 2022). Extraction of metals with acetic acid and ultrasounds was addressed in earlier research (Krasnodębska-Ostreęga and Kowalska, 2003). Due to the fact that *aqua regia* is not green method and gives much higher amounts of potassium, the aim of this study was developed: to determine the possibilities of green solvents and green preparation techniques to extract readily mobile and easily mobilizable amounts of potassium.

## MATERIAL AND METHODS

### Samples and sampling

The sampling was conducted with the aid of a plastic shovel, until the depth of 20 cm was reached. Once taken, the samples were transferred in plastic bags, labelled, and transferred to the laboratory. Ten soil samples from Butmir an agricultural soil area of the Faculty of Agriculture and Food Science in Sarajevo (label B) and ten samples from a family-owned agricultural soil in Visoko (label V) were used in this research. In total, twenty samples were investigated in two repetitions. The soil samples from Butmir are taken from a sandy loam type of soil. Sandy loam soils are characterized by portions of sand, clay and slit. The soil samples from Visoko are of a clay loam type, which is characterized by a large portion of clays (Arnold, 2004).

The samples were air dried for few days in the laboratory, homogenized with mortar and pastille, and sieved through a 2-mm sieve.

### Methods

#### *Methods for determination of basic quality parameters*

##### *pH value*

In soil samples used in this research, the pH value was measured using a potentiometric method, on a Mettler Toledo MP 220. The instrument was calibrated with buffers having pH values of 4.21 and 7.00. The soil extraction solution ratio was 1:5 (10 g soil:50 mL extraction solution), prepared as described in literature (ISO 10390, 1994). The measurement was made using two different extraction solutions: ultra-pure water and calcium chloride (0.01 mol/L).

##### *Electrical conductivity (EC)*

Electrical conductivity was measured in soil: ultrapure water (1: 5) ratio, on a Mettler Toledo MC 126 instrument. The instrument was calibrated with

standards of a known electrical conductivity (12.88 mS/cm and 1413  $\mu$ S/cm), applying the EPA 9050 method procedure.

#### *Moisture content*

Determination of moisture content was conducted in a heating oven, Memmert UN 30. 4-6  $\pm$ 0.0001 g soil was heated on 105 °C, until the constant mass was reached.

#### *Extraction of mobile forms of potassium*

Extraction of mobile forms of potassium was done with Egner-Riehm-Domingo method. The AL-method is based on the extraction of potassium from the soil with a buffer solution of ammonium lactate with a pH of 3.75.

After extraction of mobile forms of potassium with Al-solution, the content was determined by means of flame photometer (Systonic, S 935).

#### *Extraction procedures for metal analysis*

Three different metal extraction procedures were used for the purpose of this research:

- extraction with deionized H<sub>2</sub>O
- extraction in 4% CH<sub>3</sub>COOH
- extraction in *aqua regia* (HCl + HNO<sub>3</sub>) in 3:1 ratio – reference method.

Metal extractions in deionized water and acetic acid were carried out by using the shaking and ultrasounds (550 W) procedures. The *aqua regia* (reference method) was carried out in accordance with the ISO method (BS ISO 11646, 2006).

#### *Extraction with deionized water*

Water extraction was prepared as described in the literature (Séguin *et al.*, 2004). 10  $\pm$ 0.0001 g soil was placed into a polyethylene bottle with a cap and an under cap. 50 mL deionized water (1:5 ratio) was added on the soil. Two different extraction procedures were done: shaking (two hours of shaking on 180 rpm) and ultrasounds (two hours under ultrasounds). After the two-hour long 180 rpm shaking, or ultrasounds, the solution was decanted and placed in a centrifuge at 4500 rpm for 10 minutes. After centrifugation, the solution was filtered through a slow filtering paper (pore size: 2.5  $\mu$ m). The filtrate was conserved with 0.5 mL concentrated HNO<sub>3</sub>. The solution volume was brought up with deionized water, in a 100 mL volumetric flask. A 10 mL aliquot was transferred into a 50 mL volumetric flask, and 5 mL CsCl was added to make concentration of 2000 mg/L. Deionized water was conserved with 0.5 mL concentrated nitric acid in a 50 mL volumetric flask, which was used as a blank solution. After that, 5 mL acidified deionized water was placed in a 50 mL volumetric flask, into which 5 mL CsCl<sup>2</sup> solution was pipetted.

