

USING CENTER OF GRAVITY EQUATION FOR MICA AND SMECTITE IN EVALUATION OF K-STATUS IN SOME SOILS OF IRAQI KURDISTAN REGION

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ABSTRACT

Ten soil sites were chosen in Iraqi Kurdistan region, included the governorates of (Sulaimani, Arbil, and Duhok). These soils were characterized by their similarity in texture, parent material, topography, climatic conditions, and equal rainfall, in order to study the use of the center of gravity equation and mineralogical properties in evaluating the state of potassium in soils of different plant coverage (Forest, crops, and uncultivated soils). Results showed there was a variation in the values of calculated center of gravity for studied soil samples, which ranged between (0.83 – 1.63). The variation in these values was attributed to the variation between the studied soils in their ability for potassium supplying, depending on the nature of plant coverage, soil texture, mineralogical properties, and the intensity of weathering. The X-ray analyses of clay fraction revealed, that the forest soils were content a high amount of 2:1 expandable clay minerals, mica, and interstratified minerals, while the crop and uncultivated soils were contained a low amount of interstratified minerals. The distribution of minerals in studied soils, suggested the transformation of mica into 2:1 expandable clay minerals in forest soils, and no or minimal transformation of mica into 2:1 expandable clay minerals in crop and uncultivated soils.

Key words: center gravity, weathering, potassium.

الجاف

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أستعمال مركز الاجتذاب لمعادن المايكا والسمكتايت في تقييم حالة البوتاسيوم في بعض ترب أقليم كوردستان / العراق

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المستخلص

أختيرت عشرة مواقع لترب تقع في أقليم كوردستان / العراق شملت محافظات (السليمانية، أربيل، ودهوك)، إذ تميزت تلك الترب بتشابهها في النسجة، مادة الاصل، الطبوغرافية، الظروف المناخية، وتساوي كمية الامطار الساقطة، وذلك لدراسة استخدام معادلة مركز الاجتذاب، والخصائص المعدنية في تقييم حالة البوتاسيوم لترب مختلفة الاستغلال الزراعي (ترب غابات، ترب محاصيل، غير مستغلة زراعياً). أظهرت النتائج أن هناك أختلاف في قيم مركز الاجتذاب المحسوب لنماذج ترب الدراسة، والذي تراوح ما بين (0.83 – 1.63)، ويعزى هذا الاختلاف في تلك القيم الى تباين تلك الترب في قابليتها على تجهيز أيون البوتاسيوم، اعتماداً على طبيعة ونوع الغطاء النباتي، نسجة التربة، الخصائص المعدنية، وشدة عمليات التجوية. أظهرت فحوصات الاشعة السينية الحادة لدقائق مفصول الطين بأحتواء ترب الغابات على نسب مرتفعة من المعادن المتمددة 2:1، ومعادن المايكا، بالإضافة الى المعادن المتداخلة

كلمات مفتاحية: الخصائص المعدنية، البوتاسيوم، الغطاء النباتي، ترب الغابات

INTRODUCTION

Over the last few decades considerable effort has been devoted to elucidating the factors that control decomposition rates, such that we can predict rates given some information on key factors such as temperature, precipitation and chemical composition of litter. The importance of each of these factors is undisputed, rather attention has focused on assessing their inter-relationships and relative importance. (10) studied the clay minerals weathering in forest ecosystem and conclude that an increase of the 10 to 14 A^0 peak intensity ratio in the rhizosphere with respect to the bulk soil. These results underlined an upper concentration of illite-like minerals in the rhizosphere clay-sized fraction. Moreover, the K content increased in this fraction. This last observation can be interpreted as a consequence of illite-like minerals enrichment in the rhizosphere. This increase of illite-like minerals in rhizosphere can be explained according to the interpretation of (8) who defined the amount of illite-like minerals in temperate soils as a function of K status. According to these authors, the increase of exchangeable K in the top soil was correlated with an increase of illite-like minerals in the clay-sized fraction. A reversed trend was observed after decrease of K after intensive agricultural practice without fertilization. Mica weathering consists primarily of the removal of K ions from the lattice interface. This loss of K ions weakens the bonding between adjoining plates and the basal spacing expands proportionally. The maximum possible expansion without rupture of the lattice is to 14 A^0 . Intergrades from un-weathered 10 A^0 mica to highly weathered 14 A^0 mica comprises the mica weathering sequence un- weathered mica to mica intermediate to hydrated mica. Mica regard one of the most important minerals for plant nutrition because they represent a major source of the macronutrient K. The only other common potassium-rich minerals in soil were feldspar, which is less important as a source of potassium (24). Biotite is the most common trioctahedral mica, and all cation sites in octahedral sheet for biotite are filled with divalent cations such as Mg^{2+} and Fe^{2+} , that completely balance the negative charge arising. The most abundant dioctahedral mica is

