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# Comparison between Walkley- Black and Loss- on- Ignition methods for organic carbon estimation in soil from different locations

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**Abstract:**

The present study aims to find out the best method for soil carbon determination using two methods, the wet acidified dichromate oxidation, Walkley-Black (W.B) and loss on ignition (LOI) methods. This study was employed on 30 soil samples from 0-20cm depth from three Duhok, Irbil and Sulaimaniya of Kurdistan region-Iraq. The following parameters are analyzed: organic C and the particle size distribution of the soil samples. The results of LOI and W.B methods were statistically analyzed by simple linear regression equations to interpret their relationship. The highest values of soil organic carbon (SOC) were found at Loss on ignition method ranged between 4.19 - 29.70 g $kg^{-1}$ soil, whereas W-B method had the lowest values ranged between 3.0 – 19.0 g $kg^{-1}$ soil for overall sites. There was a strong relationship between these two methods, so the amount of SOC using both methods had significantly a very strong correlation ($R^2$=0. 93, $p < 0.001$), ($R^2$=0. 87, $p < 0.0001$), ($R^2$=0. 75, $p < 0.001$) in Sulaimaniya, Duhok and Irbil respectively. This study also revealed that silty clay and clay soils gave the highest values of the SOC by the two methods compared to the loamy soil. However, the soils that have more clay and carbonate contents gave higher values of SOC at high temperature using L.O.I technique. The results of this study revealed that both methods were reliable but W.B method was more accurate

and suitable for soils with high clay contents and for the calcareous soils. Also, LOI is an accurate, if the fine fraction is present in low percentage.

***Keywords*****:** *Soil organic carbon, Walkley-Black, Loss-on-ignition, Particle size distribution*

## Introduction:-

Soil organic carbon occurs in soil and derived from the decomposition of plants and animals. It considers as the main content of soil organic matter and has an important role in the global carbon cycle and influence negatively on the climate change (9). The term of the soil organic matter describes the constituents of organic matter and the carbon occurring in the soils. Wide forms of organic carbon are present in soils and begin from low decomposition forms of organic matter such as litter to high decomposition such as humus. Organic matter has a major influence on soil chemical and physical properties. Commonly the Soil organic carbon is measured by dry combustion (Loss on ignition method), or a wet acidified dichromate oxidation (Walkley and Black method) (18). The technique of Loss-on-ignition (LOI) supplies an alternative way in which the soil samples were heated at high temperature to ignite organic matter and measuring weight losses (19). This technique is easy, cheap and fewer workers needed as compared to the chemical methods. So, the LOI technique is greatly used for determining of SOM or soil organic carbon (SOC) in forest soils and sediments, and to measure carbonate in sediments (5). However, this technique is less used in soils of low fertility, although some studies have shown that the LOI technique gives an accurate estimate of carbonate for sediments (6). The standard method of W-B has been recommended for estimating the organic matter of the agricultural soil. However, there are serious issues with the routine use of this procedure. Organic carbon determined by the Walkley-Black method uses Dichromate as one of the reagents. Dichromate is Highly Toxic and Class-1 Carcinogens which pose a serious risk to health. Depending to Beaudoin(4) a very few differences were observed in the estimation of SOC between LOI and W-B methods. The previous appears good estimates of SOC, but with low accuracy (14); in soils with low organic carbon content cannot rely on other methods used, including the W-B method. In the study of soils with

organic matter and clay contents in North Wales, Ball (3) observed a good relationship between LOI and total organic carbon, using 850°C and 375°C and found a strong correlation coefficient of 0.99 between LOI at 850°C and total organic carbon measured by the W.B method. The conventional content of organic matter has been assumed on average, 58% organic carbon (10). It is necessary to select the easy method for determining of (SOC) in soils of the semi-arid region and also to evaluate methods on the basis of regression relations between LOI and W-B methods. SO the aim of this study was to assess two methods of (SOC) determination, as well as their comparability and compatibility, accuracy, the speed of determination and convenience, using reference soil.