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<sup>2</sup> CsCl was added to reduce ionization interferences in acetilene/air flame.

### *Extraction with CH<sub>3</sub>COOH (4%)*

10 ± 0.0001 g soil was placed into a polyethylene bottle with a cap and an under cap. 50 mL of 4% acetic acid was added on the soil (1:5 ratio). After a two-hour long shaking at 180 rpm, or ultrasounds, the solution volume was brought up with deionized water, until 100 mL was reached. A 10 mL aliquot was transferred into a 50 mL volumetric flask, and 5 mL CsCl was added to make concentration of 2000 mg/L. A blank solution was made by transferring 50 mL of 4% CH<sub>3</sub>COOH into a volumetric flask. After that, 5 mL acid was transferred into a volumetric flask into which 5 mL CsCl solution was pipetted. The method was modified as described in literature (Cappuyns, 2012).

### *Extraction with aqua regia*

The extraction with *aqua regia* (ISO 11464) was used in this research as a comparison (reference) method. 3 ± 0.0001 g soil was transferred in a round-bottom bottle. This was followed by adding 7 mL concentrated nitric and 21 mL concentrated hydrochloric acid. The solution was mixed and left to rest for 16 h in a digester hood. After 10 hours the solution was placed onto a heating plate under reflux, and heated at 108 °C for two hours. Solution was filtered through a slow filtering paper and brought up to a volume to 50 mL with 0.5 % nitric acid. 1 mL solution was transferred into a volumetric flask, and CsCl solution was added to make concentration of 2000 mg/L. A blank solution was prepared in the same manner, just without the sample, by mixing 7 mL nitric and 21 mL hydrochloric acid and leaving to rest for 16 hours. The solution was then heated under reflux for two hours, filtered into a 100 mL volumetric flask and volume was brought up with 5% nitric acid. 1 mL solution was transferred into a volumetric flask, where CsCl solution was added to make a concentration of 2000 mg/L.

### *Determination of potassium content*

Following the extraction procedures for metals analysis, the potassium content was measured with a FAES method, on a Varian Spectra AA240FS spectrophotometer. The measurement was carried out at 766.5 nm wavelength. The “external standards” calibration method of known potassium concentrations was used. The standards concentrations were from 0.0 to 2.0 mg/kg. The calibration curve equation was  $y = 0.357x + 0.049$  ( $R^2 = 0.9983$ ).

### *Statistical evaluation*

Statistical evaluation of the results was conducted by means of average value, standard deviation, t-test and correlation coefficients. Correlation coefficients indicating the strength of correlation between the two variables are: 0.0– 0.19 very weak correlation, 0.2 – 0.39 weak correlation, 0.40 – 0.59 moderate correlation, 0.60 – 0.79 strong correlation, 0.80 – 1.0 very strong correlation. Correlation can be uphill (the coefficient of correlation is positive), or

downhill (the coefficient of correlation is negative). The correlations were calculated in MS Office Excel.

## RESULTS AND DISCUSSION

### *Results of the basic quality parameters*

Basic quality parameters were measured in order to gain an insight into the basic characteristics of the soil samples.

The results of basic quality parameters: pH value (Water and CaCl<sub>2</sub>), EC, moisture and Al-K<sub>2</sub>O content, are shown in Table 1.

