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DETERMINATION OF ORGANIC- AND CARBONATE-CARBON IN FRESHWATER LAKE SEDIMENTS BY A MICROCOMBUSTION PROCEDURE

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A microcombustion procedure specific for the determination of total-, organic- and carbonate-C in freshwater lake sediments is described. The procedure involves combustion of the sample at 650° to obtain organic-C. Total-C is obtained by combustion at 950° and carbonate-C calculated by difference. The procedure was evaluated by differential thermal analyses of representative sediments and known carbonate minerals. A procedure for the identification of dolomite in lake sediments by differential thermal analysis under CO_2 is also described.

Determination of soil organic-C by rapid wet oxidation-back-titration methods has been accepted as a reliable procedure for most soils including those that contain significant concentrations of carbonate-C. Total C in soils is determined easily by dry combustion of the sample with subsequent determination of released CO_2 [1, 2]. The presence in lake sediments of significant concentrations of Fe^{+2}, Mn^{+2} and S^{-2} makes determination of organic-C by wet oxidation methods unreliable [3, 4]. To overcome this difficulty, sediment organic-C can be determined by dry combustion techniques provided carbonate-C is absent. Because many lake sediments contain large amounts of calcareous minerals, carbonates must be removed prior to measurement of organic-C by available microcombustion techniques which is time-consuming and requires the proper choice of reagents to minimize organic matter decarboxylation [5, 6]. Several methods are available for the rapid determination of carbonates; however, these procedures are subject to interference by organic compounds and to errors arising from slow and incomplete reaction of dolomite with acid [5—8].

The need for a rapid reliable procedure for determination of organic-C in calcareous lake sediments is apparent. The rapid procedure described herein was developed to determine total-, organic-, and carbonate-C in lake sediments including those in an anaerobic environment and containing high concentrations of reduced ionic species.

Materials and methods

The 28 lake sediment samples were obtained from 5 areas in Wisconsin, U.S.A., and varied widely in organic- and carbonate-C contents. Samples transported to the laboratory in 4-litre glass bottles were collected with either an Eckman-type or Petersen-type dredge and were dried as follows: a portion of the sediment (150 ml) was centrifuged at 10,000 rpm (16,300 g) for 10 min. to remove water associated loosely with the sediments. Following centrifugation, the sediment was air-dried and ground by mortar and pestle to pass an 80-mesh A.S.T.M. screen.

Carbonate minerals were obtained from a collection in the Department of Soil Science of the University of Wisconsin; the identity of each was verified by X-ray diffraction analyses.

Microcombustion analysis. Carbon determinations by dry combustion were made on a Sargent Programmed Microcombustion Apparatus using Ascarite and Anhydrone as trapping agents for CO_2 and H_2O, respectively. Organic-C determinations were made by programming the heating rate of the instrument from 300 to 650° in 10 minutes and maintaining temperature at 650° for 20 minutes. Total-C analyses were conducted in an identical fashion with the exception that final temperature was increased to 950°. All determinations were made with the sample in an atmosphere of pure anhydrous O_2. Because the organic-C contents of fresh-water lake sediments often were as high as 20 to 25%, sample size was chosen to yield 25 to 50 mg of CO_2 on combustion. For determination of organic-C, a furnace temperature of 650° provided complete oxidation of organic matter with no carbonate decomposition.

Differential thermal analysis. Differential thermal analysis was conducted using a Stone-Tracor differential thermal analysis system. The system is equipped with a LB-202B Recorder-Controller with dual pen recording and a JP-202 Furnace Platform (ambient temperature to 1100°) with a range of sample holders and thermocouples. Continuous exchange of the atmosphere in contact with the sample is maintained by a capillary system at the base of the sample holder. Lake sediment and carbonate samples (2 to 4 mg) were programmed from ambient temperature to 1,000° at a rate of 50°/minute in atmospheres of air or CO_2 with Al_2O_3 as the inert material.

Procedure for organic-C analysis by wet oxidation. The sediment sample (30 to 60 mg) was digested with a mixture of 10 ml 0.5*N* $K_2Cr_2O_7$ and 15 ml concentrated H_2SO_4 at boiling temperature for 30 minutes. Excess $Cr_2O_7^{-2}$ was back titrated with 0.2*N* $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ and organic-C calculated according to the procedure of Mebius [3].