**Materials and Methods:-**

Thirty soil samples were collected from three locations (10 soil samples from Erbil, Sulaimaniya and Duhok), in Iraq-Kurdistan region as shown in figure (1). They were collected at 0-20

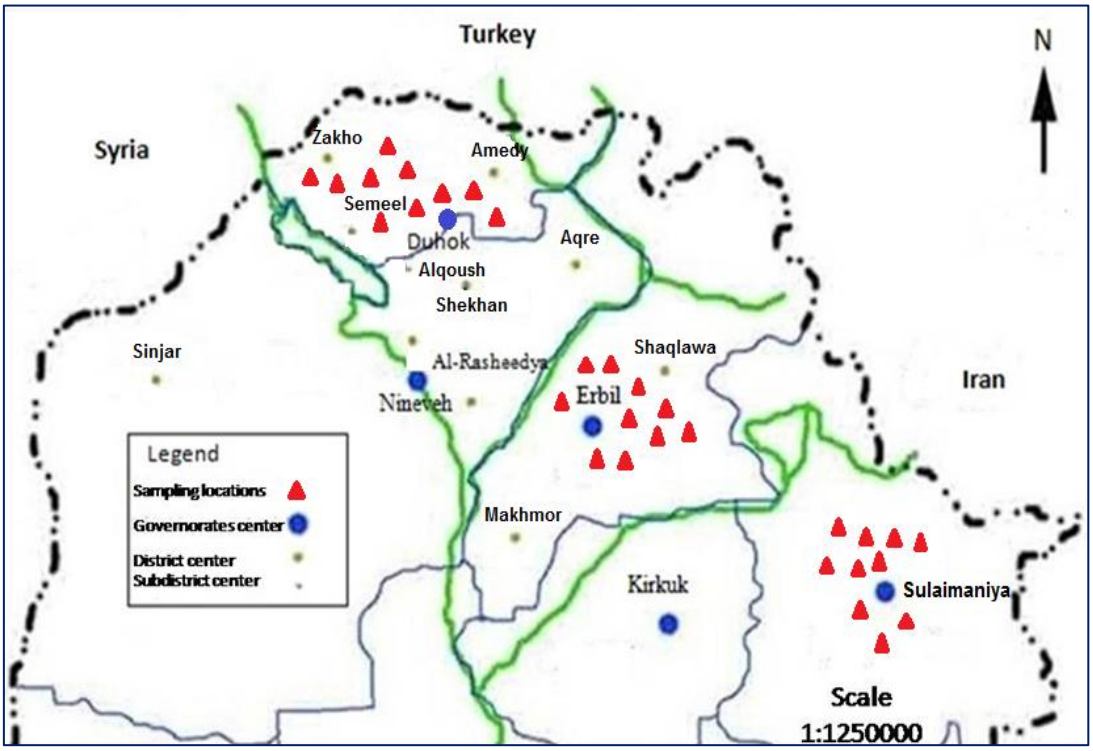


**Figure (1): Map showing the soil sampling locations**

cm depth and air dried in the laboratory. This studied soils were taken from different areas of the organic matter distributed among cultivated, non-cultivated and forest areas. While after drying and sieving soils were characterized for common chemical properties according to Spark *et.al*.(15). Particle size distribution by the hydrometer method using sodium hexametaphosphate a dispersing agent after the destruction of organic matter by hydrogen peroxide ($H_2O_2$, 6%) (8).

Soils were air-dried and sieved through a 2mm. Processed soils were analyzed for organic carbon by two recognized methods:

wet- acidified rapid dichromate oxidation (18) and loss-on-ignition (LOI)(20). Empty porcelain crucibles were placed in an oven at 105 ºC for 3 hours. The weights of crucibles were taken after it cooled in the desiccator. Oven dry soil (5g) were sieved and dried at 105 ºC for 24 hours and placed in each crucible. The crucibles then were placed in the muffle furnace and ignited at 500 ± 25 ºC for 10 – 11 hours. The crucibles then were allowed to cool in a desiccator and weighed to give a weight of ignited soil. Soil organic matter (SOM) is calculated as the weight loss between 105 ºC and 500 ºC:

$$\mathbf{SOM\ (g\ kg^{-1})} = \left(\frac{\mathbf{Weight_{105^oC} - Weight_{500^oC}}}{\mathbf{Weight_{105^oC}}}\right) \times \mathbf{100}$$

An empirical factor of 1.724 is used to convert soil organic matter into soil organic carbon (SOC), according to the assumption that SOM contains 58% organic carbon (13).

$$\mathbf{SOC\ (g\ kg^{-1})} = \frac{\mathbf{SOM\ (gkg^{-1})}}{\mathbf{1.724}}$$

Statistical Analysis:

Stepwise multiple regressions between sets of data were calculated using the Minitab software package 16. Microsoft Excel Software program was used for the data between LOI and

W.B methods and particle size distribution of the soils.

