Methods for Preparation of Soil Samples for Determination of Trace Elements

S. Krustev, V. Angelova, K. Ivanov, P. Zaprjanova

***Abstract*—**It is generally accepted that only about ten microelements are vitally important to all plants, and approximately ten more elements are proved to be significant for the development of some species. The main methods for their determination in soils are the atomic spectral techniques - AAS and ICP-OAS. Critical stage to obtain correct results for content of heavy metals and nutrients in the soil is the process of mineralization. A comparative study of the most widely spread methods for soil sample preparation for determination of some trace elements was carried out. Three most commonly used methods for sample preparation were used as follows: ISO11466, EPA Method 3051 and BDS ISO 14869-1. Their capabilities were assessed and their bounds of applicability in determining the levels of the most important microelements in agriculture were defined.

***Keywords*—**Comparative study, mineralization methods, trace elements.

I. INTRODUCTION

IT is a generally accepted notion that only about ten trace elements are essential for plant growth, and for that many more it has been proved to play an essential role in the development of some plant species [1]. Cadmium, lead, nickel and chromium do not belong to the group of elements that are absolutely necessary for plants. Indisputably copper and zinc have a dual effect on plant growth [2]. The accurate identification and regulation of their content in the soil and their transition into plants is important not only in terms of ecology. Nickel participates in the regulation of oxidative processes in plants and its deficiency causes chlorosis similar to chlorosis. At the same time it is an element forming a toxic carbonyl compound, which is considered a potential carcinogen [3]. The participation of chromium in the metabolism of plants is also still a debatable question and publications in this field are too divergent [1]. Toxic effects of lead and cadmium on life processes of almost all plants are well known [4].

Most laboratories worldwide are equipped with advanced equipment and the choice of quantification method depends primarily on specific tasks, as the atomic spectral methods - AAS and ICP-OES are most widely used. In the majority of comparative tests, the results are in good accordance [5]. However, the same can not be said about the methods and techniques for sample preparation. It is a generally accepted notion that the mineralization is a critical step in obtaining correct results for the content of heavy metals and nutrients in soil [6]-[8]. In our study we have determined that the main reasons for this are quite different composition and properties of the different soil types, as well as the wide range of connectivity options of the elements in their various factions [9], [10]. The purpose of this study was to assess the capabilities of three of the most common and standardized methods for mineralization of soil samples, by determining their boundaries of applicability in determining the content of some of the major toxic trace elements in soil samples.

II. MATERIALS AND METHODS

In the comparative study of the methods for mineralization of soil samples to determining the total content of trace elements, certified reference material Light Alluvial-deluvial Meadow Soil PS-3, SOOMET № 0003-1999 BG, SOD № 312a98 has been used, which material most closely resembles the soil composition of major grain-producing areas in northeastern Bulgaria.

Three most commonly used methods for sample preparation were used as follows:

1. ISO 11466 [11]: 1 g. air dry soil is weighed with accuracy to 0.001 g. It is moistened with 1 ml. H_2O. A mixture of 21 ml. HCl and 7 ml. HNO_3 is added. The sample stays about 16 hours at room temperature. After that the sample is heated for two hours at 180 to 200°C. The remainder is filtered and quantitatively transferred to measuring flask of 50 ml.
2. EPA Method 3051[12]: 1 g. air dry soil is weighed with accuracy to 0.001 g in PTFE containers. 10 ml. HNO_3 are added. Microwave system (Milestone 1200 MEGA) is used when preparing the samples for analysis.
3. BDS ISO 14869-1[13]: 0.250 g. air dry soil is weighed in a platinum pot and it is heated in an electric oven. For an hour the temperature is gradually increased to 450°C and it is maintained for 3.5 hours, after which the oven is cooled to room temperature. The mixture of 5.0 ml. HF and 1.0 ml. $HClO_4$ are added to the cooled sample and it is heated on a hot-plate about 30-40 minutes until the steams of the $HClO_4$ and SiF_4 disappear. The melting-pot is cooled after which 1.0 ml. nitric acid and 5.0 ml. H_2O are added. The dissolution of the sediment can be helped by careful heating. To determine the heavy metal conten in the samples atomic absorption spectrometer (Spectra AA-220, Varian, Australia) was used.

Table I shows the values of Pb, Cd, Cr, Ni, Cu and Zn in the certified sample. X_{CRM} denotes the certified value, U_{CRM} – the

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uncertainty of the certified value and σ_{CRM} – the standard deviation of the certified value.