muscovite, in ideal muscovite structure, only two out of three octahedral positions are filled with Al^{3+} . Therefore K^+ in trioctahedral mica is more readily released by weathering than K^+ in dioctahedral mica (26). The objective of this study was to evaluate the potassium availability state in some soils of Iraqi Kurdistan region through applying the Barre's equation, using the centre of gravity for mica and smectite minerals depending on results of mineralogical analysis of clay fraction, in order to predict the availability state of potassium in study soils.

MATERIALS AND METHODS

The center of gravity equation proposed by (9) has been used, and try to applied in the conditions of Iraqi soils, in order to study the status of available potassium in some soils of Iraqi Kurdistan region. The center of gravity is a fictional point moves along a distance between the peak of mica minerals (10 A^0), and that of expandable 2:1 minerals (smectite minerals group 14 A^0). The movement of this point started from peak of mica minerals towards of smectite peak, so the values of center of gravity increase in the direction of smectite peak, and decreases towards of mica peak. Stipulat that the smectite minerals should inherited from mica minerals in study soils, as it can be verified through the x-ray results. According to that all peaks fall within the distance between mica peak and smectite peak (between 10 to 14 A^0) considered as interstratified minerals in different stages of weathering, and they are product of transformation of mica to 2:1 expandable minerals. Also the measuring of the area under the curve for both mica and smectite peaks, and the d- spacing for mica and smectite peaks were using in applied the Barre's equation as follows:

$$C . g = \sum (a_i \times p_i / \sum a_i)$$

Where:

c.g – is the center of gravity, **a_i** – is the area under the curve, and **p_i** – is d- spacing for mica and smectite peakes. Also we used the critical value for available potassium in Iraqi soils (0.36 $Cmol.Kg^{-1}$) suggested by (6) as a watershed in determined the availability of potassium in studied soils. As the soils that have achieved values less than the mentioned value are considered low potassium

availability soils, while the soils that achieved values higher than the proposed critical value were considered highly potassium availability soils. Then try to compare the values of center of gravity obtained by applying the Barre's equation with the recorded available potassium values in studied soils. So according to the critical value of available potassium in Iraqi soils ($0.36 \text{ Cmol.Kg}^{-1}$) we considered the soil samples have a value of center of gravity higher than (1), are highly potassium availability, considering that the value of (1) is the halfway between 10 A^0 and 14 A^0 peaks, then the soils that register values less than the value of (1) are low potassium availability soils. Ten soil sites were selected for this study, represented by three governorates (Sulaymania, Arbil, and Duhok) in Iraqi Kurdistan region (Table 1), these soils were differ in their agricultural exploitation, whereas five of them were forest soils which are sites of number (1, 4, 6, 9, and 10), represented by forest trees of (Oak, Pine, Oak, Pine, and Oak) respectively, while the sites of

number (2, 5, and 8) were represented crop soils, and those have numbers (3 and 7) were represented an uncultivated soils. The soil samples were air dried and passed through 2 mm sieve. The particle size distribution was determined according to international pipette method as described in (25). The electrical conductivity (EC) and pH were measured according to (13). While total calcium carbonate was determined by acid neutralization method of (18). Soil organic matter was determined according to Wakley-Black method as described in (15). The mineralogical composition of the clay-sized fraction was determined by X-ray on parallel oriented clay of the Mg^{2+} and K^+ saturated clay samples. The Mg^{2+} saturated clay was treated with the X-ray in the air dry and ethylene glycol salvation. The K^+ saturated clay was heated to 350°C and 550°C . X-ray analyses were made with a Philips- P.W1840 diffractometer equipped with a graphite diffracted beam monochromatot using $\text{CuK}\alpha$ radiation.