**Results and Discussions:**

Comparison of SOC between two methods

The results regarding of 30 samples were used to measure SOC by the two methods under comparison, dry combustion (LOI) method and wet acidified rapid dichromate oxidation (W.B) method. The results of this study for determining the soil organic carbon contents revealed a good relationship between W.B and LOI methods with different soil types through producing significantly a high correlation coefficient ($r^2$=0. 87***) in the Duhok site figure (2). According to the soil samples analyzed, SOC may be calculated from LOI at 500 ± 25 ºC for 10 – 11 hours, by using this following simple linear equation:

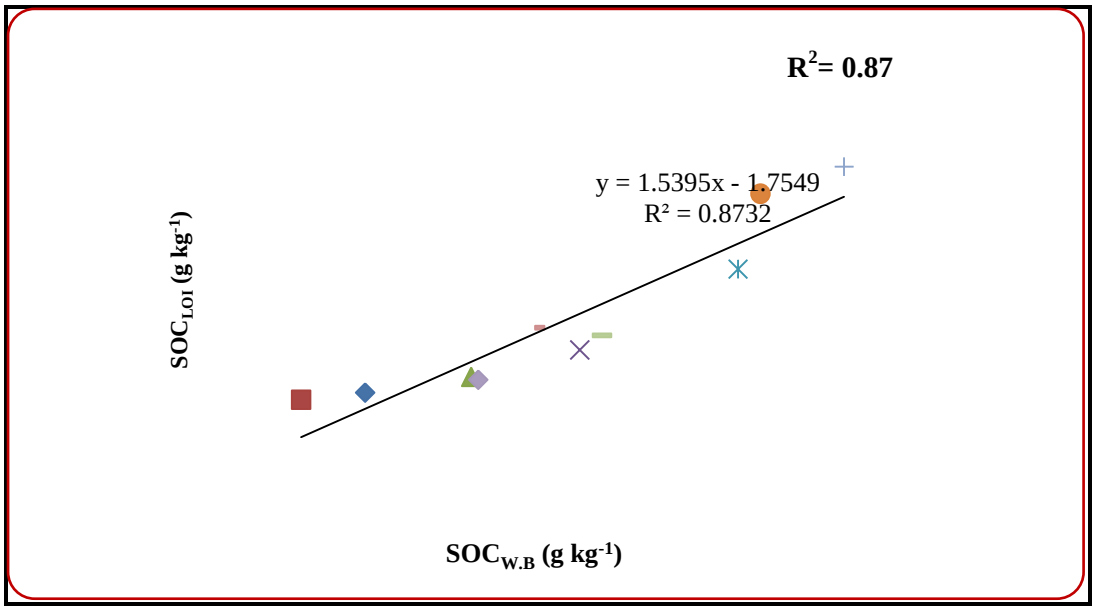


**Figure (2): Correlation between SOC measured by W.B method and LOI method for Duhok site.**

**$SOC_{LOI}$=0. 5672 $SOC_{W.B}$ + 2. 3396**

(Where, $R^2$=0. 87, n=10)

In this study, it has been found also that the Irbil site approximately has the same bias ($r^2$=0. 75**) but less significantly correlated than Duhok site

figure (3). According to the soil samples analyzed, SOC may be calculated from LOI at 500 ± 25 ºC for 10 – 11 hours, by using this following simple linear equation:

While in Sulaimaniya site gave a significant strongest correlation ($r^2$=0. 93**,) as shown in the figure (4). According to the soil samples analyzed, SOC may be calculated from LOI at 500 ± 25 ºC for 10 – 11 hours, by using this following simple linear equation:

$$\mathbf{SOC_{LOI}=0.\ 423\ SOC_{W.\ B}\ +4.\ 4755}$$

(Where, $R^2$=0. 75, n=10)

(Where, $R^2$=0. 93, n=10)

$$\mathbf{SOC_{LOI}=0.\ 5003\ SOC_{W.\ B}\ +\ 3.\ 0046}$$

The descriptive analyses of the results revealed the differences that occur by two methods and its effectiveness on the SOC estimation as shown in the table (1). It has been found that in higher SOC content, a wide difference observed were 10.70, 10.93 and 9.79 $g.kg^{-1}$ in Duhok, Irbil and Sulaimaniya sites respectively. In contrast, in low SOC content, their differences have declined sharply which were 3.57, 0.41 and 0.59 $g.kg^{-1}$ in Duhok, Irbil and Sulaimaniya sites respectively. This variation indicates that the LOI gave higher estimates, whereas W-B gave lowest one. These results are in agreement with Schinner(12) how reported that LOI technique often gives overestimates of soil organic carbon by LOI technique due to the effect of clay contents. Furthermore, W-B had more varied than LOI (1) and (8)

