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Application of X-ray and SEM–EDS evaluation of the main digestion methods for determination of macroelements in soil

K. Ivanov[1*], P. Zaprjanova[1], V. Angelova[1], L. Dospatliev[2]

[1]*Department of Chemistry, University of Agriculture, 4000 Plovdiv, Bulgaria*

[2]*Department of Pharmacology, Animal Physiology and Physiological Chemistry,*
Trakia University, Stara Zagora, Bulgaria

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Two commonly used digestion methods - acid digestion and microwave digestion in different variants (ISO 11466; EPA Method 3051; EPA Method 3052; ISO 14869-1; GB, Standing committee of analysis, ISBN 0117519081 and HNO_3 + $HClO_4$ acid mixture), were compared for digestion of three certified soil samples, corresponding to two main soil types in Bulgaria - Light Alluvial-deluvial Meadow Soil and Light Meadow Cinnamon Soil. Three main macroelements (K, Ca and Mg) were analyzed using AAS spectrometer Spektra AA 220, Varian, Australia. To elucidate the problems with elemental recovery X-Ray and SEM–EDS analysis of all residues after digestion were performed. The X-ray investigation showed the formation of $KClO_4$ when $HClO_4$ was used as a part of the acids mixture. The result was confirmed by Energy dispersive X-ray microanalysis. The use of HF at Ca and Mg determination led to the formation of $KClO_4$, CaF_2 and MgF_2.

Keywords: *digestion methods, soil, K, Ca, Mg.*

INTRODUCTION

Potassium, calcium and magnesium are essential macroelements in soil and important nutrients for plants [1]. A significant portion of potassium in the soil is in the minerals which belong to the group of feldspars (orthoclase, sanidine, microcline) and is hardly accessible for plants. The potassium contained in mica is less related and relatively easily accessible. The most important source of potassium for plants are secondary clay minerals such as illite. Calcium and magnesium are present in the crystal lattice of soil minerals in exchangeable form easily assimilated by plants, as well as salts (chlorides, sulfates, nitrates, carbonates and phosphates). They determine to a significant extent some of the important soil characteristics and the related fertility. Calcium improves the overall physical, physico-mechanical and aqueous properties of the soil. In the less fertile podzolic soils, which are characterized by a small amount of calcium and magnesium, the soil reaction is highly acidic. This favours the decomposition of carbonates and the destruction of soil, as well as the blocking of phosphorus in Al- and Fe-phosphates [2]. For these reasons, of essential importance is the determination not only of the mobile and easily absorbed by plants forms of K, Ca and Mg, but their total amounts, defining some of the basic soil characteristics.

The objective of the study is to assess the capabilities of the most common standardized and non-standardized methods of mineralization and to outline their boundaries of applicability in determining the total amount of the main macroelemets in soil.

MATERIALS AND METHODS

Three certified soil samples corresponding to two main soil types in Bulgaria were used in the study: Light Alluvial-deluvial Meadow Soil PS-1, SOOMET № 0001 BG, SOD № 310a98; Light Meadow Cinnamonic Soil PS-2, SOOMET № 0002 BG, SOD №311a98 and Light Alluvial-deluvial Meadow Soil PS-3, SOOMET № 0003 BG, SOD № 312a98. The content of K, Ca and Mg in the certified samples is presented in Table 1.

Table 1. Content of K, Ca and Mg (as oxides, %) in the certified samples. X_{CRM} is the certified value and U_{CRM} - the indefiniteness of the certified value.

Element	**PS – 1**		**PS – 2**		**PS – 3**	
	X_{CRM} %	U_{CRM} %	X_{CRM} %	U_{CRM} %	X_{CRM} %	U_{CRM} %
K_2O	2.26	0.13	2.75	0.12	2.38	0.13
CaO	14.73	0.36	2.88	0.09	7.34	0.18
MgO	3.07	0.15	1.65	0.12	2.28	0.12

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

- ISO 11466 [3]: 1 g air-dried soil + 21 ml HCl and 7 ml HNO_3, heating two hours at 180 – 200 °C.