TABLE I
THE CONTENT OF TRACE ELEMENTS IN THE CERTIFICATED FORM

Element	X_{CRM} mg/kg	U_{CRM} mg/kg	σ_{CRM} mg/kg
Pb	87.50	11.68	6.74
Cd	0.67	0.10	0.058
Cr	88.15	7.00	4.04
Ni	51.75	4.23	2.44
Cu	53.80	2.30	1.33
Zn	125.56	11.68	6.74

III. RESULTS AND DISCUSSION

The results from the determination of the total content of Cd, Pb, Cr ,Ni, Cu and Zn in the three certified soil samples are presented in Tables II-VII. For evaluation of the correctness of the results, in our research [10], we have used three generally accepted criteria, as follows:

1. $D = X - X_{CRM}$, where X is the measured value in Tables II-VII. When D is in the range of $\pm 2\sigma_{CRM}$, the result is considered to be good; when D is in the range of $\pm 3\sigma_{CRM}$ the result is satisfactory and beyond these limits the result is unsatisfactory.
2. $D\% = D/X_{CRM}.100$ – the difference expressed as a percentage.
3. $Z = X - X_{CRM} /\sigma_{CRM}$. The result is considered to be good when Z <2 , when Z is in the range from 2 till 3 the result is satisfactory, when Z > 3 - unsatisfactory. We have introduced K criterion which shows the extent of extraction of the element in percents. When the measured value X is within the range of the sum $X_{CRM} + U_{CRM}$ we accept that the extent of extraction is 100%.

The presented results show that the degree of extraction depends both on the defined element and the method of sample preparation. The degree of extraction of Cd and Pb is 100%. The use of aqua regia gives good results, but total extraction is observed only in methods involving the use of HF. Most likely this is related to the content of silicate materials in the soil sample. In determining the total content of Cd and Pb, most appropriate is the BS ISO 14869-1 method. The degree of extraction of chromium ranges from 79 to 100%, as incomplete extraction is observed only for independent use of nitric acid. In this case, dominant factor is the method of sample preparation, as the full extraction of the element requires the use of HF. The partial extraction of the element with aqua regia shows that part of it is associated with the silicate matrix of the tested samples. And in determining the content of nickel, dominant factor is also the method of sample preparation, as the results for the three soils are close. Its content ranges from 85.6 to 100%.

TABLE II
EFFICIENCY OF THE MINERALIZATION METHODS IN DETERMINING THE CONTENT OF CD

Method	**X** mg/kg	**U_x** mg/kg	**σ_x** mg/kg	**D**	**D,%**	**Z**	**K**
1.	0.70	0.06	0.02	0.03**	4.47**	0.52**	100
2.	0.70	0.06	0.12	0.03**	4.47**	0.52**	100
3.	0.81	0.07	0.15	0.14*	20.90*	2.41*	100

* - “satisfactory” result; ** - “good” result

TABLE III
EFFICIENCY OF THE MINERALIZATION METHODS IN DETERMINING THE CONTENT OF PB

Method	**X** mg/kg	**U_x** mg/kg	**σ_x** mg/kg	**D**	**D,%**	**Z**	**K**
1.	77.00	7.24	1.39	10.50**	12.00*	1.56**	100
2.	76.00	7.14	1.75	-11.50**	-13.14**	1.71**	100
3.	94.00	8.84	3.56	6.50**	7.43**	0.96**	100

* - “satisfactory” result; ** - “good” result

TABLE IV
EFFICIENCY OF THE MINERALIZATION METHODS IN DETERMINING THE CONTENT OF CR

Method	**X** mg/kg	**U_x** mg/kg	**σ_x** mg/kg	**D**	**D,%**	**Z**	**K**
1.	69.90	6.57	3.66	-18.3	-20.76	4.52	79.3
2.	62.40	5.87	2.98	-25.8	-29.27	6.37	70.8
3.	93.62	8.80	3.10	5.47**	6.21**	1.35**	100

* - “satisfactory” result; ** - “good” result

TABLE V
EFFICIENCY OF THE MINERALIZATION METHODS IN DETERMINING THE CONTENT OF NI

Method	**X** mg/kg	**U_x** mg/kg	**σ_x** mg/kg	**D**	**D,%**	**Z**	**K**
1.	47.70	4.48	0.45	-4.05**	-7.83**	1.66**	100
2.	44.40	4.17	0.10	-7.35	-14.20	3.01	85.8
3.	55.60	5.17	1.32	3.85**	7.44**	1.58**	100

* - “satisfactory” result; ** - “good” result

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TABLE VI
EFFICIENCY OF THE MINERALIZATION METHODS IN DETERMINING THE CONTENT OF CU

Method	**X** mg/kg	**U**$_x$ mg/kg	σ_x mg/kg	**D**	**D,%**	**Z**	**K**
1.	53.40	5.02	5.02	-0.40**	-0.73**	0.30**	100
2.	43.20	3.89	5.89	-10.60	-19.70	7.97	80.3
3.	54.80	5.15	5.15	1.00**	-1.86**	1.40**	100

* - “satisfactory” result; ** - “good” result

TABLE VII
EFFICIENCY OF THE MINERALIZATION METHODS IN DETERMINING THE CONTENT OF ZN

Method	**X** mg/kg	**U**$_x$ mg/kg	σ_x mg/kg	**D**	**D,%**	**Z**	**K**
1.	122.46	9.80	0.59	-3.10**	-2.47**	0.46**	100
2.	107.50	8.60	0.08	-18.06	-14.38	2.68	85.6
3.	121.40	9.71	3.11	-4.16**	-3.31**	0.62**	100

* - “satisfactory” result; ** - “good” result

In this case, however, insufficiently effective is only the independent use of HNO_3 while all acid mixtures lead to its complete extraction. This indicates that in the tested samples the nickel is not associated with the silicate matrix.

