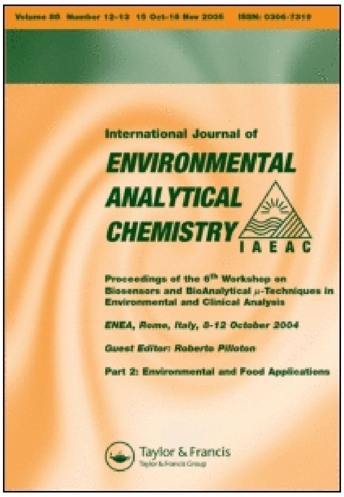

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Towards a Standard Method for the Measurement of Organic Carbon in Sediments

C. M. Lee[a]; D. L. Macalady[a]
[a] Colorado School of Mines, Golden, Colorado, USA

To cite this Article Lee, C. M. and Macalady, D. L.(1989) 'Towards a Standard Method for the Measurement of Organic Carbon in Sediments', International Journal of Environmental Analytical Chemistry, 35: 4, 219 — 225

To link to this Article: DOI: 10.1080/03067318908028396

URL: http://dx.doi.org/10.1080/03067318908028396

Intern. J. Environ. Anal. Chem., Vol. 35, pp. 219–225
Reprints available directly from the publisher
Photocopying permitted by license only

TOWARDS A STANDARD METHOD FOR THE MEASUREMENT OF ORGANIC CARBON IN SEDIMENTS

C. M. LEE and D. L. MACALADY

Colorado School of Mines, Golden, Colorado, 80401, USA

(Received 12 July 1988; in final form 20 September 1988)

The precisions achieved by two different methods for analysis of organic carbon in soils and sediments were determined and compared. The first method is a rapid dichromate oxidation technique (Walkley–Black) that has long been a standard in soil chemistry. The second is an automated coulometric titration method for which commercial instrumentation is available. The latter method shows relative standard deviations that are six to twenty times smaller than the dichromate oxidation technique. Development of a standardized sediment with a low level of organic carbon is recommended in order to facilitate the evaluation of the precision and accuracy of organic carbon measurement techniques.

KEY WORDS: Organic carbon, sediments, coulometric titration, Walkley–Black titration.

INTRODUCTION

Organic carbon has unquestioned importance in many environmental chemical and physical processes. Examples include the sorption of pollutants by sediments and soils and environmental reduction-oxidation reactions. Karickhoff[1] suggested that sorption of hydrophobic compounds by natural materials may be modeled successfully by considering only the fraction of organic carbon in the soil or sediment. He defines a partition coefficient based solely on organic carbon as

$$K_{oc} = K_p / oc$$

where K_p is the partition coefficient and *oc* is the fraction organic carbon.[2] Several researchers have commented on the role of natural organic carbon compounds in redox reactions involving pesticides in the environment.[3–6] Southwick and Willis[3] and Tratnyek[6] suggested that possible reducing agents for particular pesticides include key components of natural organic matter.

In these cases and others, the precise measurement of organic carbon in soils, sediments and natural waters is crucial to the study of the process. Yet, there is no universally accepted analytical method for determining organic carbon in such systems. Many different methods of varying accuracy and precision have been employed making valid comparisons of the findings published in the environmental literature quite difficult. According to Powell *et al.*,[7] instrumental techniques are not the limiting factor as long as high-temperature combustion is included.

Table 1 Characteristics of EPA sediments[10]

Sediment	*pH*	*CEC (meq/100 g)*	*Total N (%)*	*Organic carbon (%)*	*Sand (%)*	*Clay (%)*	*Silt (%)*
EPA-10	7.80	14.58	0.183	2.10	6.3	21.8	71.9
EPA-16	6.50	10.50	0.116	1.20	0.5	39.0	60.5

In our laboratory, we require accurate measurements of organic carbon in materials such as soils, sediments, and aquifer materials. We compared two methods: (1) the Walkley–Black titration as described by Allison,[8] and (2) automated coulometric titration.[9]

Hassett *et al.*[10] used the Walkley–Black method to determine the organic carbon content of a group of soils and sediments that have since been widely used for environmental studies. The Walkley–Black has long been a standard method for organic carbon determination in the soil sciences. The method uses materials and equipment readily available at reasonable cost. It is simple to use and does not require extensive sample preparation.