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[*] To whom all correspondence should be sent.
E-mail: kivanov1@abv.bg

- 1 g air-dried soil + 15 ml HNO_3 and 5 ml $HClO_4$, heating two hours at 180 - 200 °C [4].
- EPA Method 3051 [5]: 1 g air-dried + 10 ml HNO_3, digestion in microwave system Milestone 1200 MEGA.
- EPA Method 3052 [6]: 1 g air-dried soil + 9 ml HNO_3, 3 ml HF, 2 ml HCl and 2 ml H_2O_2, digestion in microwave system Milestone 1200 MEGA.
- ISO 14869-1 [7]: 0.25 g air-dried soil in a platinum melting-pot, dry ashing for 3 hours at 450 °C + 5.0 ml HF and 1 ml $HClO_4$ (after cooling to room temperature). Second heating until the dense steams of the $HClO_4$ and SiF_4 disappear. After cooling to room temperature 1.0 ml nitric acid and 5.0 ml H_2O are added.
- ISBN 01175 19081 [8]: *Part 1*: 3.0 g air-dried soil + 22.5 ml HCl and 7.5 ml HNO_3, heating to boiling for 2 hours, filtration and dilution to 100 ml with 12.5% nitric acid *Part 2*: drying of the remaining undissolved part after the first stage at 105 °C and transferring in a teflon container with a well closing lid + 5 ml HF acid and heating for 30 minutes at 140-150 °C. Finally, after cooling 50 ml saturated solution of boron acid is added.

The XRD patterns were recorded on a Philips PW 1050 diffractometer, equipped with Cu Kα tube and a scintillation detector. SEM images were recorded in a JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with ultrahigh resolution scanning system (ASID-3D)

To determine the elements content in the solution after digestion of the samples atomic absorption spectrometer (Spectra AA-220, Varian, Australia) was used.

RESULTS AND DISCUSSION

The results from the determination of the total content of K, Ca and Mg in the three certified soil samples are presented in Table 2, where R shows the extent of extraction of the element in percents from the certified value ($R = X / X_{CRM}.100$).

Determination of potassium

The unsatisfactory results for the three certified samples in the use of methods 1 to 3 (48.5 - 61.6%) and practically the complete extraction of potassium with the use of methods 4 and 6 make an impression. It is well known that the independent use of HNO_3 leads to a partial extraction of potassium from the soil samples [9]. Its combination with HCl acid (method 1) insignificantly increases the rate of recovery. The results are consistent with the results of Kackstaetter and Heinrichs [10] according to which aqua regia provides a satisfactory extraction of many basic elements, but limited extraction of Al and K.

Unsatisfactory results (<75%) in the study of river sediments and soils are received also by Krause *et al.* [11]. The use of $HClO_4$ (methods 2 and 5) leads to different results depending on the composition of the acid mixture. The result of its combination with HNO_3 (method 2) is unsatisfactory. This is probably due to the incomplete dissolution of aluminosilicate matrix and the formation of a sediment of an insoluble potassium perchlorate. To clarify this problem, we studied the insoluble sediment after decomposition of the samples by methods 2 by X-Ray and SEM-EDS analysis. The results of powder X-ray analysis presented in Fig. 1 indicates the presence of roentgenoamorphous phases (the so called halopeaks) that differ low intensity and great half-width x-ray diffraction peaks of high disperse phases, among which the largest is the percentage of $KClO_4$ (PDF - 70-0488). This result is also confirmed by the SEM-EDS analysis of the same sediment (Fig.2 and Table 3). The results of the integral elemental analysis (Table 3) show that only part of the potassium is linked in $KClO_4$. The rest is obviously included in the insoluble siliceous matrix.

The inclusion of HF in the acidic mixture used in the mineralization is not sufficient for the complete extraction of potassium from the soil samples. This is confirmed by the results obtained by method 5 (HNO_3 + $HClO_4$ + HF). Even though to a lesser degree, in this case the formation of sediment is observed in the mineralization of all samples.

