

AN ABSTRACT OF THE THESIS OF

Glenn Wood Simkins for the M.S. in Chemistry
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Title THE POTASSIUM IODATE METHOD FOR DETERMINING ORGANIC
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(Major Professor)

The chemical literature contains numerous references to various methods used in estimating the organic content of soils. All of these which have been proposed or adopted are subject to rather serious limitations. These various types of methods and their limitations are discussed. Probably the greatest weakness of both dry and wet combustion methods lies in the necessity of employing a factor which is based on the assumption of the percentage of carbon in the organic matter.

Two general types of measurements are used. In one method the CO_2 evolved is measured, and in the other method the reducing capacity of the soil is measured. In the method suggested, the writer has attempted to combine both of these measurements into a single determination with the hope that the combination might give a truer index as to both the amount and the nature of the organic matter and perhaps give a means of establishing the true value of this factor.

KIO_3 , a new oxidizing agent for soil carbon determinations, was selected in this procedure because of its stability at high temperatures and its ability to oxidize organic compounds completely to CO_2 with no evolution of free oxygen during the reaction (a property that is lacking in most oxidizing agents, notably $\text{K}_2\text{Cr}_2\text{O}_7$).

The ease of oxidation of several series of pure organic compounds was determined to find the optimum conditions for complete combustion.

For the soil analyses a closed system was used. The CO_2 evolved was absorbed by standard alkaline solution, and from this measurement the amount of carbon calculated. The excess oxidizing agent after the reaction has taken place was measured and from this the amount of reducing material in the soil calculated.

Results indicated that probably a great portion of the organic matter in most soils is of carbohydrate nature. The determination of the organic matter from the measurement of CO_2 evolved appears to be more reliable than the determination of the soil's reducing capacity.

No correlation was found between ratio of oxygen consumed to carbon and the factor used to convert mg. of carbon to mg. of soil organic matter. However, it does indicate when a soil contains inorganic carbonates.

ABSTRACT (Cont.)

The combined data (percent of organic matter by loss-on-ignition by Rather's method, CO_2 produced by wet combustion, and KIO_3 used) gave some clue as to the nature of these organic constituents. On the assumption that these compounds were composed of hydrogen, oxygen, and carbon only, the percentages of each element in soil organic matter was calculated for soil samples studied. It is hoped that this data may give some means of measuring the biological activity of the soils.

THE POTASSIUM IODATE METHOD FOR DETERMINING
ORGANIC MATTER IN SOILS

by

GLENN WOOD SIMKINS

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APPROVED:


Assistant Professor of Chemistry

In Charge of Major


Head of Department of Chemistry


Chairman of School Graduate Committee


Chairman of College Graduate Council

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THE POTASSIUM IODATE METHOD FOR DETERMINING
ORGANIC MATTER IN SOILS

The chemical literature contains numerous references (1) (6) (8) (9) (10) (11) (12) to various methods used in estimating the organic content of soils. All of these which have been proposed or adopted are subject to rather serious limitations.

The loss-on-ignition method which has been used considerably in the past has inherent errors that make it practically worthless as an index of the organic matter of a soil. Attempts have been made to eliminate these sources of error by a modification suggested by Rather (10). This modification consists of pre-treating the soil by digestion with a mixture of HCL and HF to remove the carbonate, the hydrated, and the unoxidized minerals from the soil prior to ignition. This pretreatment eliminates those factors which interfere with the accuracy of this determination so that it is now believed that with this modification the method is superior to the organic carbon determination.

While some investigators have attempted to measure the soil organic matter from a nitrogen determination, it is generally recognized that such estimations are not trustworthy because of the great variations in the carbon-nitrogen ratio (2) (9).

Many investigators consider dry combustion methods to

be the most precise available (9). In view of the fact that the employment of this method requires the use of a factor (based on the assumption of the percentage of carbon (9) in the organic matter) this method at best is only an approximation. It has been demonstrated that the percentage of carbon of organic material removed from the soil by solvents varies between 44 and 64% (10). In addition, other errors arising from carbonate and elementary carbon are inherent in this determination.

Wet combustion methods are more convenient, though perhaps not as precise as the loss-on-ignition methods. The results from these methods may be obtained from two different types of measurements. Some measure the organic matter in terms of the CO_2 evolved, employing a factor as in dry combustions. Others measure the amount of reducing material in the soil by determining the amount of oxidizing agent required for complete combustion of the organic material.