Generally, the difference in the results for assessing the level of SOC as low, medium and high revealed that both methods are suitable in minimum values of SOC contents, and this is in agreement with Oscar(11) who reported that W-B is only suitable for determining low levels of organic matter in mineral soils whereas LOI is suitable for determining both higher organic matter levels usually in organic soils and the low levels of organic matter in mineral soils. Oxidized forms of carbon could be measured by W.B method while the loss of

decomposed and undecomposed organic matter by the LOI technique. The results are affected by other factors, particularly using the LOI technique for soil samples containing high content of carbonates and bicarbonates like calcareous soils and soils with a high content of clay minerals that trapped hygroscopic water within the interlayer spaces. The losses of water and $CO_2$ from the carbonates give inaccurate determination.

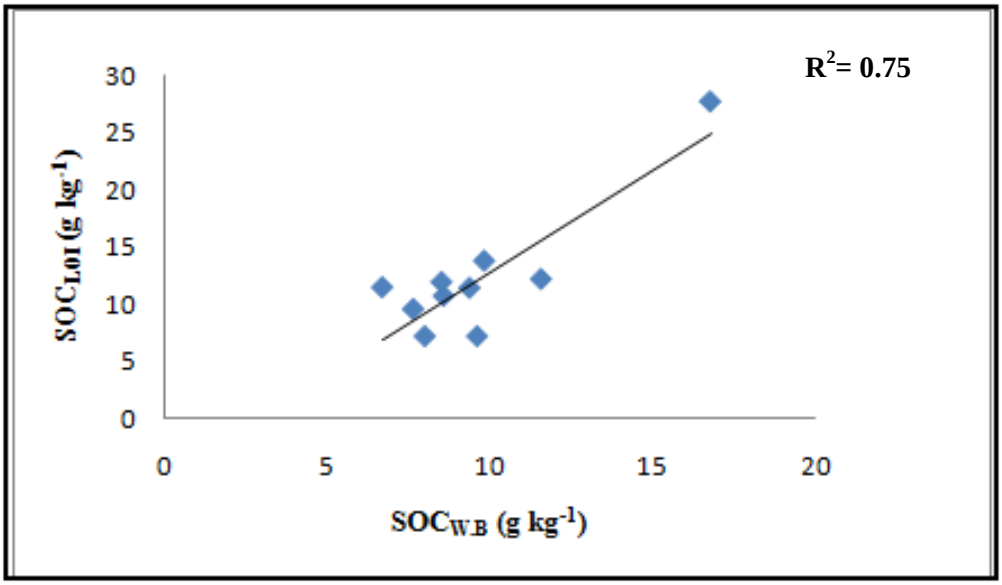


**Figure (3): Correlation between SOC measured by W.B method and LOI method for Irbil site.**

Variability of SOC determined by two methods vs. particle size distributions of soils

From 30 soil samples of different soils consisting; 13 were clay, 9 clay loam, 2 silty clay loam, 3 silty clay, 2 loam and1sandy loam. Their color varied from light brown to red-brown. Figure (5) shows the relationship between the SOC values of these two methods against particle size distributions of studied soils. Silty clay and clay soils gave the highest values of SOC contents by W-B and LOI techniques compared to the sandy loam and loam, gave the lowest values. Therefore, low

clay and high sand contents can contribute to low soil organic carbon contents. As a result, the amounts of SOC that obtained by W-B method were less than by LOI method. This indicates that the amounts of organic carbon revealed to be less when the soils are smaller in particle size. It may be due to the types of organic carbon associated with the soil fractions differ (17 and 16), so most of the organic carbon stored in the clay fractions (2);

**Table (1): Descriptive analyses of soil organic carbon contents (g $kg^{-1}$) determined by two methods in different soils of studied soil locations.**

| Governorate | LOI Method | | W.B Method | | Differences | |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Minimum | Maximum | Minimum | Maximum |
| Duhok | 6.57 | 29.70 | 3.00 | 19.00 | 3.57 | 10.70 |
| Irbil | 7.09 | 27.72 | 6.68 | 16.79 | 0.41 | 10.93 |
| Sulaimaniya | 4.19 | 27.50 | 3.60 | 17.71 | 0.59 | 9.79 |