Fig. 3 presents the results of powder X-ray analysis of a soil sample, digested by method 5. The analysis of the roentgenogram shows the presence of almost roentgen-amorphous phases (the so called halopeaks) that differ low intensity and great half-width x-ray diffraction peaks of high disperse phases, among which the largest is the percentage of $KClO_4$ (PDF - 70-0488), MgF_2 (PDF - 38-0882), CaF_2 (PDF - 77-2094). There is a presence and a small amount of SiO_2 (PDF 88-2302), as well as aluminosilicate phase, containing magnesium and iron - probably $Mg_{0.8}Fe_{0.2}Al_2Si_2O_6(OH)_4$ (PDF -83-1944).

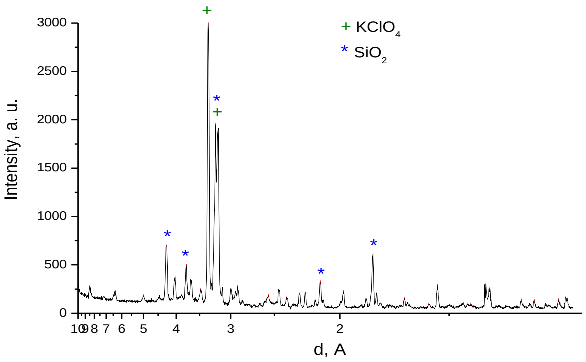

Fig. 1. X-ray pattern of the residue after digestion of the certified sample by mixture of HNO_3 and $HClO_4$

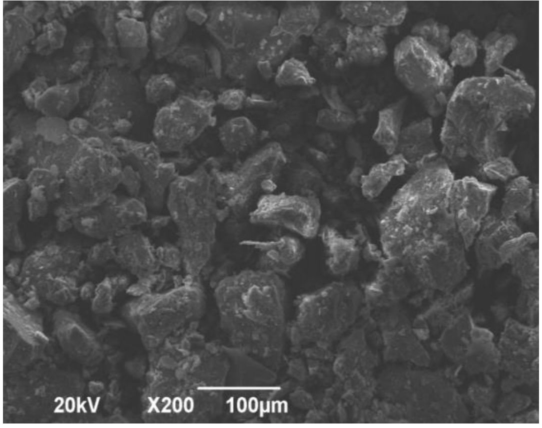

Fig. 2. SEM images of the residue after digestion of the certified sample by mixture of HNO_3 and $HClO_4$

Table 2. Efficacy of the digestion methods at the determination of Ca (as CaO), Mg (as MgO) and K (as K_2O). in certified soils. * - “acceptable” results

Element		**K**			**Ca**			**Mg**		
Soil	**Method**	**X, %**	**U_x, %**	**R**	**X, %**	**U_x, %**	**R**	**X, %**	**U_x, %**	**R**
PS-1	1	0.68	0.05	30.1	12.12	0.36	82.3	2.31	0.16	75.2
	2	0.75	0.05	33.2	13.00	0.39	88.3	2.20	0.15	71.7
	3	0.57	0.04	25.2	13.42	0.40	91.1	2.04	0.14	66.5
	4	2.15	0.15	95.1	12.50	0.38	84.9	2.50	0.18	81.4
	5	2.01	0.14	88.9	12.90	0.39	87.6	2.54	0.18	82.7
	6	2.28	0.16	100.9	14.00	0.42	97.0	2.89	0.20	98.1
PS-2	1	0.55	0.04	20.0	1.29	0.04	44.8	0.95	0.07	57.6
	2	0.60	0.04	21.8	1.38	0.04	47.9	0.98	0.07	59.4
	3	0.42	0.03	15.3	1.54	0.05	52.1	0.82	0.06	49.7
	4	2.68	0.19	97.5	2.20	0.07	76.4	1.26	0.09	76.4
	5	2.39	0.17	86.9	2.36	0.07	81.9	1.57	0.11	95.2
	6	2.80	0.20	101.8	2.50	0.08	96.8	1.60	0.11	96.9
PS-3	1	0.51	0.04	21.4	3.90	0.12	53.1	1.44	0.10	63.2
	2	0.53	0.04	22.3	3.60	0.11	49.0	1.42	0.10	62.3
	3	0.50	0.04	21.0	3.80	0.11	51.8	1.34	0.09	58.8
	4	2.15	0.15	90.3	6.10	0.18	83.1	2.10	0.15	92.1
	5	2.10	0.15	88.2	6.25	0.19	85.1	2.17	0.15	95.2
	6	2.34	0.16	98.3	7.31	0.22	99.6	2.21	0.15	96.9