**Table 1.** Basic quality parameters

	pH (H <sub>2</sub> O)	pH (CaCl <sub>2</sub> )	EC μS/ cm	Moisture (%)	K <sub>2</sub> O mg/ 100g		pH (H <sub>2</sub> O)	pH (CaCl <sub>2</sub> )	EC μS/cm	Moisture (%)	K <sub>2</sub> O mg/ 100g
B <sub>1</sub>	6.02	5.08	231	11.34	25.2	V <sub>1</sub>	6.71	6.10	1068	11.95	53.3
B <sub>2</sub>	6.10	5.11	263	16.28	28.0	V <sub>2</sub>	6.46	6.60	626	12.67	53.1
B <sub>3</sub>	6.13	5.34	270	17.47	17.6	V <sub>3</sub>	6.75	6.09	598	12.98	39.2
B <sub>4</sub>	7.61	6.86	492	15.03	23.1	V <sub>4</sub>	5.89	4.90	187	10.17	10.6
B <sub>5</sub>	6.29	5.30	300	17.22	25.8	V <sub>5</sub>	5.85	4.96	289	10.24	31.1
B <sub>6</sub>	6.85	6.14	617	14.24	73.3	V <sub>6</sub>	6.99	6.25	600	14.17	61.6
B <sub>7</sub>	6.06	6.03	452	15.83	34.6	V <sub>7</sub>	6.95	6.21	466	11.65	49.2
B <sub>8</sub>	6.60	6.02	362	17.91	34.5	V <sub>8</sub>	6.60	5.94	501	12.98	25.8
B <sub>9</sub>	7.00	6.25	333	17.63	31.4	V <sub>9</sub>	6.96	6.23	658	13.11	46.8
B <sub>10</sub>	6.51	5.63	323	10.40	25.0	V <sub>10</sub>	6.97	6.11	685	14.13	35.0
SD	0.51	0.57	120.9	0.47	15.3	SD	0.43	0.56	239.2	1.09	15.4
Aw.	6.53	5.78	364.3	10.87	40.5	Aw.	6.61	5.94	567.8	13.04	31.8

All results of pH measurement indicate a slight acidity of the medium. The maximum value of pH was found in B<sub>9</sub> sample and the minimum in V<sub>5</sub> sample. The average value of pH measurement for B samples was 6.53 and for V samples 6.61. These pH values define soils under the investigation as neutral soils (Sirsat *et al.*, 2017). The pH measurement in calcium chloride is, in each case, lower than pH in water. This result is expected, because calcium removes some of the hydrogen ions from soil matter, thus causing higher amount of H<sup>+</sup> in solution and lower pH (Minasny *et al.*, 2017).

The average value of electrical conductivity was higher in V labelled samples (567.8 μS/cm). The average value for electrical conductivity in B samples was 364.3 μS/cm. The maximum value was found in sample V<sub>1</sub>, and minimum in sample V<sub>4</sub>. Since electrical conductivity is the measure of the concentration of ions that are extractable by water, it could be concluded that V samples (clay loam) contain more ions, which is expected, since clays have a highly active surface attracting ions from solution (Yuehmin *et al.*, 2016). Moisture content was quite uniform. The higher average value of water content was found in V samples (13.06 %). The Al-solution extraction of potassium resulted in higher concentration in V samples, than in B samples.

The correlations between basic quality parameters are shown in Table 2.

**Table 2.** Correlations between the measured values

	pH	pH (CaCl <sub>2</sub> )	EC	Moisture	K <sub>2</sub> O
pH	1				
pH (CaCl <sub>2</sub> )	0.856	1			
EC	0.649	0.648	1		
Moisture	0.171	0.196	-0.135	1	
K <sub>2</sub> O	0.423	0.550	0.690	-0.062	1

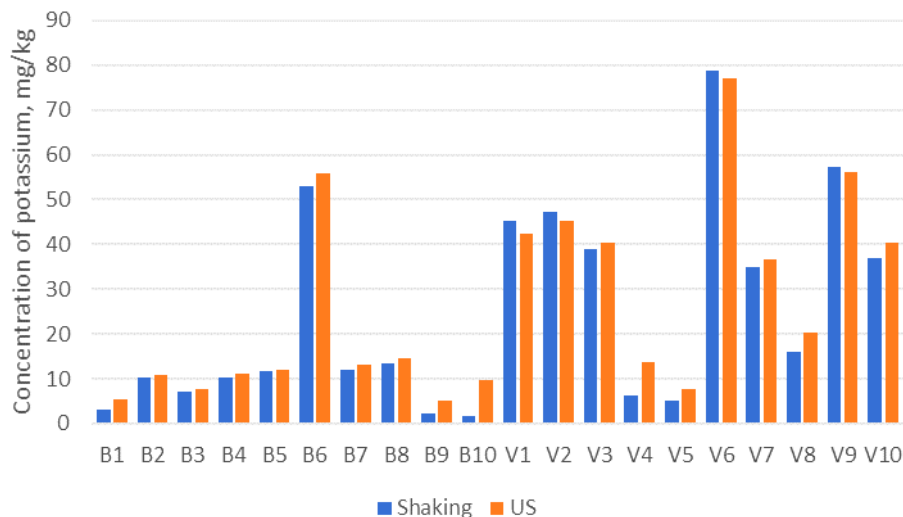
The expected very strong correlation was observed between the results of pH in water and pH in calcium chloride. Those two parameters are very similar because they represent the amount of H<sup>+</sup> ion. The moderate correlation between pH and EC is the result of the fact that a higher EC is derived from a higher ions content. The less acidic pH value is derived from the OH<sup>-</sup> ion presence in soil, which could give higher EC.

