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# **Application of the Walkley-Black titration for organic carbon quantification in organic rich sedimentary rocks**

Faina Gelman, Ruth Binstock and Ludwik Halicz

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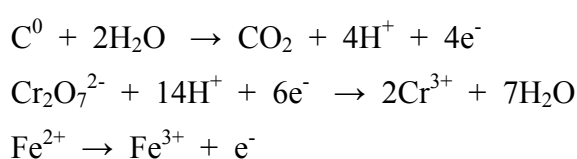
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## **Abstract**

Forty-three samples of Israeli organic-rich sedimentary rocks (oil shales) have been analyzed for organic carbon content by a modified Walkley-Black titration method and dry combustion method. A good correlation ( $R^2 = 0.92$ ) between the OC results obtained by two methods is observed, but a correction equation is suggested to be applied to OC results obtained by the Walkley-Black method ( $OC = 1.14 \cdot OC_{WB} - 0.83$ ). Considering the simplicity of the modified Walkley-Black titration method its general applicability to the analysis of total organic carbon content in the oil shale deposits may be preferable in many cases.

## 1. Introduction

The Walkley-Black (WB) titration method is one of the classical methods for rapid analysis of organic carbon (OC) in soils and sediments. The method is based on the oxidation of organic matter by potassium dichromate ( $K_2Cr_2O_7$ )-sulfuric acid mixture followed by back titration of the excessive dichromate by ferrous ammonium sulfate ( $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ ). The average oxidation number for organic carbon is considered as zero and the reactions involved into the WB titration method are as following:



Although the method is widely used for OC analysis in soils and sediments, the accuracy of the method remains an issue. One of the questionable points of the method is the extent of the oxidation by dichromate. In the early variations of the method (Walkley and Black 1934; Walkley 1947), the soil samples were not heated during the oxidation step and the mean recovery of OC was found to be about 76%. Therefore it was proposed to introduce a correction factor of 1.32 for the quantification of the OC content in the soil samples (Walkley and Black 1934). Afterwards it was proposed to apply extensive heating of the sample during oxidation (Mebius et al. 1960; Heanes et al. 1984) to overcome the concern of incomplete digestion of the organic matter. In that case, no correction factor was required. However, the temperature of the oxidation must be strictly controlled due to the possible decomposition of acidic dichromate above 150°C. This complicates appreciably the procedure and does not always lead to satisfactory results (Ayub and Boyd 1994).

In order to evaluate the accuracy of the WB titration, it is necessary to compare the results with those obtained by other methods. One of the most reliable methods for the OC analysis is a dry combustion based on the high-temperature oxidation of a sample, appropriately pretreated in order to remove completely inorganic carbon.

Numerous studies comparing the OC results obtained by these two methods have been conducted previously. However the deduced conclusions were not decisive. Thus, for example, a good agreement between the results was found for some types of Australian soils (Wang et al. 1996), whereas some underestimation in soil organic carbon content by WB titration for Indian soils was reported (Krishan et al. 2009). In the study comparing TOC in recent marine sediments, Leong and Tanner found that the values obtained by the dichromate method were too high for anoxic sediments and too low for oxic sediments (Leong and Tanner 1999).

Despite the numerous studies concerning the use of the dichromate titration for TOC analysis, the practical applications of the method are mainly limited to analysis of soils and recent marine sediments. In the present study we examined the use of the modified WB titration method for organic carbon analysis of oil shales. Exploitation of oil shale reservoirs for the fuel production has resumed its importance due to the increasing demand for fuel in the last decade. Organic carbon content is a primary decisive characteristic for the determination of the economic potential of the deposits. Nowadays, OC analysis of the oil shales is performed mostly by a dry combustion technique using different types of TOC analyzers. However, in many cases method utilization is restricted due to high instrumental expenses. In addition, sample pretreatment for the complete removal of inorganic carbon is required when the dry combustion method is used. Obviously, no necessity for inorganic carbon removal for the Walkley-Black titration considerably simplifies the procedure.