Table 1. GPS reading for the studied sites

Site No.	Location	Latitude	Longitude
1	Sulaimani	$35^\circ 44 40.37$	$45^\circ 33 27. 01$
2	Sulaimani	$36^\circ 18 12. 30$	$44^\circ 39 55. 78$
3	Sulaimani	$36^\circ 13 41. 50$	$45^\circ 18 33. 55$
4	Sulaimani	$36^\circ 27 37. 44$	$45^\circ 23 27. 47$
5	Arbil	$36^\circ 07 33. 25$	$44^\circ 18 11. 13$
6	Arbil	$36^\circ 17 20. 57$	$44^\circ 37 30. 41$
7	Arbil	$36^\circ 10 12. 30$	$44^\circ 20 17. 10$
8	Duhok	$37^\circ 06 39. 22$	$43^\circ 15 03. 87$
9	Duhok	$36^\circ 55 30. 73$	$43^\circ 12 37. 17$
10	Duhok	$36^\circ 40 19. 50$	$43^\circ 17 30. 06$

RESULTS AND DISCUSSIONS

Chemical and Physical

properties of studied soils: Results in Table 2 showed that all studied soils were non-saline, reflected by low values of EC ($0.22 - 0.41 \text{ dS.m}^{-1}$). The rang of pH values was between ($7.14 - 7.48$) reflecting that the reaction of all soil samples was moderate alkali, due to effect of calcareous parent material of these soils. The total amounts of CaCO_3 was ranged between ($125.72 - 306.50 \text{ g.Kg}^{-1}$), and indicating that all studied soils are calcareous by nature. Also the results of Table 2 showed

that the total contend of O.M was ranged between ($21.66 - 36.43 \text{ g.Kg}^{-1}$), and the highest values were obtained in forest soils, also the difference between the amounts of organic matter in the studied soils may be due to many factors such as types of plant covering, difference between plant residual decomposition, and the ability of organic matter decomposition. The values of cation exchange capacity CEC were ranged between ($22.81 - 45.21 \text{ Cmol.Kg}^{-1}$), in general the results showed that the forest soil samples have a higher values of CEC, and suggest the

effect of organic matter and /or clay content in these soils. Results of particle size distribution in Table 2 showed that the amount of clay in forest soil samples (1, 4, 6, 9, and 10) was ranged between (409.71 – 481.42 g.Kg⁻¹), in general the forest soil samples were recorded a high amount of clay comparing with its counterparts in soil samples of numbers (2, 3, 5, 7, and 8), the difference between the amounts of clay in studied soils my attributed to the effect of geomorphic processes specially

erosion of fine fractions from surrounding upland soils and deposition of materials on low plan soils causing to increase clay content in forest soils (22) . In general the amounts of silt and sand were lower than that of clay content in all studied samples and they ranged from (234.42 -420.91 g.Kg⁻¹) and from (190.86 – 505.73 g.Kg⁻¹) respectively. From the results of particle size distribution, it is obvious that the texture of studied soils was ranged from clay to silty clay loam.

Table 2. Some chemical and physical properties of studied soils

Site No.	PH	EC ds m ⁻¹	O.M g Kg ⁻¹	CaCO ₃ g Kg ⁻¹	CEC Cmol Kg ⁻¹	Clay gm Kg ⁻¹	Silt gm Kg ⁻¹	Sand gm Kg ⁻¹	Texture Class
1	7.35	0.29	31.17	195.80	34.67	420.74	255.44	323.82	C
2	7.42	0.31	27.70	220.51	29.32	371.52	331.82	296.66	CL
3	7.48	0.41	22.34	125.72	31.18	355.33	420.91	223.76	CL
4	7.29	0.33	33.37	130.02	37.20	409.71	370.51	219.78	C
5	7.14	0.22	27.15	211.66	32.73	390.82	384.44	224.74	CL
6	7.46	0.35	35.32	235.11	41.15	452.91	356.23	190.86	C
7	7.43	0.23	29.82	306.50	22.81	259.85	234.42	505.73	SCL
8	7.42	0.27	21.66	184.20	28.78	274.30	245.47	480.23	SCL
9	7.31	0.30	36.43	206.32	45.21	481.42	246.89	271.69	C
10	7.28	0.32	34.20	237.93	42.19	463.78	258.18	278.04	C