Potassium amounts available to plants (K<sub>2</sub>O) showed strong correlation with EC. pH value showed moderate correlation with K<sub>2</sub>O value. (Kassa, 2021) had similar finding. Available potassium, same as the H<sup>+</sup> ion contributes to electrical conductivity.

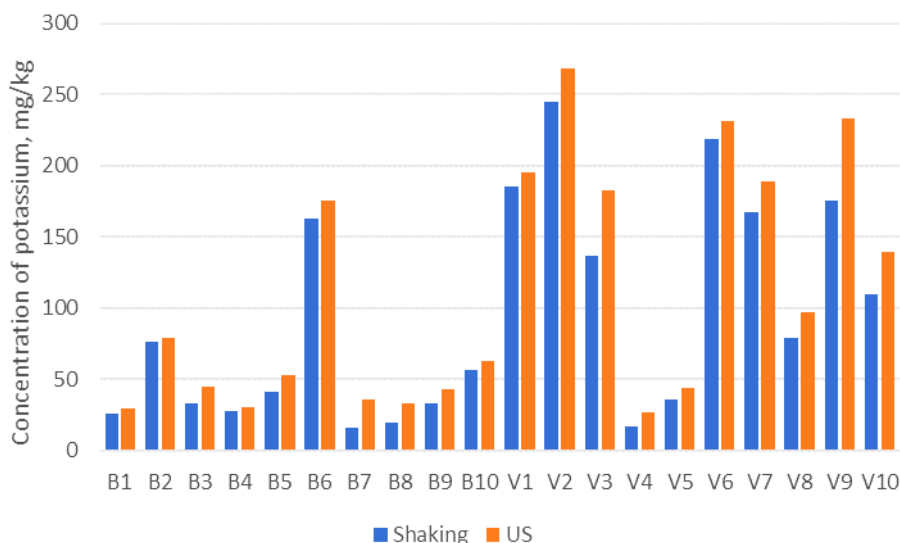
### *Extraction of potassium by means of different solvents and different intensification techniques*

The results obtained for the extraction of potassium from soil samples using demineralized water and acetic acid and shaking or ultrasounds as intensification technique are presented in Figures 1-3.

Water, as extractant, was used for the extraction of mobile fractions of potassium. The extractions were conducted by applying the ultrasounds or the shaking technique.

**Figure 1.** Shaking and US extraction with water

The extraction with water resulted with lowest amount of potassium. The average concentration of potassium using the ultrasounds field extraction was 26.29 mg/kg, and 24.59 mg/kg using the shaking method. The application of ultrasounds resulted in slightly higher average concentration. The higher concentrations of mobile amounts of potassium were found in samples from Visoko, where the average value was 36.69 mg/kg. The V samples showed the higher amount of bioavailable potassium content (AL-K<sub>2</sub>O). The average value of mobile fraction of potassium in B samples was 12.49 mg/kg. The higher concentration of potassium in V samples was expected due to the higher electrical conductivity of these samples. Recent research (Lu, 2021) resulted in similar potassium content. Diluted acetic acid was the second extraction solution used for measuring the mobilizable fractions of potassium. Potassium concentrations gained with acetic acid extraction with two different extraction techniques, shaking and ultrasounds are presented in Figure 2.