In the present study we examined a possibility of application of a modified classical dichromate oxidation method for the analysis of organic carbon in oil shales, comparing the results with those obtained by a dry combustion method.

## **2. Materials and methods**

### **2.1 Samples for OC analysis**

Forty three samples of organic rich sedimentary rocks (oil shales) collected from various depths of oil shale deposits from different parts of Israel were analyzed for OC content. Prior to the analysis the samples were dried at 60°C and ground down to 74  $\mu$  (200 mesh). Major inorganic elements of oil shales (Ca, Al, Si, P and Fe) contained in the samples were determined by ICP-OES (Optima 5300V - Perkin-

Elmer) by the standard analytical methods. Standard rock reference materials (SGR-1, SO-3, BCR-32) were analyzed repeatedly and compared with the certificate data to determine accuracy and precision of the analytical method.

## 2.2 OC analysis by modified Walkley-Black titration

A weighed amount (20-50 mg) of the dried, ground organic-rich sedimentary rock samples with of a variable quantity of organic carbon (6-18%) was treated with 5 ml of 0.4 N potassium dichromate solution ( $K_2Cr_2O_7$ ) followed by addition of 10 ml of concentrated sulfuric acid. The mixture was gently swirled and left at room temperature in a fume hood for 16-18 hours and then, 100 ml of triple-distilled water was added to the mixture. The excess of dichromate was back-titrated potentiometrically with the standard 0.2 N ferrous ammonium sulfate ( $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ ) solution. Blank titration of the acidic dichromate with ferrous ammonium sulfate solution was performed at the beginning of the batch analysis using the same procedure with no sedimentary rock added. One ml of 0.2 N ferrous ammonium sulfate is equivalent to the 0.009807 gr of  $K_2Cr_2O_7$  or 0.0006 gr of carbon. Organic carbon content in the sample was calculated as:

$$\text{Organic carbon (\%)} = (B - S) \times 0.0006 / m \times 100$$

where  $B$  is the volume of ferrous solution used in the blank titration,  $S$  is the volume of ferrous solution used in the sample titration,  $m$  is the mass of the sample in gr used in the analysis. No correction factor was applied to the OC content calculation.

## 2.3 OC analysis by the dry combustion method

Analysis of the organic carbon by dry combustion method was performed by an Elemental Analyzer (1112 Flash EA, Thermo-Finnigan) interfaced with an Isotope Ratio Mass Spectrometer (EA-IRMS Delta V Plus, Thermo Scientific), enabling simultaneous measurements of carbon quantity and carbon isotope ratio ( $\delta^{13}C$ ).

Aliquots of the ground sedimentary rock (~ 300 microgram) were weighed in silver capsules (5 mm X 8 mm). The silver capsules were placed into a specially machined ceramic block. The block was then placed inside a glass desiccator along with a dish containing 100 mL of the fresh concentrated HCl in order to remove any inorganic carbon. The desiccator was cleaned prior to use to ensure the absence of paraffin

grease and other organic materials. The samples were exposed to HCl vapor for 16 hours at room temperature, then removed (while remaining in the ceramic block) and heated in the oven for 1 hour at 60 °C to drive off residual HCl. To achieve higher temperature of the combustion (up to 1700°C) and then ensure a complete conversion of the organic carbon into CO<sub>2</sub>, the treated samples in silver capsules were wrapped in tin capsules (5 mm x 8 mm). The tin capsules were closed, folded into cube-shaped parcels and transferred to the autosampler tray of the CN Analyzer. Analysis of the carbon was performed by the CN analyzer interfaced to an Isotope Ratio Mass Spectrometer at the following conditions: the oxidation reactor filled with chromic oxide over silvered cobaltous-cobaltic oxide was maintained at 1020°C. The reduction reactor filled with reduced copper wire was maintained at 650°C. The chromatographic column for the gas separation was maintained at 50°C. Helium carrier gas flow was 100 ml/min. For the quantitative analysis of the organic carbon the instrument was calibrated by the high organic sediment standard OAS B-2151 (6.72%C, Elemental Microanalysis) in the range from 10 µg to 60 µg of carbon. Validity of the calibration curve over the time was checked by quantitative analysis of B-2151 standard and urea (laboratory standard) after every 6 samples. δ<sup>13</sup>C analysis was performed against a laboratory CO<sub>2</sub> standard gas calibrated relatively to PVB.