Potassium forms in studied soils

Table 3 shows that the amount of soluble potassium ranged between (0.01 – 0.07 Cmol.Kg⁻¹) in all studied soils. These results agree with (7 and 17), who studied some Iraqi soils. In general the values of soluble potassium appears low in all studied soils, and this attributed to effected the studied soils by precipitation and leaching of potassium. (23) found that one of the important factor which affects potassium release from soils is leaching, and the concentration of potassium was affected by the equilibrium and kinetic reactions that occur between the forms of soil potassium, the soil moisture content, and the concentrations of divalent cations in solution and on the exchangeable sites . The amount of exchangeable potassium ranged between (0.17 – 0.97 Cmol.Kg⁻¹), from these results we can fined that all samples of forest soils recorded values above the critical value of exchangeable potassium in Iraqi soils found by

(6), (0.36 Cmol.Kg⁻¹), and the highest value of exchangeable potassium was found at oak forest soils. These results are agree with finding of (22) who been working on effect of plant coverage on transformation of mica to an expandable minerals in some forest soils of Iraqi Kurdistan region. In general these results indicate the effect of accumulation of organic matter and their decomposition on weathering process of clay minerals in these soils, and reflected the effect of tree species and their biodegradation. (20) found that the soil characterized by an accumulation of organic matter in the upper layers of forest soils means that the soils are in a very active pedogenetic state with a high intensity of weathering and high release rate of metal cations and pedogenetic oxides, and tree species have all been shown to influence minerals weathering in the forest floor or soil, and this influence has been attributed at least partly to their effect on rate of litter decay.

Table 3. Forms of potassium in Cmol. Kg⁻¹ for studied soils

Site No.	Agri. Exploitation	Soluble-K	Exch.-K	Available-K	Non-Exch.K	Mineral-K	Total-K
1	Forests-Oak	0.07	0.97	1.04	15.67	19.70	36.41
2	Crops	0.06	0.25	0.31	18.55	22.60	46.86
3	Uncultivated	0.03	0.21	0.24	23.16	26.45	49.85
4	Forests-Pine	0.05	0.43	0.48	16.77	20.21	37.46
5	Crops	0.03	0.35	0.38	19.32	28.11	47.81
6	Forests-Oak	0.06	0.52	0.58	18.45	20.62	39.65
7	Uncultivated	0.03	0.17	0.20	20.17	21.45	41.82
8	Crops	0.06	0.22	0.28	14.05	26.16	40.49
9	Forests-Pine	0.01	0.45	0.46	17.22	22.10	39.78
10	Forests-Oak	0.01	0.67	0.68	18.65	26.53	45.86

Results in Table 3 showed the values of available potassium in studied soils, which ranged between (0.20 – 1.04 Cmol.Kg⁻¹). The results showed that there is a clear difference in the values of available potassium in studied soils, and some of them were exceeded the critical value of available potassium in Iraqi soils (0.36 Cmol.Kg⁻¹). This variance in values attributed to the variation in the clay minerals content of those soils, in addition to the weathering processes effecting to the potassium bearing minerals, which consider the main source of potassium supplying, especially those that have the ability to fixed and released of potassium such as mica minerals . In addition to the role of soil texture to keep the potassium in soil, as indicated by the publications of the International Potash Institute, (14) . The results also showed that the highest values of available potassium were recorded in forest soils, and the lowest in uncultivated soils. These results reflect how the factor of soil exploitation affects the availability of potassium in these soils, and were in agreement with many studies conducted on Iraqi soils (2). Also results in Table 3 showed that forest soils recorded a low values of non-exchangeable potassium ranged between (15.67 – 18.65 Cmol.Kg⁻¹), and mineral potassium (19.70 – 26.53 Cmol.Kg⁻¹), comparing with uncultivated soils (20.17 – 23.16 and 21.45 – 26.45 Cmol.Kg⁻¹) respectively and crop soils (14.05 – 19.32 and 22.60 – 28.11 Cmol.Kg⁻¹) respectively, which confirm that the amount of potassium release from the structure of potassium bearing