The coulometric method we used also involves little sample preparation and is a simple, rapid technique. It does, however, require a substantial initial instrument cost.

The analyses reported herein are presented to provide comparison of the widely-used Walkley–Black technique to an instrumental method. No such comparisons are available in the literature. Also, the precision of the coulometric method has not been reported for analyses of soils and sediments. We compare the two methods by determination of the organic carbon content of three sediment samples. Two were collected and characterized by Hassett *et al.*[10] for the U.S. Environmental Protection Agency (EPA) and one was collected by workers from our laboratory.

MATERIALS AND METHODS

The two EPA sediments, EPA-10 and EPA-16, were used as received. Table 1 lists the characteristics of these sediments as determined by Hassett *et al.*[10] The New Hampshire (NH) sediment was collected in June 1986 from Lake Pemigewasset near New Hampton, NH (USA). The NH sediment was air-dried and sieved through a #30 mesh brass screen. No attempt was made to ensure the homogeneity of the samples other than shaking the container for less than a minute by hand before removing any material.

Walkley–Black Method

Ten ml of 1 N potassium hydroxide (Baker Chemical Co., primary standard grade) was mixed with about 0.5 g of sediment in a 500 mL wide-mouth Erlenmeyer flask.

To this mixture, 20 mL of concentrated sulfuric acid was added. The combination was swirled for 1 minute, then allowed to stand for 30 minutes. After the mixture had cooled additions included 200 mL deionized water, 10 mL concentrated phosphoric acid, and 4 drops of *o*-phenanthroline-ferrous complex, which was the indicator. The mixture was not filtered before titration with 0.5 N ferrous sulfate. The ferrous sulfate was standardized daily to establish its normality by titrating a blank that contained all the reagents, but not the sediment.

Coulometric Method

For the coulometric method we used instruments manufactured by Coulometrics, Inc. (Model 5011 Coulometer, Model 5120 Total Carbon Combustion Apparatus, and Model 5030 Carbonate Carbon Apparatus).

Organic carbon was determined as the difference between the total and inorganic carbon. To determine total carbon, no more than 125 mg of sediment was weighed into a platinum boat. The boats were placed into a combustion chamber at 900 °C via a delivery system which was purged with oxygen for about 1 minute to remove any introduced CO_2. The sample remained in the combustion chamber until a stable measurement was obtained, which required about 7 minutes. The evolved CO_2 is swept into a coulometric cell where it is titrated. The CO_2 stream passes through a magnesium perchlorate scrubber and a NO_x scrubber made of acid dichromate on silocel and manganese dioxide. The cell is in the path of a light source and a detector. The cell contains silver and platinum electrodes in a partially aqueous proprietary solution that includes ethanolamine and a colorimetric indicator. Initially, the mixture is basic and has a blue color due to the indicator. The incoming CO_2 reacts with the ethanolamine quantitatively to form N-carboxy-2-amino ethanol.

$$CO_2 + HOCH_2CH_2NH_2 \rightarrow HOCH_2CH_2NHCOOH.$$

As the N-carboxy-2-amino ethanol dissociates, the acidity of the solution increases, which causes the indicator color to fade

$$HOCH_2CH_2NHCOOH \rightarrow HOCH_2CH_2NHCOO^- + H^+.$$

As the color fades and the percentage of transmittance increases, current is supplied to the electrodes. The reaction at the platinum electrode produces OH^-

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-.$$

As the solution returns to its original basic pH and color, transmittance is reduced and the current to the cell is turned off. The amount of current necessary to reach the endpoint is electronically integrated and the result is displayed digitally as micrograms of carbon (or whatever units have been preset).[9,11]

To determine inorganic carbon, less than 0.2 g of the sediment was weighed into

Table 2 Percentage of organic carbon

Sediment	*Walkley–Black*	*Coulometric*	*EPA*[10]
EPA-10	1.998±0.220[a]	1.894±0.083[b]	2.10
EPA-16	1.073±0.187	1.114±0.017[c]	1.20
New Hampshire	0.112±0.116	0.160±0.008[c]	n.a.