### **3. Results and discussion**

In this study we investigated the applicability of the WB method for the organic carbon analysis in oil shales. Numerous investigations performed on the Israeli oil shale reservoirs revealed that the main mineralogical phases of the organic rich sedimentary rocks are carbonates, clay minerals and apatite; other minor constituents are pyrite, gypsum and quartz (Shirav and Ginzburg 1983; Halicz 1984). Forty three samples of oil shale deposits from different parts of Israel were examined in the present study. Table 1 represents the major chemical content of these samples. As can be seen from the data, the samples vary in their chemical composition.

In principle, chemical components of the samples may affect the results of the WB titration. For example, the presence of chlorides or Fe<sup>2+</sup> can cause overestimation of the organic carbon due to the competitive reactions with dichromate. However this interference is supposed to be negligible for the Israeli oil shale samples due to a low

content of the dissolved Cl (< 0.1%) and the reduced Fe (< 0.2%) (Halicz, 1984). Another important factor potentially affecting the results of the WB titration is the composition of the organic matter. Unlike organic matter of the soils and sediments consisting mostly of humic substances, major components of the oil shales are kerogeneous materials. Due to a more aromatic and less oxidizable character of kerogen, incomplete OC oxidation by dichromate leading to underestimation of the OC content may be expected if no heating is applied. At the same time, it is likely to suggest that a less oxidizable structure of the kerogens may result in a more reduced carbon oxidation state as compared to that found in humic matter. Nevertheless, in the present study we assumed the complete oxidation of the OC and did not apply any correction factor adopting the assumption of classical WB method stating zero carbon oxidation state independently of the soil origin.

In order to confirm the accuracy of OC analysis by the modified WB method used in our study, we compared the OC results obtained by WB titration and Elemental Analyzer (EA). As it has been already mentioned, OC analysis by EA is based on the dry combustion technique and requires inorganic carbon removal from the sample prior to the analysis. In the present study the fumigation method was used for the carbonate removal (Komada et al. 2008). According to the standard procedure, the samples are exposed to HCl vapors for several hours, enabling simultaneous treatment of a large number of samples. Although in some cases, only a partial removal of the carbonate by fumigation were reported in the literature (Schubert et al. 2000), we assumed complete elimination of inorganic carbon based on the  $\delta^{13}\text{C}_{\text{org}}$  values of the treated samples. Taking into account that  $\delta^{13}\text{C}_{\text{org}}$  of Israeli organic rich sedimentary rocks is  $\sim -29\text{‰}$  (Schneider-Mor et al. 2007) and  $\delta^{13}\text{C}$  of inorganic carbon is usually close to  $0\text{‰}$ , even relatively small amounts of incompletely removed carbonate should cause a noticeable shift of  $\delta^{13}\text{C}$  to the more positive values. In our study all measured  $\delta^{13}\text{C}_{\text{org}}$  values of the treated samples ranged between  $-28.5\text{‰}$  to  $-29.4\text{‰}$ , indicating complete carbonate removal.

Analytical results for the organic carbon content obtained by the modified WB titration and EA were compared by regression analysis (Fig.1). The comparison of the data reveals a linear regression equation  $\text{OC}_{\text{EA}} = 1.14 \cdot \text{OC}_{\text{WB}} - 0.83$  with a correlation coefficient ( $R^2$ ) of 0.92. Although a good correlation ( $R^2 = 0.92$ ) between the results of these two methods is achieved, the obtained intercept significantly deviates from zero. This “intercept effect” caused by a more pronounced underestimation of the OC

by WB titration method in the samples with higher content of the organic matter ( $\sim\text{OC} \geq 10\%$ ). We suppose that this underestimation phenomenon could be explained by the change of the mechanism of organic matter conservation in sedimentary rocks of different OC content (Bushnev and Burdel'naya, 2009).