minerals (mica minerals) in forest soils was higher than other studied soils. Many studies (16 and 19) have shown that the type of plant cultivated in particular soil has a clear effect on concentrations of available potassium, and this depends on plant species, type of root system and its density, and metabolism activity of plant. Also they showed that plant species and plant density were effect on the concentrations of available potassium in soil.

Mineralogical properties of Studied soils

The clay samples have been taken from all studied soils in order to study the mineralogical properties particularly of mica minerals and group of 14 A⁰ 2:1 expandable minerals using X-ray diffraction, in order to investigate and diagnostic of these minerals, and then study their transformations, to reflect that on the liberation of potassium in study soils. Results of X-ray inspections for clay fractions in Figs. (2 and 3) showed the presence of diffraction (13.92 – 14.72 A⁰) in air-dried Mg-saturated treatment in all clay samples of studied soils, which expanded his d-spacing to reach (16.55 – 17.05 A⁰) in ethylene-glycol salvation, also the K-saturated and heating to 350⁰C treatment led to collapsed the diffraction (13.92 – 14.72 A⁰), and transforming it to the d-spacing of (9.87 – 10.27 A⁰), this was accompanied by an increase in diffraction intensity of (10 A⁰) at the expense of diffraction of (14 A⁰), these results confirms the presence of smectite minerals in the clay samples, and that the smectite was inherited from mica minerals, and it characterized by mica characteristics in

terms of the highly layer charges and fixed or release of potassium ion (11). The continued presence of diffraction ($13.92 - 14.72 \text{ \AA}^0$) in all treatments, and accompanied by its third order diffraction at the d-spacing of (4.72 \AA^0), confirms the presence of real chlorite in the samples, and that this case was found in most of the soils exploited by crops, as well as the uncultivated soils. Whereas, the disappearance of ($13.92 - 14.72 \text{ \AA}^0$) diffraction in K-saturated and heating to 550°C treatment with the continued presence of its third order (4.72 \AA^0) in all treatments confirms the presence of swelling chlorite, this case was found in clay samples of forest soils. The variations in the presence of chlorite types in studied soils, it may be due to many reasons, including: variation in intensity of weathering, plant coverage, and pedological processes. But according to our belief that the high content of swelling chlorite in forest soils, can be attributed to the high organic matter content in these soils, which in turn encourages the occurrence of chloritization phenomenon leading to the transformation of the 2:1 expandable minerals towards of swelling chlorite, these results are in agreement with finding of (5), who found that the among of encouraging factors for the occurrence of chloritization phenomenon in some soils of northern of Iraq, it is the highly content of organic matter, especially in forest soils. Also, results showed the presence of diffraction ($10.04 - 10.65 \text{ \AA}^0$) in air-dried Mg-saturated

treatment, and remains the same in all treatments, this confirms the presence of mica minerals in clay samples of studied soils, whereas the appearance of the second order of mica at a d-spacing of (5 \AA^0) in weak intensity reveal that the Biotite mineral is present in clay samples. These results are in agreement with many studies conducted on Iraqi soils (5 and 4), which showed that the Biotite mineral was dominant in Iraqi soils among the mica minerals, despite his weak resistance to weathering compared with Muscovite mineral, and they attributed this to dominance of Biotite in the parent materials of Iraqi soils. In forest soil samples (1,4,6,9,and 10), the presence of diffractions (12.11 and 12.99 \AA^0) in air-dried Mg-saturated treatment confirmed the presence of irregular interstratified (M-S) mineral while the appearance of diffraction in two d-spacing (12.11 and 12.99 \AA^0) reflecting the presence of interstratified mineral in different stages of weathering. Also the appearance of diffraction (16.31 \AA^0) in air-dried Mg-saturated treatment confirmed the presence of second order d_{002} of regular interstratified (M-S) mineral in these soils, and the intensity of clarity of the mentioned diffraction was increased in ethylene-glycol salvation, and k-saturated and heating to 350°C and 550°C , these results were in agreement with finding of (1) during his study for the nature and formation of interstratified minerals in some Iraqi soils.