The results of the XRD analysis were verified by the SEM-EDS analysis (Fig. 4). The majority of the particles contained in the sediment are larger than 20 µm and are covered with mini crystallites (<0.1 µm) in the form of a sponge. The integrated EDS analysis shows the contents of K, Ca, Mg, F and Cl, included in the composition of the less soluble fluorides of calcium, magnesium and $KClO_4$, as well as the presence of Al, Si, Fe and Na. The use of HF in the absence of $HClO_4$ (Method 6) results in the complete extraction of potassium by the three certified samples (Table 2). The results presented in Tables 2 and 3 and Figures 1-4 show that the digestion method is a dominant factor in determining the content of K in soils.

Table 3. SEM/EDS examination (integral spectrum) after digestion of the certified sample by mixture of HNO_3 + $HClO_4$ + HF (ISO14869-1)

Element	Weight %	Atom %
Al	6.68	4.84
Si	26.08	18.15
Cl	0.61	0.34
K	2.23	1.11
Na	1.94	1.65
Ca	1.17	0.57
Ti	0.88	0.36
Fe	0.95	0.33
O	59.47	72.65

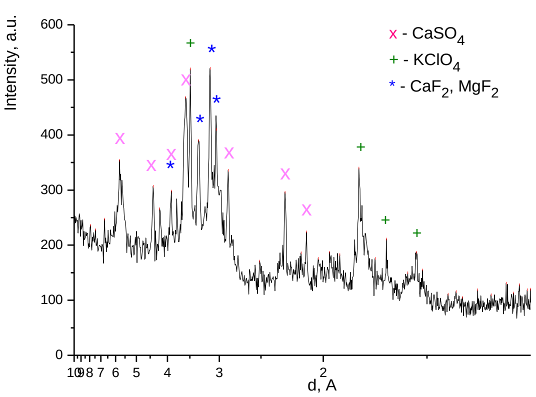

Fig. 3. X-ray pattern of the residue after digestion of the certified sample by mixture of $HNO_3 + HClO_4 + HF$ (ISO14869-1).

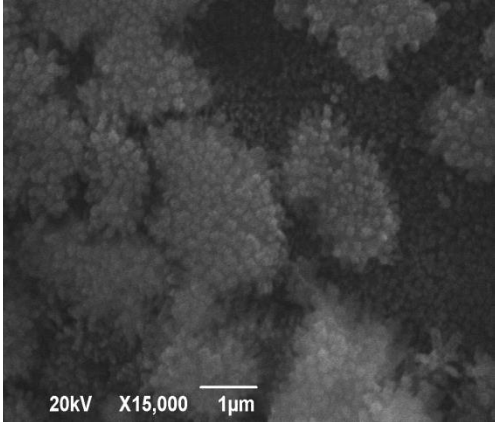

Fig. 4. SEM images of the residue after digestion of the certified sample by mixture of $HNO_3 + HClO_4 + HF$ (ISO14869-1).