The former measurement (evaluation of organic matter in terms of CO_2) does not give results including elementary carbon, but does include carbonate carbon as well as having other limitations. In the case of certain oxidizing agents (notably $\text{K}_2\text{Cr}_2\text{O}_7$, which is most generally used) most organic compounds are not oxidized completely to CO_2 under the conditions employed (5).

The Schollenberger method (11) or its modifications

is probably the most widely adopted of the wet combustion procedures. According to his method the soil sample is oxidized with excess $K_2Cr_2O_7$ in 36 N H_2SO_4 . This charge is heated to 175 degrees in 90 seconds, cooled and titrated to determine the extent of the reduction. The organic matter is estimated from these results.

The wide-spread use of this method has been largely due to its simplicity, rapidity, and convenience. The determination appears to be purely empirical. Many investigators have shown that most organic compounds are not completely oxidized under the conditions suggested by Schollenberger, and that in an oxidation involving dichromate both CO and oxygen are evolved (5). While no claim is made as to the precision of the method, it has so many sources of error (factor, etc.) that results obtained by this procedure can at best give only a rough estimate.

Obviously the greatest weakness of both the dry and wet combustion methods lies in the necessity of employing a factor.

It is ~~also~~ surprising that no attempt has been made to combine both measurements (CO_2 evolved, and reducing capacity) into a single determination. It is quite possible that these measurements might give a truer index as to both the amount and nature of the organic matter and perhaps give a means of establishing the true value of this factor. The writer has made an attempt to do this

in the method to be discussed.

EXPERIMENTAL

Of all the possible oxidizing agents for such a determination KIO_3 appeared to offer the greatest possibilities. It is stable, easy to obtain pure, capable of oxidizing organic compounds completely to CO_2 , (13) (4) and gives no evolution of free oxygen during the reaction.

Although it has been reported in the literature that KIO_3 is stable in H_2SO_4 solutions up to 250 degrees centigrade (13), initial experiments were conducted to check its stability in 36 N H_2SO_4 . The results of these tests indicated a slight decomposition with temperatures as low as 210 degrees. Further work, however, showed that it was possible to heat this mixture to 200 degrees for as long as one hour without measurable decomposition.

In order to determine the relative ease of oxidation under these conditions, several series of pure organic compounds were tested. Sucrose, succinic acid, mercuric acetate, benzoic acid, and salicylic acid were oxidized with no difficulty. These results merely confirmed the work of Strebinger (13). Potassium acid phthalate, however, was found to be very resistant to oxidation by this method, and under the above conditions was only partially oxidized. This has been confirmed by Williams and his co-workers (4) who have reported a few compounds which are not easily

attacked by KIO_3 . However, since compounds reported (nicotinic acid and phthalate) are not likely to be present in soils in appreciable amounts, the inability to oxidize them should not introduce a serious objection.

The apparatus that was finally adopted was a modification of that used by Heck (8). In the opinion of the writer there were several objections to the original system:

1. The reaction was carried out in a 500 ml. rubber-stoppered flask at temperatures of boiling acid.
2. The CO_2 absorption column appeared to be too short to insure complete absorption of the gas.
3. The volume of the system was entirely too large to be easily flushed prior to and following the reaction.

In addition, changes had to be made in the construction of the original apparatus to remove the free iodine which was liberated. This was accomplished by passing the gases through solutions of KI and $Na_2S_2O_3$; the bulk of the iodine being removed by the KI and last traces by the thio-sulphate.

The apparatus that was used in the present investigation is illustrated in Figure I. The reaction chamber, constructed from a Pyrex No. 20 standard taper, measured 12 inches over all. In order to cut the time of flushing to a minimum, the absorption vessel M was equipped with a

siphon. This permitted the vessel to be filled with distilled water which was easily removed and replaced by CO_2 free air.

The three-way stopcock J served to by-pass the flushing gas during the initial flushing. The absorption column N was 36 inches long.