(16) more clay particles provides more capable of including more stable organic carbon. So it has probably been more difficult to oxidize more stable organic carbon with W.B method in which it always retrieval only easily oxidizable of organic carbon. In addition, the types of organic carbon that combined with the soil of different sizes have an affect on the W-B method as well as, some soils that were easily oxidized would produce the soil organic carbon values close to the values of LOI method,

whereas other soils that were more difficult oxidized contribute to yield more difference between these two methods.

which calculated by LOI method. Hence, it will be very useful for determining SOC in soils with a large amount of SOM and low contents of clay. The amount of SOC that calculated by LOI method gave the highest values in silty clay and clay soils because clay adsorbs the water as the hygroscopic moisture between oven-drying and ignition occurring.

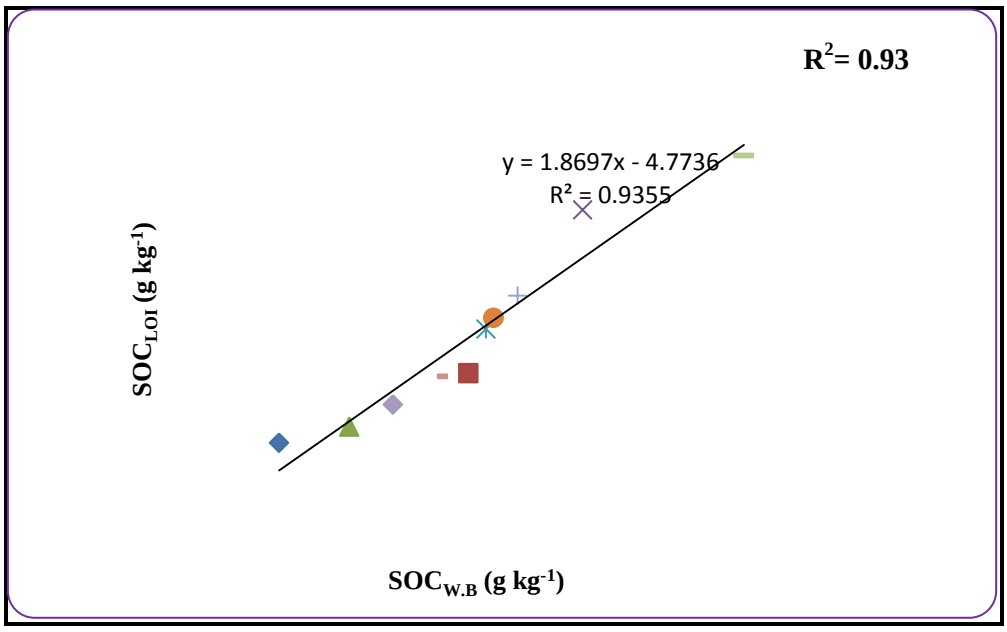


**Figure (4): Correlation between SOC measured by W.B method and LOI method for Sulaimaniya site**

More laboratories are transitioning from the W.B method to the LOI method due to the human health problems and environmental conditions. The overestimated of SOC contents in the case of LOI method might be due to a temperature that selected which was not accurate enough to reveal the differences of SOC in arid and semi-arid regions, it should be investigated the efficiency of