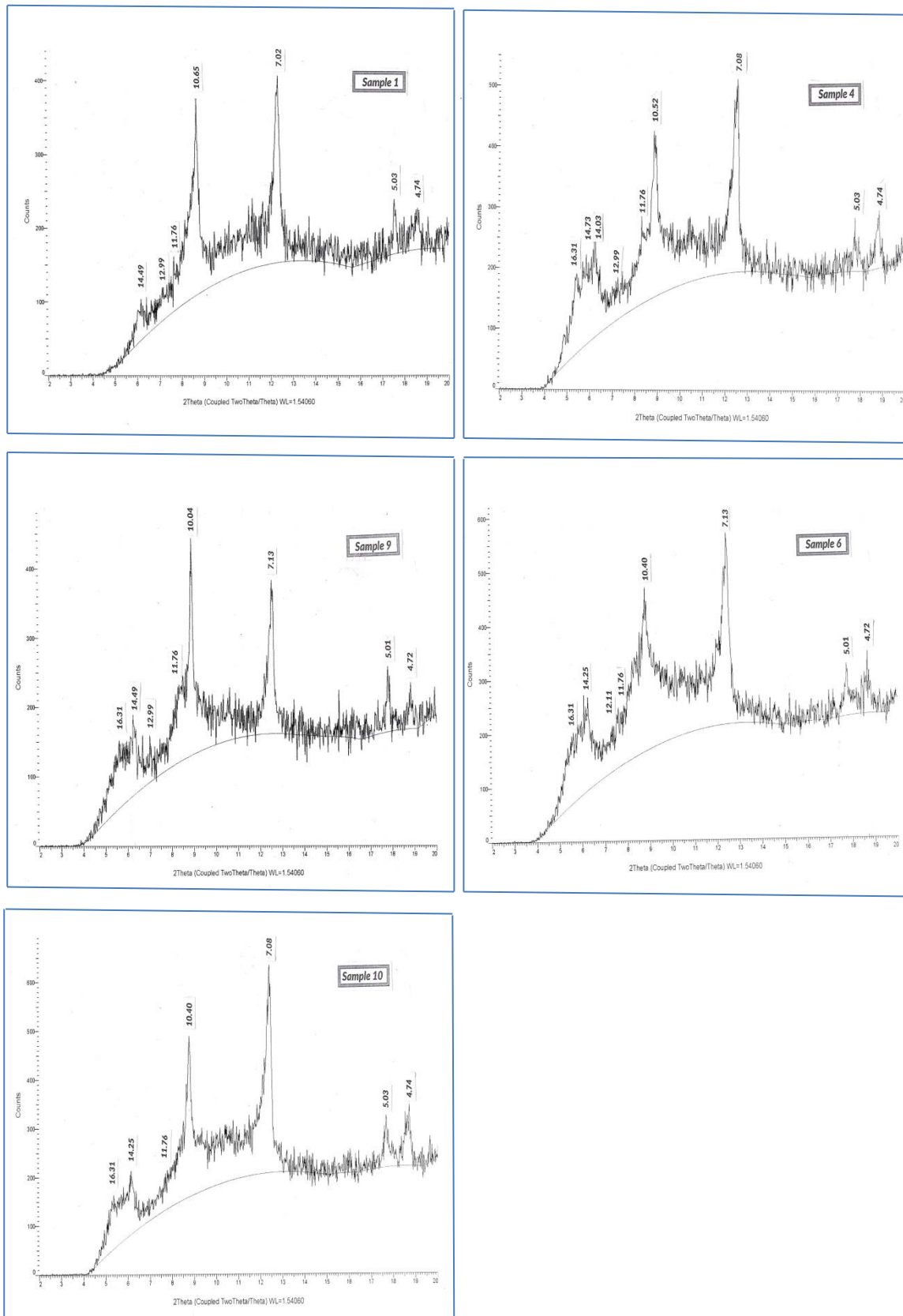


Figure 1. X-ray diffraction patterns of Mg- saturated (air dry) clay fraction of samples No.(1, 4, 6, 9, and 10).