[a] 95% confidence limit.

[b] Organic carbon for EPA-10 was determined by the difference between total carbon (2.929±0.045) and inorganic carbon (1.035±0.038).

[c] Total carbon. Inorganic carbon negligible.

Table 3 Measure of the precision of the two methods

Sediment	*Walkley–Black*			*Coulometric*		
	SD	*Variance*	*RSD* (%)	*SD*	*Variance*	*RSD* (%)
EPA-10	0.398	0.158	19.9	0.082[a]	0.007	2.80
				0.068[b]	0.005	6.57
EPA-16	0.339	0.115	31.6	0.031[c]	0.001	2.78
New Hampshire	0.211	0.044	188.4	0.015[c]	0.0002	9.38

[a] Total carbon.

[b] Inorganic carbon.

[c] Total carbon. Inorganic carbon negligible.

a glass tube. The tube was then attached to the carbonate carbon apparatus and purged with air for about 1 minute to remove any introduced CO$_2$ before it was placed on a heating element. Three ml of approximately 2 M reagent grade perchloric acid was added to the sediment. The maximum amount of time required for this particular group of sediments was 8 minutes. The CO$_2$ is swept into the coulometer cell after passing through a silver nitrate scrubber to remove interfering gases. The coulometric determination proceeds as the total carbon determination.

RESULTS AND DISCUSSION

To determine the accuracy of the measurement of organic carbon in an environmental sample is very difficult. However, the determination of the precision of such a measurement is entirely possible. The Walkley–Black results contain a correction factor of 1.33 as recommended by the standard procedure.[8] Table 2 contains the means of the 15 replicate measurements for each sediment.

In all cases, the confidence limits for the coulometrically determined means were less than those for the Walkley–Black method. The relative standard deviations for all the coulometric measurements were also less than those for the Walkley–Black measurements. Table 3 lists the standard deviations, variances, and relative standard deviations for the three sediments.

The precision of both methods declined as the amount of organic carbon decreases, as is typically the case. EPA-10 had the largest percentage of organic carbon as determined by both methods and the smallest relative standard deviation, 19.9% by the Walkley–Black method and 2.80% for total carbon by the coulometric method. The New Hampshire sediment with less than 0.50% organic carbon had the largest relative standard deviations, 188.4% by the Walkley–Black method and 9.38% for total carbon by the coulometric method. However, the lower precision was markedly less extreme for the coulometric method. For the New Hampshire sediment, the Walkley–Black method produced negative results for 11 of the 15 replicates. The negative values were treated as 0.0 for purposes of this analysis. None of the 15 replicates for the coulometric method for the determination of total carbon of the New Hampshire sediment resulted in negative values.

The Walkley–Black method relies on the principle that the potassium dichromate oxidizes any organic carbon present in the sediment. This assumes that all the organic carbon has an average oxidation state of zero.[12] The coulometric method makes no assumptions as to the average oxidation state of the organic carbon. The Walkley–Black method also assumes that the heat of dilution of concentrated sulfuric acid is adequate for the complete oxidation of organic carbon. However, other investigators have found that additional heat is required for a quantitative oxidation because the heat of dilution oxidizes only the most active forms of organic carbon.[12] Therefore, a correction factor should be used in the calculation of the percentage of organic carbon. In this analysis, we used a correction factor of 1.33 based on the findings of Walkley and Black[13] that an average of 76% of the organic carbon was oxidized for a group of 20 soils. The coulometric method assumes that all forms of carbon are oxidized to CO_2 in the total carbon determination and only inorganic carbon is oxidized in the inorganic carbon determination.

Chloride and iron (II) can produce positive errors and the higher oxides of manganese can produce negative errors by the Walkley–Black method.[12] None of these substances cause interferences with the coulometric method.

The coulometric method required substantially less sample than the Walkley–Black method. For example, the mean of the weights for the Walkley–Black measurement of EPA-16 was 0.528 g and that for the coulometric measurement was 0.065 g. For highly heterogeneous materials, the small sample size could be a disadvantage.