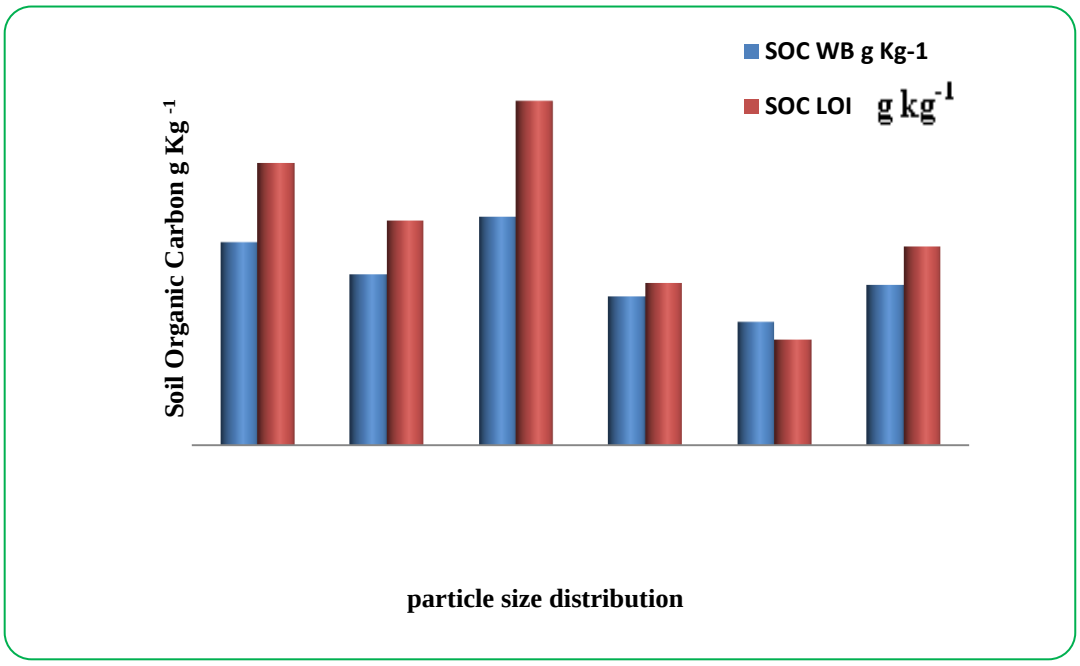


**Figure (5): Soil organic carbon by using LOI/W.B methods versus to particle size distribution of studied soils.**

the LOI method for arid soils with lower SOM content. So we recommended doing some study at different temperatures with the different time of ignition

## . Conclusion:

The values obtained by LOI methods significantly differed from the values generated by W.B method. It was observed in this study that the two methods were reliable but W.B method was more suitable, so the latter was suggested for soils with high clay content and also for calcareous soils. Therefore, the amount of clay had some potential on SOC content estimation

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# مقارنة بين طريقتي ولكي بلاك والفقد بالحرق لتقديرالكربون العضوي في ترب من مواقع مختلفة

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## المستخلص

ان الغرض من هذه الدراسة هو لأيجاد افضل طريقة لتقديرالكربون العضوي في التربة (SOC) بطريقتين، طريقة أكسدة دايكرومات المحمضة الرطبة، ولكي بلاك (W-B) وطريقة الفقد بالحرق (LOI). اجريت هذه الدراسة على 30 عينة من التربة بعمق (0-20) سم لثلاث مواقع من كل من محافظة دهوك وأربيل والسليمانية (اقليم كردستان-العراق). و قدرت البراميترات الاتية: الكاربون العضوي والتوزيع الحجمي للدقائق. وتم تحليل النتائج احصائيا بالطريقتين سابقتي الذكر بواسطة معادلات الانحدار الخطي البسيط. وجد أعلى القيم من محتوى الكاربون العضوي في التربة مع طريقة (LOI) وبقيم (29.70 - 4.19) غم كغم$^{-1}$ تربة, بينما كانت اوطأ القيم مع طريقة (W-B) وبقيم (19.0- 3.0) غم كغم$^{-1}$ تربة لكل المواقع المذكورة اعلاه. حيث وجدت علاقة ارتباط قوية بين هاتين الطريقتين و بمعامل الارتباط ($R^2$=0. 75, $p < 0.001$) ($R^2$ = 0. 93, p < 0.001), ($R^2$=0. 87, $p < 0.0001$) لكل من السليمانية ودهوك وأربيل بالترتيب. اظهرت هذه الدراسة ايضا بان الترب الطينية الغرينية والطينية اعطت أعلى قيم الكاربون العضوي باستخدام كلا الطريقتين مقارنة بالمزيجية التي اعطت اوطأ القيم. لذا فإن التربة التي تحتوي على نسبة طين وكربونات اكثر أعطت قيم عالية للكاربون العضوي في التربة باستخدام تقنية LOI عند درجة الحرارة العالية. واظهرت نتائج هذه الدراسة ايضا بان كلتا الطريقتين كانتا مناسبتين ولكن طريقة W-B مناسبة اكثر للتربة التي تحتوي على نسبة طين عالية وكذلك بالنسبة للتربة الكلسية.

الكلمات المفتاحية: الكاربون العضوي للتربة، ولكي بلاك، الفقد بالحرق، التوزيع الحجمي للدقائق .