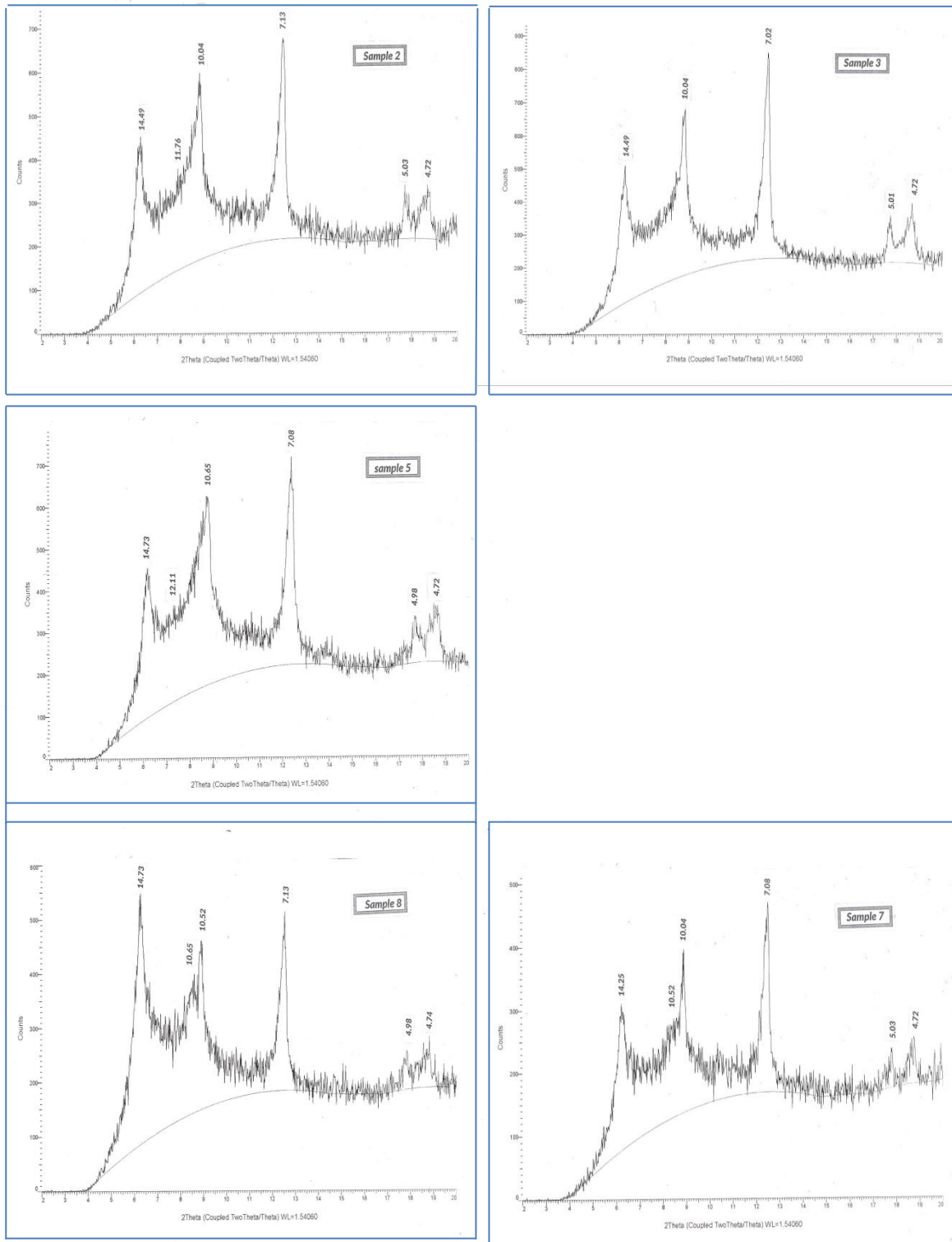


Figure 2. X-ray diffraction patterns of Mg- saturated (air dry) clay fraction of samples No. (2, 3, 5, 7, and 8).