#### **4. Conclusions**

While the Walkley-Black titration method was developed as a convenient method for the determination of the organic carbon content in soils and marine sediments, it appears to be applicable for the analysis of organic rich sedimentary rocks as well. Based on the linear regression analysis of the results obtained in the present study, a correction equation is suggested to be applied to OC quantified by the Walkley-Black method ( $\text{OC} = 1.14 \cdot \text{OC}_{\text{WB}} - 0.83$ ). Considering that the modified WB titration is a simple technique as only basic equipment is required for the analysis and no carbonate removal pretreatment of the sample is needed, its use for the organic carbon content analysis in the oil shale deposits could be preferable for many cases. Supplementary research, regarding the applicability of a modified WB method for the organic carbon analysis in oil shales from elsewhere in the world, is being performed.



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## Appendix

Figure 1. Regression analysis of WB titration and EA dry combustion results.

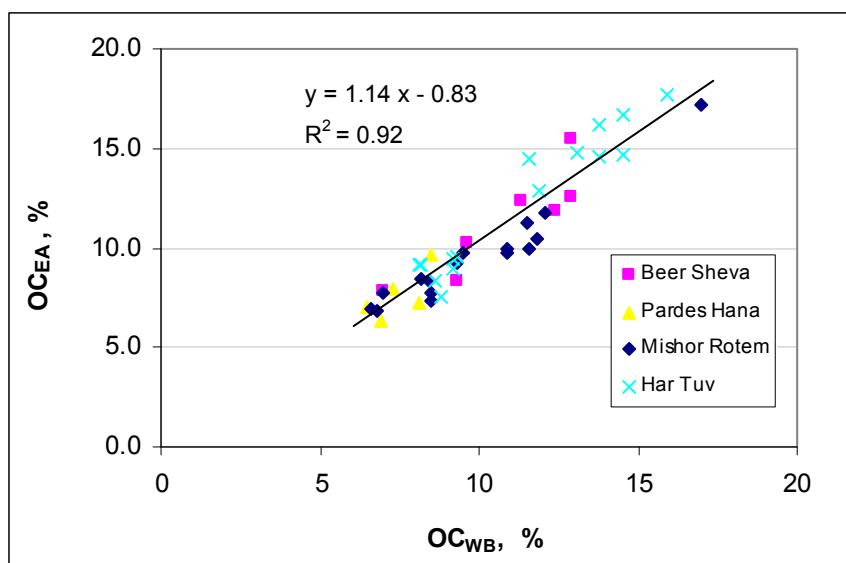


Table 1. Chemical composition of the sedimentary rocks samples

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	As	Ba	Cd	Cr	Cu	Mn	Mo	Ni	Pb	Sr	U	V	Zn	TOC (EA)	TOC (WB)
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	(%)	(%)
HT-1	8.7	2.4	0.9	0.15	28.7	0.6	3.0	4.6	0.3	6.6	360	0.8	280	75	30	7	139	2.6	970	19	81	217	16.7	14.5
HT-2	5.5	1.3	0.5	0.09	34.6	0.4	2.0	4.6	0.3	5.8	265	0.7	243	79	20	7	202	1.5	933	16	54	214	16.2	13.8
HT-3	5.4	1.5	0.6	0.09	35.5	0.4	2.0	4.3	0.3	6.7	260	0.8	221	64	24	9	172	1.6	954	16	59	182	14.5	11.6
HT-4	5.6	1.5	0.6	0.09	33.9	0.5	1.9	4.6	0.3	6.9	303	0.8	219	85	22	9	141	2.2	1094	19	45	217	14.7	14.5
HT-5	7.4	2.3	0.8	0.13	30.3	0.5	1.2	5.5	0.3	7.3	269	0.6	232	67	21	7	123	2.2	849	14	53	185	17.7	15.9