Procedure for carbonate analysis by gasometric method. Concentrated HCl was used to liberate CO_2 from the calcareous lake sediments (100 mg). The volume of CO_2 produced was determined by H_2O displacement according to the procedure of Leo [6].

Results and discussion

The organic-C contents of 28 lake sediment samples were determined by $Cr_2O_7^{-2}$ oxidation and microcombustion at 650° (Table 1). With one exception (sample 11) organic-C values by the microcombustion technique were lower than

Table 1

Comparison of organic-C contents of Wisconsin lake sediments obtained by $Cr_2O_7^{-2}$ oxidation and microcombustion

Sediment No.	Lake	Location (county)	Lake type*	Organic-C (%) by $Cr_2O_7^{-2}$ oxidation (a)	Organic-C (%) by Microcombustion (b)	Difference $\left(\frac{a-b}{b}\right)100$, %
1	Wingra	Dane	H	7.8	7.0	11.4
2	Wingra	Dane	H	8.8	7.9	11.4
3	Wingra	Dane	H	9.7	7.8	19.6
4	Wingra	Dane	H	9.8	8.9	10.1
5	Wingra	Dane	H	10.8	8.7	24.2
6	Wingra	Dane	H	8.4	8.2	2.4
7	Wingra	Dane	H	6.6	6.2	6.5
9	Monona	Dane	H	7.3	6.9	5.8
11	Mendota	Dane	H	8.6	8.8	—2.3
12	Labelle	Waukesha	H	6.0	5.2	15.4
13	Labelle	Waukesha	H	8.3	6.9	20.3
14	Nagawicka	Waukesha	H	7.5	6.8	10.3
15	Nagawicka	Waukesha	H	6.5	6.2	4.8
16	Devil's	Sauk	S	8.5	8.4	1.2
19	Little John	Vilas	S	25.9	25.4	2.0
20	Crystal	Vilas	S	24.2	24.0	0.8
22	Tomahawk	Oneida	S	3.3	2.9	13.8
23	Plum	Vilas	S	21.7	20.9	3.8
24	Tomahawk	Oneida	S	20.3	19.8	2.5
25	Pickeral	Oneida	S	18.4	17.9	2.8
26	Mendota	Dane	H	8.0	7.7	3.9
29	Trout	Vilas	S	12.5	12.4	0.8
40	Delavan	Walworth	H	8.2	7.8	5.1
41	Delavan	Walworth	H	8.0	7.5	6.7
42	Geneva	Walworth	H	6.5	5.4	20.4
43	Geneva	Walworth	H	6.6	5.6	17.9
45	Minocqua	Vilas	S	13.1	13.0	0.8
46	Minocqua	Vilas	S	16.3	16.0	1.9

* H is Hardwater, S is Softwater.

those obtained by $Cr_2O_7^{-2}$ oxidation. The percentage deviations between organic-C values by the two methods were more pronounced with calcareous sediments (average deviation – 10.6%) than with the noncalcareous samples (average deviation – 3.0%). The calcareous sediments were sampled from hard water lakes which had reached generally a high degree of eutrophication. Thus, the sediments were formed under more reduced conditions than the noncalcareous samples taken from oligo- and mesotrophic lakes. However, sediments from both lake types contained appreciable concentrations of reduced ionic species. The sediment samples contained from 2 to 15% total Fe, 50 to 500 ppm total Mn and 500 to 3000 ppm reduced S. At present, no acceptable techniques are available for the evaluation of the oxidation status of the several species of these elements existing in lake sediments. For this reason, it is impossible to derive a reliable factor for correcting the C-contents for interferences from inorganic oxidizable ions in wet oxidation procedures [3]. The microcombustion technique is not subject to these interferences and it was decided to evaluate the technique for the determination of organic- and inorganic-C in lake sediments. For the determination to be specific and accurate, reliable data on the thermal reactions leading to formation of CO_2 from organic compounds and carbonates are required.