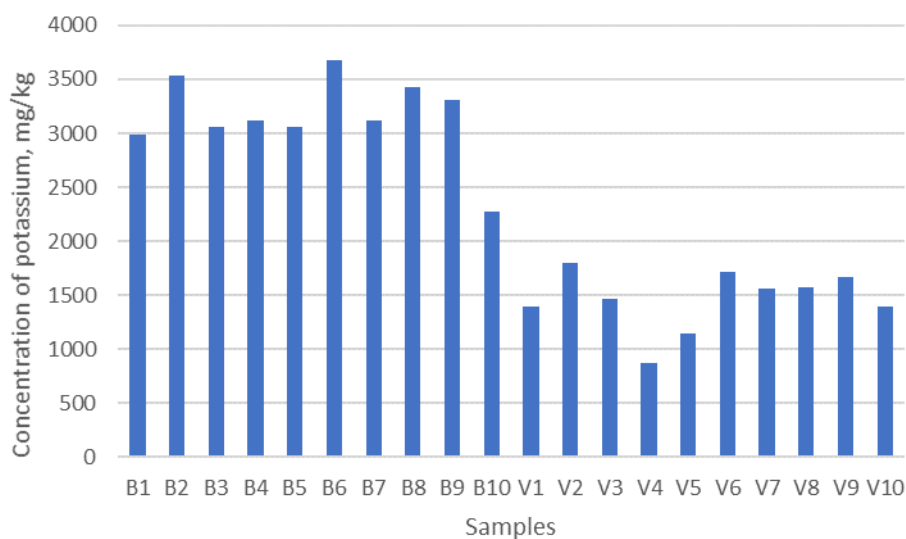
**Figure 2.** Shaking and US extraction with acetic acid

The ultrasounds field extraction with acetic acid resulted in the average value of 109.65 mg/kg, while the shaking technique recorded the average value of 93.01 mg/kg. Some recent studies show similar results (Linguist *et al.*, 2022). The average value in case of acetic acid shaking-assisted extraction for B samples was 49.04 mg/kg, and 58.71 mg/kg in case of ultrasounds-assisted extraction. V samples analysis resulted in 136.99 mg/kg of potassium with shaking, and 160.59 mg/kg with ultrasounds. The results gained with acetic acid were higher than in case of water. The reason lies in the fact that acetic acid is more aggressive than water. The higher amount of potassium recorded with the use of the ultrasound's technique is probably due to the fact that ultrasounds produce more energy than shaking. Ultrasound-assisted extraction of metals is based on the cavitation



phenomenon. The cavitation process comprehends formation, expansion, and collapse of microbubbles. Ultrasounds waves pass through the medium, inducing cycles of expansion and compression in the particles resulting in microbubbles that, upon reaching a critical size, collapse violently and release large amounts of energy (Rutkowska *et al.*, 2017).

Determining the amount of pseudo-total potassium content was conducted with *aqua regia* extraction. The results of potassium content extracted with *aqua regia* are shown in Figure 3.



**Figure 3.** Extraction with *aqua regia*

The potassium concentrations were quite uneven because of the fact that samples under the investigation were very heterogenous. The results of water and acetic acid extractions were compared with the results obtained by the *aqua regia* extraction. Amounts of potassium extracted with *aqua regia* were much higher than those extracted with water or acetic acid. The average value for B samples was 3.16 g/kg, while the average amounts for V samples were 1.46 g/kg. Although the electrical conductivity was higher in the V samples, the *aqua regia* extraction showed much smaller amounts of potassium (two times smaller). This means that there are other ions, e.g., calcium, magnesium, hydrogen etc., present in the “V” samples contributing to electrical conductivity. If the results of metal extraction from B labelled soils were compared to each other, it is possible to extract only 0.62% of potassium with distilled water, and only 3.4 % with acetic acid. In the case of V labelled samples, it is possible to extract only 5.1 % of potassium with distilled water, and only 10.21 % with acetic acid. The samples from Visoko showed higher amounts of mobile and easily mobilizable potassium. Very large difference between pseudo-total and mobile or easily mobilizable fractions of metals was observed. Potassium is mostly present in

forms that are not available to plants. It is believed that it is structurally incorporated in very stable minerals, e.g., silicates. Silicate minerals that contain potassium in soils are mainly muscovite, biotite and feldspars. K-feldspars can directly release potassium into soil, but K in micas is tightly bonded (Singh and Goulding, 1997). Extraction of potassium from soil with ISO method could lead to an inadequate insight into the potassium presence in the soil.

The results obtained by three different extraction methods were also subjected to correlation calculation. Correlations between the extraction methods are shown Table 3.