Center of gravity and Available potassium status: Results in Table 4 showed the values of center of gravity for studied soils, which ranged between (0.83 – 1.63), from these results were found that the soil samples of numbers (1, 4, 6, 9, and 10) were recorded values of center of gravity (1.36, 1.33, 1.53, 1.40, and 1.63) respectively, which considered

a highly potassium availability soils, were the available potassium values in their soils exceed of the critical value of available potassium in Iraqi soils (0.36 C mole Kg⁻¹). Whereas the soils have numbers (2, 3, 5, 7, and 8) recorded low values of center of gravity (0.86, 0.94, 0.89, 0.81, and 0.77) respectively and considered a low to medium potassium

availability soils. These variations in values of center of gravity can be attributed to the soil texture, as the results of Table 2 show that the texture of soils (1, 4, 6, 9, and 10) was clay, while the texture of soils (2, 3, 5, 7, and 8) was ranged between sandy clay loam to clay loam. As we expected that the increasing of sand fraction content is negatively effect on the available potassium concentration. These results are in agreement with finding of (3) who state that the concentration of available potassium was increased with increasing of clay fraction content in Iraqi soils, and share that opinion (4) which found that the values of the center of gravity were decreasing when the sand fraction content was increased during her study on potassium availability in some Iraqi soils, and attributed this to the soil texture which effects on potassium availability in these soils. Also, the X- ray results showed that the peaks of mica minerals in soil samples (1, 4, 6, 9, and 10) were recorded a high d-spacing ranged between (10.04 – 10.62 Å⁰), this is superior to its counterparts in soil samples of numbers (2, 3, 5, 7, and 8), which is explained according to our opinion the increased exposure of the interlayers of mica minerals to shrinking and swelling, and caused to increasing the size of mineral particles in the direction of the vertical axis, which in turn leads to an increase the d- spacing of mica minerals, and increases the transformation of potassium ions from unavailable to exchangeable and soluble forms. (12) state that the exposing of mica minerals to the weathering process leads to effect on the interlayers of mineral, converting bonds between layers into weak bonds, and increases the size of the mineral along the vertical axis (C), and thus increasing the d- spacing of mineral. As we believe that the mica minerals in soils of numbers (1, 4, 6, 9, and 10) were exposed to weathering and transfer to 2:1 expanding clay minerals or illite, which can be attributed to the nature and type of plant coverage in those soils, all of which are considered forest soils. (8) defined the transformation of mica to 2:1 expanding clay minerals in forest soils as a function of K status, they state that the increase of exchangeable K after litter mineralization in top soil correlates with an increasing the rate

of transformation of mica to 2:1 expanding minerals and illite-like minerals in clay fraction . (27 and 21) have observed an enrichment of exchangeable K in surface horizon and solution of different mature tree species. This increase in K concentrations in surface horizons of forest soils could be due to positive differences between element input fluxes, principally by mass flow, mineral weathering, organic matter mineralization, and element output fluxes. To confirm the exposure of mica minerals to weathering processes, and to increase the availability of potassium within samples of (1, 4, 6, 9, and 10), the results of mineralogical analysis by X-ray showed the existence of (M-S) interstratified mineral which appeared in two d- spacing (12.11 – 12.99 Å⁰) in Mg-saturation air dry treatment, reflecting the presence of interstratified mineral in different stages of weathering, which we saw at the time that the presence of this mineral is a product of weathering of mica minerals in situ.

Table 4. Values of calculated center of gravity and available – K in studied soils

Site No.	C . g Calculated	Available – K Cmol.Kg ⁻¹
1	1.36	1.04
2	0.86	0.31
3	0.94	0.24
4	1.33	0.48
5	0.89	0.38
6	1.53	0.58
7	0.81	0.20
8	0.77	0.28
9	1.40	0.46
10	1.63	0.68

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