The inorganic portion of the coulometric method has some operational drawbacks. The reaction of the inorganic carbon with the perchloric acid appears to be incomplete and to depend to a certain extent on sample size. There is no mechanism to ensure complete mixing of the acid and the sample. Another potential problem is that perchloric acid as recommended by the manufacturer of the coulometer may oxidize a portion of the organic matter which would result in a positive error in the inorganic measurement.[9] A limited check of the inorganic measurements was made by determining the amount of inorganic carbon in $CaCO_3$. The measurements resulted in a mean of 12.79% inorganic carbon, which is greater than the expected 12.00%. The standard deviation was 2.51 and the relative standard deviation was 19.63%.

The problem of the inorganic determination can be avoided by pretreating the sample with acid to oxidize the inorganic portion before using the total carbon analyzer. The operations manual for the coulometer also suggests that reducing the furnace temperature to less than 700 °C will prevent the oxidation of inorganic carbon by the total carbon analyzer.[9] This method should be carefully evaluated.

CONCLUSIONS

Based on the analysis of three sediments, the coulometric method of determining organic carbon content was found to be more precise than the Walkley–Black method. Both methods lose precision as the amount of organic carbon decreases. However, the decline in precision is markedly less for the coulometric method than for the Walkley–Black method. The coulometric method experiences fewer interferences than the Walkley–Black and requires less sample. The initial cost for the Walkley–Black method is much less than the coulometric method but more time is required to perform the Walkley–Black measurement.

The coulometric method should be evaluated against other instrumental methods for organic carbon determination. The development of a standard low organic carbon sediment that could be made widely available to environmental researchers would aid in establishing the precision as well as the accuracy of various methods. Perhaps then an agreement on the best method for the measurement of organic carbon can be reached and used as a standard in environmental research.

Disclaimer

Although the research described in this article has been supported by the United States Environmental Protection Agency through cooperative agreement #811654 to the Colorado School of Mines, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

References

1. S. W. Karickhoff, *J. Hydraulic Engin.* **110,** 707 (1984).
2. S. W. Karickhoff, D. S. Brown and T. A. Scott, *Water Research* **13,** 241 (1979).
3. L. M. Southwick and G. H. Willis, Abstracts of papers, 178th National Meeting of the American Chemical Society, *Div. Pestic. Chem.* (1979).
4. P. A. Wahid, C. Ramakriskna and N. Sethunathan, *J. Environ. Qual.* **9,** 127 (1980).
5. N. L. Wolfe, B. P. Kitchens, D. L. Macalady and T. J. Grundl, *Environ. Toxicol. Chem.* **5,** 1019 (1986).
6. P. G. Tratnyek, Abiotic reduction of nitro-aromatic pesticides in anaerobic laboratory systems designed to model dissolved organic matter. Ph.D. thesis, Colorado School of Mines, Golden, CO (1987).
7. R. M. Powell, B. E. Bledsoe, G. P. Curtis and R. L. Johnson, submitted to *Environ. Sci. Technol.* (1987).
8. L. E. Allison. In: *Methods of Soil Analysis*, Part 2: *Chemical and Biological Properties*, C. A. Black, ed. (American Society of Agronomy, 1965), pp. 1367–1378.

Coulometrics, Inc. *Instruction Manual Model 5010 CO_2* (Coulometer, 1985).

10. J. J. Hassett, J. C. Means, W. L. Banwart and S. G. Wood, Sorption properties of sediments and energy-related pollutants, NEPA-600/3-80-041 (1980).
11. E. W. D. Huffman, *Microchemical J.* **22,** 567 (1977).
12. D. W. Nelson and L. E. Sommers. In: *Methods of Soil Analysis,* Part 2: *Chemical and Microbiological Properties,* A. L. Page, ed., (American Society of Agronomy, Inc. and Soil Science Society of America, Inc., 1982), 2nd edition, p. 573.
13. A. Walkley and I. A. Black, *Soil Sci.* **37,** 29 (1934).