**Table 3.** Correlations between the extraction methods (shaking and ISO)

	Water	Acetic acid	ISO
Water	1		
Acetic acid	0.904	1	
ISO	-0.515	-0.605	1

A very strong correlation between water and acetic acid extraction was found. It means that mobile and mobilizable amounts of potassium have very similar solubility characteristics. They differ slightly only in amount. Another thing that can be noted is that there is a moderate correlation between ISO method and water/acetic acid extraction – a negative one. The negative correlation actually proves that potassium is mainly present in highly insoluble compounds in soil. On the one hand, similarity between results obtained with shaking and ultrasounds as intensification techniques, could be seen in their high correlation ( $r = 0.998$ ). On the other hand, the t-test (paired, uneven variance) showed that shaking and ultrasound field were statistically significantly different ( $t\text{-test} = -3,487$ ;  $p = 0.001$ ).

When extractions with shaking and ultrasounds from Butmir and Visoko are separately compared, the results from Butmir do not show significant difference between methods ( $t\text{-test} = -0.468$ ;  $p=0.645$ ), but samples from Visoko do ( $t\text{-test}= -5.230$ ;  $p=0.000$ ). The samples from Butmir are characterized as sandy loam. Samples from Visoko are clay loam. From the results of the t- test, we can conclude that sandy loam is more suitable for extraction with ultrasounds, than clay loam. This can be explained by the fact that clays are mostly aluminum – potassium silicates, which contain large amounts of potassium, which could be partially released by ultrasound. Ultrasounds are high in energy. Because of that, ultrasounds field extraction gives a larger amount of potassium. Average difference in potassium content when shaking and ultrasounds are compared in case of Butmir samples is 1.6 mg/kg, Samples from Visoko resulted in 16.06 mg/kg difference (ten times higher - clay loam).

## CONCLUSIONS

It is possible to extract mobile and easily mobilizable fractions of potassium from soil with the use of green solvents and with application of shaking or ultrasounds. There is a very large difference in the amounts of mobile

and easily mobilizable fractions of potassium when compared to the pseudo-total amounts. The aqua regia extraction could lead to an inadequate insight into the potassium status in soil.

## REFERENCES

- Arnold, R.W. (2004). Classification of Soils. *Encyclopedia of Soils in the Environment* Elsevier, Amsterdam, 204–210. DOI: 10.1016/B0-12-348530-4/00003-5.
- BSI (2006) BS ISO 11464: - Soil Quality. Pretreatment of Samples for Physicochemical Analysis. Available at: <https://www.iso.org/standard/37718.html> (accessed 27 April 2021).
- Byrne, F.P., Jin, S., Paggiola, G., Petchey, H.M.T., Clark, H.J., Farmer, J.T., Andrew, J., Hunt, C., Robert, McElroy & James, Sherwood. (2016). Tools and techniques for solvent selection: green solvent selection guides. *Sustainable Chemical Processes*, 4 (7), 1–24. DOI: 10.1186/S40508-016-0051-Z.
- Câmara, J.S., Perestrelo, R., Berenguer, C.V., Andrade, C.F.P., Gomes, T.M., Olayanju, B., Kabir, A., M.R. Rocha, C., Teixeira, J.A., Pereira, J.A.M. (2022). Green Extraction Techniques as Advanced Sample Preparation Approaches in Biological, Food, and Environmental Matrices: A Review. *Molecules*, 27 (9), 1-29. <https://doi.org/10.3390/molecules27092953>
- Capello, C., Fischer, U. and Hungerbühler, K. (2007). What is a green solvent? A comprehensive framework for the environmental assessment of solvents, *Green Chemistry* 9, 927–93. DOI: 10.1039/b617536h.
- Cappuyns, V.A. (2012). Critical evaluation of single extractions from the SMT program to determine trace element mobility in sediments, *Applied and Environmental Soil Science*, 1-15, DOI: 10.1155/2012/672914.
- Gupta, S.K., Vollmer, M.K. and Krebs, R. (1996). The importance of mobile, mobilisable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management. *Science of the Total Environment*, 178(1–3), 11–20. DOI: 10.1016/0048-9697(95)04792-1.
- ISO 10390: (1994): Soil Quality - Determination of pH. International standard.
- Kassa, M., Kebede, F., Haile, W. (2021). Forms and Dynamics of Soil Potassium in Acid Soil in the Wolaita Zone of Southern Ethiopia, *Applied and Environmental Soil Science*, 1-10.
- Krasnodębska-Ostręga, B. and Kowalska, J. (2003). Ultrasound-Assisted Acetic Acid Extraction of Metals from Soils, *Chemical Analysis*, 48 (967).
- Linquist, B.A., Campbell, J.C., Southard, R.J. (2022). Assessment of potassium soil balances and availability in high yielding rice systems, *Nutrient Cycling in Agroecosystems*, 122/3, 255-271. DOI: 10.1007/s10705-022-10200-w
- McBride, M.B. (1994). *Environmental Chemistry of Soils*, Oxford University Press, New York, DOI: 10.2134/jeq1995.00472425002400010029x (1994).
- Minasny, B., Mcbratney, A.B., Brough, D.M., Jacquier, D. (2011). Models relating soil pH measurements in water and calcium chloride that incorporate electrolyte concentration, *European Journal of Soil Science*, 62(5), 728–732. DOI: 10.1111/j.1365-2389.2011.01386.x.
- Néel, C., Soubrand-Colin, M., Piquet-Pissaloux, A., Bril, H. (2007). Mobility and bioavailability of Cr, Cu, Ni, Pb and Zn in a basaltic grassland: Comparison of selective extractions with quantitative approaches at different scales. *Applied Geochemistry*, 22(4), 724–735. DOI: 10.1016/j.apgeochem.2006.11.008.