PROCEDURE

The reaction vessel was charged with 1 gm. of oven-dried soil and 1 gm. of recrystallized KIO_3 . The stopcock C on the reaction vessel and the ground-glass joint were lubricated with syrupy phosphoric acid. The absorption unit MN was filled with distilled CO_2 free water, and the suction bottle with tap water. By adjusting stopcock J, the unit MN was cut out of the system, and water permitted to siphon rapidly from the suction bottle R. Three liters of flushing gas will remove any residual CO_2 that might have been in the system. After J was closed, the stopper at the upper end of column N was replaced with a drying tube filled with soda-lime, while the water was siphoned from N through O; then with the original stopper replaced in N, after closing pinchclamp Q, J was again opened and as the water siphoned from vessel M, the CO_2 absorption unit was emptied of water and filled with CO_2 free air.

After stopcock J and pinchclamp O are closed, exactly

50 ml. of standard NaOH was introduced by means of a burette through the upper end of column N, and N was so adjusted that the solution stands a little more than half way up in the column. Pinchclamps Q and S were opened, stopcock J was opened and the siphoning permitted to proceed at about 1 drop per second.

One half ml. of distilled water was pipetted into the reaction chamber through BC, then 10 ml. of concentrated H_2SO_4 which had been boiled to insure removal of organic matter.

The bath (phosphoric acid mixture (3)) was adjusted to surround the lower 4 or 5 cm. of the reaction chamber, and the temperature raised slowly to 200 degrees centigrade. If there was much organic matter present, rapid reaction began around 100 degrees. Care had to be exercised to prevent a reaction so rapid as to cause "backing up". The temperature was maintained at 200 degrees with a micro-burner.

After 60 minutes the bath was removed and the system again flushed with 3 liters of air. The contents of the reaction vessel were neutralized with NaOH and boiled to expel iodine. While cooling this solution and drying the reaction vessel in the oven, the contents of the CO_2 absorption unit was titrated with standard HCL (the absorbed CO_2 is precipitated with $BaCl_2$). From this titration it was possible to calculate the weight of carbon

which was oxidized.

After this titration, the absorption unit was again filled and put in place in the system.

When the KIO_3 solution from the reaction vessel was cool, it was made alkaline to precipitate iron that was present in all of the samples. The resulting precipitate, along with the siliceous material, was filtered out and aliquots of the filtrate were titrated with thiosulphate (7). From this titration the amount of KIO_3 required for the oxidation of the soil can be calculated.