HT-6	12.2	5.1	2.0	0.21	23.9	0.5	1.1	3.7	0.4	7.1	150	0.4	287	59	42	5	134	5.7	1000	10	85	146	9.1	8.1
HT-7	7.8	3.1	1.5	0.13	29.4	0.3	1.2	3.4	0.3	7.0	90	0.5	201	51	34	5	108	4.0	1091	10	61	114	9.1	8.2
HT-8	4.5	1.1	0.4	0.07	31.3	0.6	3.1	5.4	0.2	6.1	172	0.8	232	70	17	8	128	2.3	1164	20	59	202	14.6	13.8
HT-9	5.1	1.5	0.6	0.08	34.4	0.5	1.1	5.5	0.2	9.5	125	0.7	182	89	18	9	150	1.8	1177	14	35	199	14.8	13.1
HT-10	13.1	5.2	2.9	0.19	23.5	0.9	0.8	5.1	0.3	15.1	277	0.4	260	31	31	9	85	3.7	749	8	71	88	9.4	9.2
HT-11	11.1	4.4	2.0	0.19	29.5	0.5	1.2	3.5	0.3	7.9	263	0.6	245	60	44	8	139	5.2	966	13	83	147	8.3	8.6
HT-12	4.3	1.0	0.4	0.06	37.2	0.4	2.1	4.2	0.1	6.8	97	0.8	213	64	20	7	111	2.2	1099	22	57	178	12.9	11.9
HT-13	6.4	2.3	1.0	0.10	37.2	0.4	2.8	3.8	0.2	9.3	121	0.7	212	49	22	33	106	2.9	1185	23	48	140	8.9	9.2
HT-14	6.3	2.1	1.1	0.10	35.4	0.8	2.2	3.3	0.1	5.6	2159	0.5	187	41	30	10	100	2.1	1095	15	43	155	9.5	9.3
HT-15	7.5	2.6	1.4	0.11	36.5	0.5	1.5	3.6	0.2	8.9	146	0.4	175	31	33	9	80	3.0	916	11	47	81	7.5	8.8
MR-1	7.4	1.7	0.8	0.1	41.8	1	1.3	12.2	nd	89	59	2.1	465	129	53	30	244	4.7	1442	42	140	380	17.0	17.2
MR-2	7.9	2.3	1.5	0.11	50.1	1	3.5	9	nd	35	51	1.4	333	97	54	29	184	4.1	1575	33	142	216	9.5	9.7
MR-3	11.9	4.3	2.8	0.17	47.6	1	3.8	12.9	nd	21	63	1.3	400	108	78	33	210	5.6	1506	40	161	253	10.9	9.7
MR-4	18.2	8.3	4.4	0.28	37.5	0.9	2.1	9.7	nd	30	75	0.8	390	89	105	22	181	8.4	1397	25	166	177	7.0	7.7
MR-5	12.8	5.7	2.8	0.21	44.7	0.6	1.2	7.1	nd	11	45	0.5	232	61	45	11	126	4.0	1331	13	89	126	6.8	6.8
MR-6	19.6	9.9	4	0.32	35.2	0.7	1.5	6.8	nd	11	59	0.6	300	67	59	10	129	6.3	1072	16	126	136	6.6	6.9
MR-7	16.2	7.1	3.1	0.26	31.1	0.8	1.7	8.3	nd	11	435	0.7	323	75	42	20	164	4.4	934	22	117	194	11.5	11.3
MR-8	15.1	6.7	2.7	0.25	41.3	0.6	1.7	7.4	nd	9	51	0.5	265	63	48	11	128	4.0	1112	14	99	132	8.5	7.7
MR-9	21.4	9.3	4	0.35	32.3	0.9	2.1	9.4	nd	17	58	0.5	314	70	64	13	149	5.6	897	16	123	146	9.3	9.2