- Neugschwandtner, R.W., Száková, J., Pachtrog, V., Tlustoš, P., Kulhánek, M., Cerný, J., Kaul, H.P., Wagentristl, H., Moitzi, G., Euteneuer, P. (2022). Exchangeable and Plant-Available Macronutrients in a Long-Term Tillage and Crop Rotation Experiment after 15 Years. *Plants*, 11 (565), 1-11. <https://doi.org/10.3390/plants11040565>
- Rutkowska, M., Namieśnik, J. and Konieczka, P. (2017). Ultrasound-Assisted Extraction. *The Application of Green Solvents in Separation Processes*. Elsevier, Amsterdam, 301–324. DOI: 10.1016/B978-0-12-805297-6.00010-3.
- Séguin, V., Gagnon, C. and Courchesne, F. (2004). Changes in water extractable metals, pH and organic carbon concentrations at the soil-root interface of forested soils, *Plant and Soil*, 260, pp. 1–17. DOI: 10.1023/B:PLSO.0000030170.49493.5f (2004).
- Singh, B. and Goulding, K.W.T. (1997): Changes with time in the potassium content and phyllosilicates in the soil of the Broadbalk continuous wheat experiment at Rothamsted, *European Journal of Soil Science*, 48(4), 651–659. DOI: 10.1111/j.1365-2389.1997.tb00565.x
- Sirsat, M.S., Cernadas, E., Fernández-Delgado, M., Khan, R. (2017). Classification of agricultural soil parameters in India, *Computers and Electronics in Agriculture*, 135, 269-279. DOI: 10.1016/j.compag.2017.01.019.
- Soumaré, M., Tack, F.M.G. and Verloo, M.G. (2003). Characterisation of Malian and Belgian solid waste composts with respect to fertility and suitability for land application. *Waste Management*, 23(6), 517–522. DOI: 10.1016/S0956-053X(03)00067-9.
- Yebra, M.C. (2012). A green analytical method using ultrasound in sample preparation for the flow injection determination of iron, manganese, and zinc in soluble solid samples by flame atomic absorption spectrometry. *Journal of Analytical Methods in Chemistry*, 1(1), 1-5. DOI: 10.1155/2012/298217.
- YuehMin, C., JinBo, G., Yoing Quiang, Y., Jun, M., Shen, Y. (2016). Relationship between heavy metal contents and clay mineral properties in surface sediments: Implications for metal pollution assessment, *Continental Shelf Research*, 124, 125–133. DOI: 10.1016/j.csr.2016.06.002.
- Zörb, C., Senbayram, M. and Peiter, E. (2014). Potassium in agriculture - Status and perspectives. *Journal of the Plant Physiology*, 171(9). 656–669. DOI: 10.1016/j.jplph.2013.08.008