In determining the content of nickel, the dominant factor is also the method of sample preparation, as the results for the three methods are close. Its content ranges from 85.6 to 100%. In this case, however, insufficiently effective is only the independent use of HNO_3 while all acid mixtures lead to its complete extraction. This indicates that in the tested samples the nickel is not associated with the silicate matrix. The results of the Cu presented in Table VI are quite different. Complete extraction is achieved with aqua regia and with the participation of fluoride hydrogen acid using method 3. This shows that the inclusion of Cu in the silicate matrix of the soil is insignificant. This is also confirmed by the results presented in Table I. It can be seen that practically the whole quantity of the metal is extracted in the first stage of the process which does not affect the primary and a significant part of the secondary soil minerals. In this the dominating factor is the method of sample preparation.

The results of the Zn have presented in Table VII are similar to those of the Cu. The effectiveness of the nitric acid is again the lowest and the complete extraction is achieved through aqua regia and all the methods using fluoride hydrogen acid. In this case as in the case with Cu the inclusion in the silicate matrix is insignificant which is confirmed by the results presented in Table I. By contrast with the mixture zinc is sensible to the method of sample preparation and the soil type. Its composition varies from 67.5% to 100%. All the results with PS-3 are good and satisfactory while with. Obviously here as well the usage of aqua regia is the most suitable.

IV. CONCLUSIONS

The comparative study of the 3 most widely used methods for mineralization of soil samples for analysis of the content of the main trace elements and toxic metals, shows that:

1. The degree of extraction of the tested elements is different and depends on the mineralization method and the soil composition. In determining the content of elements which are not linked or are weakly linked with the silicate matrix of the soil, the dominant factor is the mineralization method. In lead and cadmium, the composition of the soil samples is also essential. The large amount of siliceous compounds hinder the accurate determination of the total content of these elements.
2. The determination of the total chromium content in all cases requires the use of hydrofluoric acid.
3. The most appropriate method for mineralization of the three compared methods with simultaneous determination of lead, cadmium, chromium and nickel is BS ISO 14869-1 due to the relatively easy implementation and high efficiency.

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REFERENCES

[1] H.J.M. Bowen., *Environmental Chemistry of the Element*, Academic Press, New York,1979,333.

[2] A. Kabata-Pendias, and H. Pendias,” *Trace elements in soil and plants*”. 3nd ed. CRC Press, Boca Raton, FL, USA, 2001

[3] B. J. Alloway, D.C. Ayres, *Chemical Principals of Environmental Pollution*, 1st edition, Springer-Verlag,140-174, 1994.

[4] D.C. Adriano, *Trace Elements in the Terrestrial Environment*, Springer-Verlag, Berlin, Germany, 2001.

[5] A. L. Ward, M. Arciello, L. Carrara, V. Luciano, „Simultaneous determination of major, minor and trace elements ia agricultural and biological samples by inductively coupled argon plasma spectrometry”, *Spectroscopy letters*,13 (11), 803-831, 1980.

[6] Pyle, S., J. Nocerino, S. Deming, J. Palasota and J. Palasota.1996. Comparison of AAS, ICP-AES, PSA and XRF in determining lead and cadmium in soil. *Environ.Sci.Technol*, 30: 204-213

[7] Poykio, S., H. Torvela, P. Peramaki and T. Ronkkomaki. 2000. Comparison of dissolution methods for multi-element analysis of some plant materials used as a bioindicator of sulphur and heavy metal deposition determined by ICP-AES and ICP-MS. Analusis, 28: 850-854

[8] M. Hoenig, H. Baeten, S. Vanhentenrijk, E. Vassileva, Ph. Quevauviller, “Critical discussion on the need for an efficient mineralization procedure for the analysis of plant material by atomic spectrometric methods”, *Analytica Chemica Acta*, 358, 85-94, 1998.

[9] P. Zaprjanova, V. Angelova and K. Ivanov, Correlation between soil characteristics and copper and zinc content in the boveground biomas of Virginia tobacco, *Journal of International Scientific Publications, Ecology and Safety,* Vol.4, Part.2, 180-187, 2010.

[10] P. Zaprjanova, L. Dospatliev, V. Angelova and K. Ivanov, A Comparative Study of the Methods for Preparation of Soil Samples for Analysis, *Bulgarian Journal of Agricultural Science*, 12 (2006), 375-385

[11] ISO 11466. 1995. Soil quality-extraction of trace elements soluble in aqua regia.
[12] EPA Method. 1996. Mikrowave assisted acid digestion of sediments, sludge, soils.
[13] BDS ISO 14869-1.2002. Quality of the soils. Mineralization for the determining the total content of elements.

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