MR-10	14.5	6.2	2.3	0.23	39.5	0.7	1.7	7.4	nd	8	52	0.5	264	62	38	10	127	3.8	1123	15	98	143	8.2	8.4
MR-11	14.9	6.4	2.7	0.23	40.2	0.7	2	7	nd	10	52	0.5	251	64	39	10	126	4.3	1067	15	91	143	8.4	8.3
MR-12	10.6	3.6	1.8	0.14	42.7	0.9	2.6	7.7	nd	13	41	0.7	255	70	40	15	127	3.5	1033	21	91	150	10.9	10.0
MR-13	11.5	4	2	0.16	48	1.3	2.8	9.8	nd	13	45	0.9	290	71	34	15	135	3.0	1180	25	96	164	11.8	10.5
MR-14	8.6	2.2	1.6	0.11	43.7	1	3.5	9.3	nd	23	46	1.3	307	72	24	37	137	3.2	1109	34	116	185	12.1	11.8
MR-15	8.4	1.3	0.5	0.11	44.1	1	3.9	8.4	nd	15	54	1.8	260	63	16	33	128	1.6	1100	38	100	210	11.6	9.9
MR-16	18.9	8.3	3.2	0.29	38.1	0.7	2	7	nd	11	62	0.5	285	73	46	7	146	5.0	1061	19	93	157	8.5	7.3
BS-1	6.1	1.9	0.7	0.11	33.0	0.5	2.3	5.9	0.3	10	104	0.8	269	90	27	12	141	2.2	1182	21	76	246	15.5	12.9
BS-2	4.6	1.4	0.7	0.07	35.0	2.2	4.0	5.4	0.1	12	57	1.5	212	40	22	36	94	0.8	1152	27	59	147	11.9	12.4
BS-3	9.3	3.2	1.1	0.17	31.2	1.8	1.6	5.5	0.3	19	48	0.8	246	37	22	14	89	1.9	901	19	65	121	12.4	11.3
BS-4	7.7	3.0	1.8	0.14	34.0	0.5	1.8	5.7	0.3	16	309	0.7	231	80	65	15	120	5.1	1228	17	117	175	10.3	9.6
BS-5	9.4	4.2	1.6	0.19	31.0	0.5	1.6	6.3	0.3	16	67	0.3	366	65	35	7.7	113	3.0	1163	13	66	167	12.6	12.9
BS-6	2.8	1.0	0.4	0.05	45.3	0.4	2.4	3.5	0.1	6	31	0.8	132	35	16	18	74	0.7	1428	19	39	136	7.8	7.0
BS-7	8.8	3.8	2.3	0.16	30.1	1.4	1.2	6.3	0.3	27	33	0.7	235	29	27	15	69	2.6	809	12	72	95	8.3	9.3
PH-1	5.4	1.7	0.8	0.10	41.8	0.5	1.0	3.1	0.2	7	305	0.4	115	48	39	10.4	74	59.2	1228	11	47	329	6.3	6.9
PH-2	8.3	3.0	1.1	0.15	36.4	0.6	1.3	3.7	0.3	11	156	0.4	164	38	30	9	70	2.2	1368	10	50	117	7.2	8.1
PH-3	8.5	2.5	1	0.13	30.5	0.7	1.9	3.4	0.3	9	80	0.6	184	55	40	12	98	3	1035	17	60	140	9.6	8.5
PH-4	8.6	3	1.2	0.14	30.6	0.6	1.1	2.9	0.2	9	65	0.5	170	38	35	9	78	3	930	12	57	108	7.0	6.5
PH-5	6	2.2	0.9	0.1	33.2	0.6	1	3.1	0.2	10	40	0.5	173	40	30	8	92	2	940	14	78	125	7.9	7.3

HT - Har Tuv    MR - Mishor Rotem    BS - Beer Sheva    PH - Pardes Hana