Determination of Ca and Mg

The results for Ca and Mg extraction (Table 2) are very different from those of potassium and are specific for each certified soil. In this case, the efficiency of extraction depends on the method of sample digestion, and on the soil type. The better extraction of Ca by PS -1 through all methods (> 80%) demonstrates the significant influence of soil type on results. In this model the basic amount of Ca is linked in an easily soluble calcium (16%) and dolomite (9%). The content of these components in the PS-3 significantly reduces as opposed to quartz and hardly soluble primary soil minerals, and PS - 2 contains only 2% calcite. This leads to a significant reduction in the rate of extraction in these samples through the first 3 methods. The relatively low level of leaching of calcium through methods 4 and 5 despite the use of acid mixtures disrupting largely silicate matrix. This leads to a significant reduction in the rate of extraction in these samples through the first 3 methods. The relatively low level of extraction of calcium through methods 4 and 5 is noteworthy despite the use of acid mixtures significantly disrupting the silicate matrix. The reason for this is the formation of insoluble fluorides which precipitate and significantly reduce the final result. This is confirmed by the results of the XRD and SEM–EDS analysis of insoluble sediment after digestion of the sample by method 5 (BSS/ISO14869-1), presented Fig. 3 and Table 3. Although crystal phases are highly dispersed, the presence of CaF_2 in the sediment is undeniable. The addition of H_3BO_3 in method 6 links the unreacted HF and prevents the formation of such fluorides, allowing the measurement of the total quantity of extracted calcium.

Comparable with the results for Ca are the results obtained in the determination of the content of Mg. The highest degree of extraction by methods 1, 2 and 3 has been established in soil sample PS-1, containing easily soluble dolomite (9%) and magnesium (2%). In the other certified samples these components are missing, which explains the lower results. Significant increase of the results for all samples (> 80% extraction) is observed in the use of HF (methods 4, 5 and 6).

The comparative study of six of the most widely used methods of mineralization of soil samples for analysis of the content of K, Ca and Mg shows that:

1. The degree of extraction of the various elements is different and depends on the method of mineralization, as well as on the soil type. Acceptable results (over 80% extraction) for all tested elements can only be obtained by the methods of mineralization, involving the use of HF, and total extraction is only possible by method 6 (ISBN 19 081 01175)
2. The degree of extraction of K strongly increases with the increase of the aggressiveness of the acid mixture used. In this case, the method of sample preparation is dominant. In Ca, Mg the degree of extraction depends on the aggressiveness of the acid mixture used, as well as on the soil type.
3. The use of $HClO_4$ in the determination of K and HF in the determination of Ca and Mg leads to inaccurate results due to the formation of poorly soluble sediments from $KClO_4$, CaF_2 and MgF_2.

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ПРИЛОЖЕНИЕ НА РЕНТГЕНОСТРУКТУРНИЯ АНАЛИЗ И ЕЛЕКТРОННАТА МИКРОСКОПИЯ ПРИ ОЦЕНКАТА НА ОСНОВНИТЕ МЕТОДИ ЗА ПОДГОТОВКА НА ПОЧВЕНИ ПРОБИ ЗА АНАЛИЗ НА МАКРОЕЛЕМЕНТИ

К. И. Иванов[1], П. А. Запрянова[1], В. Р. Ангелова[1], Л. К. Доспатлиев[2],

[1]*Катедра „Обща химия“, Аграрен университет, 4000 Пловдив, България*

[2]*Катедра „Фармакология, физиология на животните и физиологична химия“,*
Тракийски университет, Стара Загора, България

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(Резюме)

Сравнени са два от най-често използваните методи за разлагане на почвени проби при анализ на микро- и макроелементи - киселинно разлагане и микровълнова минерализация, в различни варианти (ISO 11466; EPA Method 3051; EPA Method 3052; ISO 14869-1; GB, Standing committee of analysis, ISBN 0117519081 и смес от HNO_3 и $HClO_4$ киселина). Използвани са 3 сертифицирани почвени образци, отговарящи на 2 типа почви, широко разпространени в България: Светла алувиално-делувиална ливадна почва и Светла ливадно канелена почва. Определено е съдържанието на три основни макроелементи (K, Ca и Mg), като количествените измервания са извършени на атомно абсорбционен спектрометър Spektra AA 220, Varian, Australia. За да се изясни проблема със степента на извличане на елементите и факторите, които влияят върху нея, неразтворимите утайки след разлагане на пробите са изследвани с рентгеноструктурен анализ и сканираща електронна микроскопия. Установено е, че използването на $HClO_4$ при определяне съдържанието на K и на HF при определяне съдържанието на Ca и Mg води до формирането на неразтворими утайки от $KClO_4$, CaF_2 и MgF_2**.**

Ключови думи: *пробоподготовка, почва, K, Ca, Mg.*