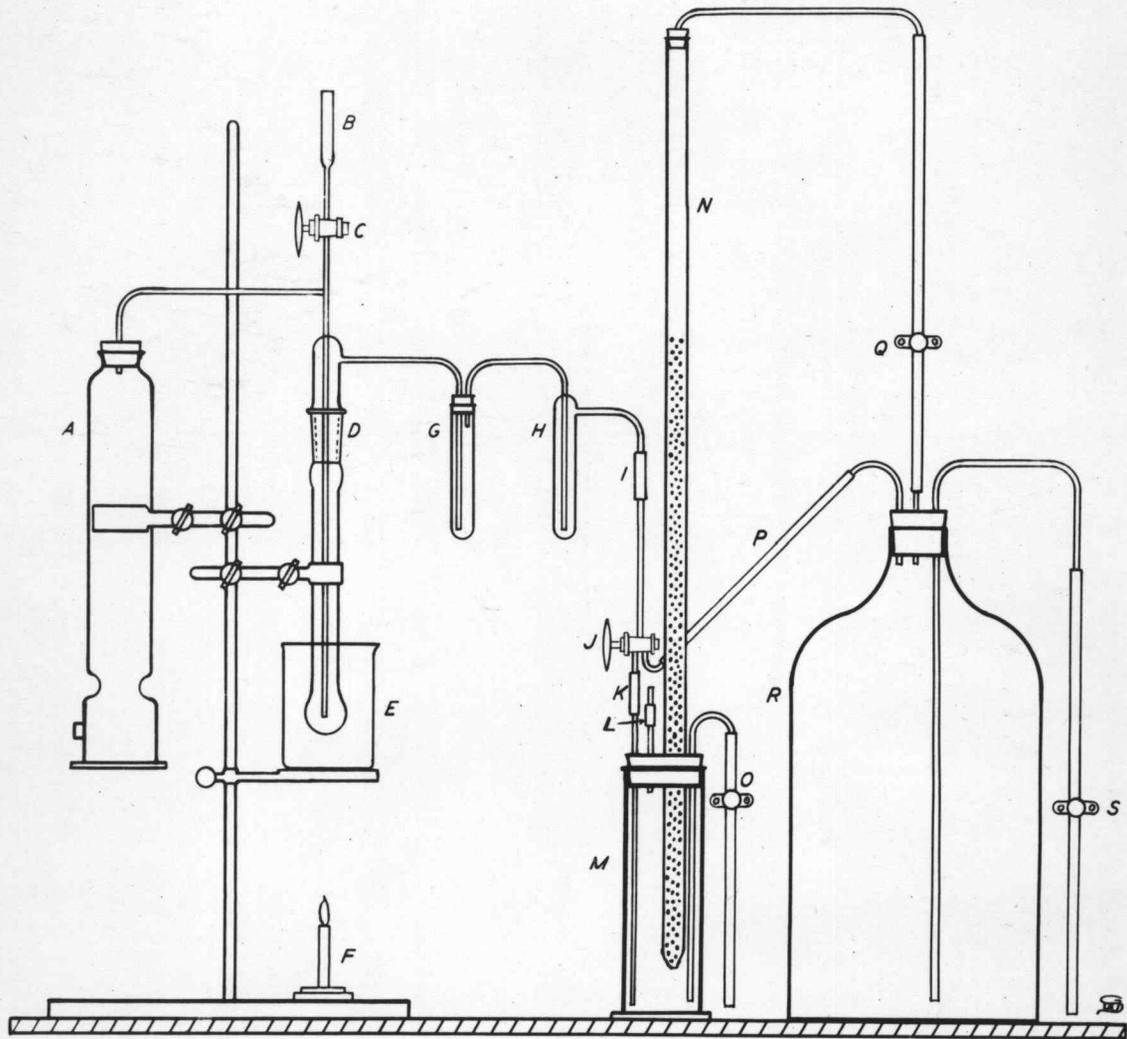


FIGURE 1.

DISCUSSION AND RESULTS

Results obtained by the use of KIO_3 are given in Tables I, II, and III.

The percentage of carbon calculated from KIO_3 used in the oxidation was based on the assumption that the soil organic matter was carbohydrate in nature and hence the oxygen consumed was a measure of the carbon content.

From this work it is evident that the determination of organic matter from measurement of CO_2 evolved is more reliable than the determination of its reducing capacity.

The percentage of organic matter obtained for the CO_2 data was made on the assumption that soil organic matter should on the average contain 58% carbon (9).

Oxygen consumed to carbon ratios were calculated in an attempt to find some correlation between this ratio and the factor used to convert mg. of carbon to mg. of soil organic matter. As far as the writer was able to determine, no correlation exists between these values. The determination of oxygen consumed gave no indication as to the true value of the factor. However, it does indicate when a soil contains inorganic carbonates.

The combined data (percent of organic matter by loss-on-ignition by Rather's method (10), CO_2 produced by wet combustion, and KIO_3 used) gave some clue as to the nature of these organic constituents. On the assumption that

these compounds were composed of hydrogen, oxygen, and carbon only, the percentages of each element in soil organic matter was calculated for soil samples studied. Although all samples used were supposed to have been carbonate free, analyses indicate that some of them must have contained carbonate carbon. It is hoped that this data may give some means of measuring biological activity of the soils. The results from these calculations are tabulated in Table III.

The following abbreviations are used in Tables I and III under the columns headed "Type".

S-----Sandy or sand
C-----Clay
L-----Loam
Crs.--Coarse
F-----Fine
Si-----Sitly
G-----Gravelly

TABLE I.

Sample	Depth	Type	% C--Meas'd.	% C--Calc'd. from KIO ₃ used
Umatilla				
19064	0-8	SCL	2.95	2.98
19065	8-27	SCL	1.24	1.25
19066	27-42	SCL	.55	.63
Rupert				
19076	0-8	Crs.S	1.66	1.78
19077	8-21	Crs.S	.80	.84
19078	21-38	Crs.S	.56	.58
Umatilla				
19079	1½-8	FSL	1.59	1.50
19080	8-18	FSL	1.26	1.14
19081	18-28	FSL	.43	.36
Palouse				
19116	0-4	Si.L	2.26	2.33
19117	0-8	Si.L	2.44	2.50
19118	4-21	Si.L	2.35	2.62
Umatilla				
19162	0-14	Onyx L	1.08	1.37
19163	14-40	Onyx L	.56	.89
Josephine County				
19903	0-8	GL	1.16	1.22
19904	8-18	GL	.54	.57
19905	18-36	GL	.34	.42
Josephine County				
19906	0-8	FSL	.91	.94
19907	8-18	FSL	.63	.62
19908	18-36	FSL	.28	.29
Salem				
19909	0-8	SL	1.21	1.19
19910	8-18	SL	.60	.58
19911	18-36	SL	.34	.34
Josephine County				
19912	0-7	GL	2.16	2.25
19913	8-18	GL	.25	.31
Umatilla				
19061	0-5	L	1.97	2.21
Pilot Rock				
19067	0-8	Si.L	.99	1.32
Walla Walla				
19070	0-8	Si.L	1.00	1.34

TABLE II.

Sample	O-C ratio	% Org. Matt. from CO ₂	% Org. Matt. OSC Exp. Sta.
Umatilla			
19064	2.69	5.09	5.17
19065	2.71	2.14	2.33
19066	3.03	.96	.99
Rupert			
19076	2.85	2.87	3.26
19077	2.82	1.38	1.65
19078	2.73	.95	1.09
Umatilla			
19079	2.53	2.74	1.74
19080	2.43	2.17	1.26
19081	2.26	.74	.96
Palouse			
19116	2.75	3.90	4.00
19117	2.75	4.04	4.42
19118	2.99	4.05	4.09
Umatilla			
19162	3.39	1.86	2.07
19163	4.28	.97	1.21
Josephine County			
19903	2.80	2.05	1.92
19904	2.80	.93	.74
19905	3.26	.59	.41
Josephine County			
19906	2.73	1.57	1.38
19907	2.62	1.09	.81
19908	2.73	.49	.41
Salem			
19909	2.64	2.08	1.95
19910	2.60	1.04	.91
19911	2.66	.58	.62
Josephine County			
19912	2.77	3.73	3.52
19913	3.36	.44	.45
Umatilla			
19061	2.99	3.40	3.34
Pilot Rock			
19067	3.56	1.70	1.82
Walla Walla			
19070	3.55	1.73	1.85

TABLE III.

Sample	Depth	Type	Soil organic matter		
			% C	% H	% O
Umatilla					
19064	0-8	SCL	57.2	5.0	38.0
19065	8-27	SCL	53.5	5.4	41.3
19066	27-42	SCL	56.3	7.2	36.7
Rupert					
19076	0-8	Crs.S	51.0	6.2	42.5
19077	8-21	Crs.S	48.5	7.2	44.3
19078	21-38	Crs.S	51.3	5.8	42.7
Umatilla					
*					
19081	18-28	FSL	44.9	4.1	51.3
Palouse					
19116	0-4	Si.L	56.5	5.4	38.3
19117	0-8	Si.L	55.3	5.4	39.4
19118	4-21	Si.L	57.5	6.1	36.4
Umatilla					
19162	0-14	Onyx L	51.8	9.2	38.6
19163	14-40	Onyx L	46.5	13.8	39.6
Josephine County					
19903	0-8	GL	60.5	5.2	34.4
19904	8-18	GL	73.0	4.1	23.0
19905	18-36	GL	83.0	7.3	9.8
Josephine County					
19906	0-8	FSL	65.9	4.3	29.7
19907	8-18	FSL	77.8	1.9	20.4
19908	18-36	FSL	68.3	3.9	27.8
Salem					
19909	0-8	SL	61.5	4.1	34.4
19910	8-18	SL	66.0	3.3	30.8
19911	18-36	SL	54.9	5.0	40.2
Josephine County					
19912	0-7	GL	61.3	4.9	33.8
19913	8-18	GL	55.6	9.3	35.1
Umatilla					
19061	0-5	L	59.0	6.7	34.4
Pilot Rock					
19067	0-8	Si.L	54.3	10.5	35.2
Walla Walla					
19070	0-8	Si.L	54.1	10.4	35.5

* 19079 and 19080 appear to contain carbonates.

SUMMARY

1. An apparatus for determination of total carbon and reducing capacity of soils is reported.
2. A method is given for the determination of the nature of soil organic matter.
3. A new oxidizing agent for soil carbon determinations is suggested.

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