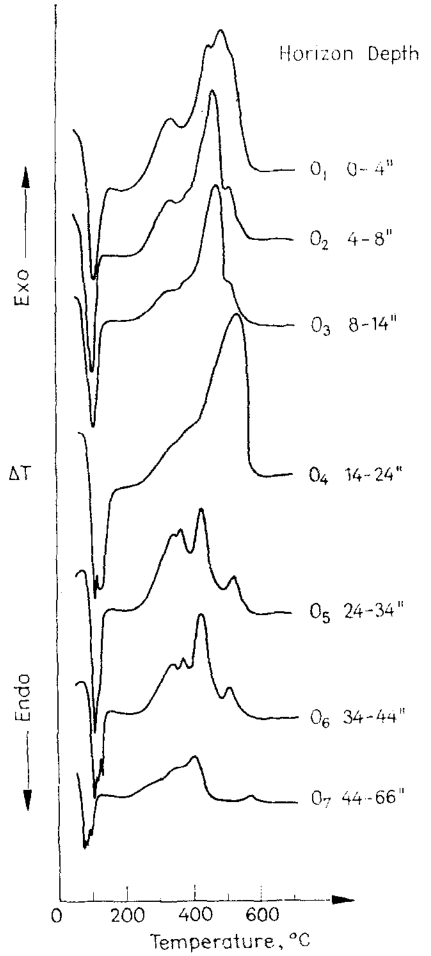

Fig. 1. DTA curves in air of a peat profile of the Horizon series

Differential thermal analyses in air of standard organic acids and various natural products such as lignins, woods, celluloses and proteins show that all thermal reactions occurring below 600° can be ascribed to water loss and formation of CO_2 [9]. Thermal reactions in air of the several horizons of a peat profile are complete by 600° (Fig. 1). From this evidence it was concluded that complete oxidation of organic-C occurs at temperatures below 600°. Therefore, quantitative oxidation of organic-C to CO_2 would occur in the microcombustion technique at temperatures in excess of 600°. However, many lakes have highly calcareous sediments and oxidation of organic-C must be accomplished at a temperature below which carbonates are decomposed thermally. With this in mind, the thermal decomposition characteristics of carbonate minerals were investigated.

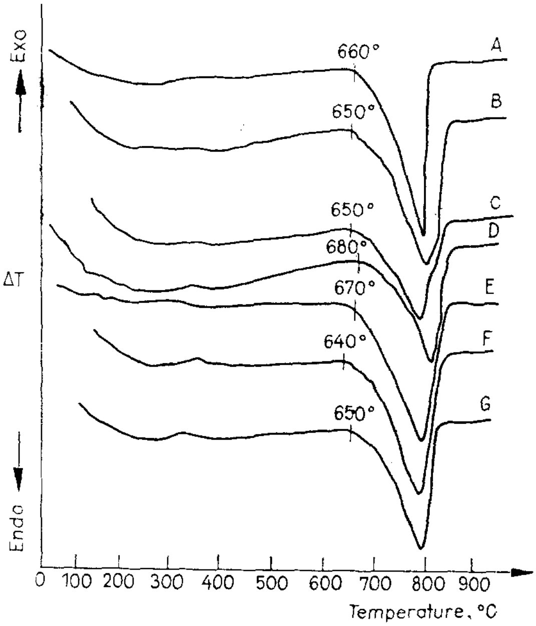

Fig. 2. DTA curves in air of carbonate minerals. A — aragonite; B — calcite; C — dolomite; D — calcite + dolomite; E — dolomite + aragonite; F — calcite + aragonite; G — calcite + dolomite + aragonite

Differential thermal analysis patterns of calcite, dolomite, aragonite and various mixtures of each in air are shown in Fig. 2. The loss of CO_2 characterized by endothermic reactions was initiated between 640° and 680° and completed by 850°. Similar thermal patterns were obtained for each of the pure mineral carbonates and were not influenced by the presence of other carbonate minerals. From the data in Fig. 2, it was concluded that organic-C could be determined in the presence of carbonates if the maximum temperature of the microcombustion furnace is maintained between 600° and 650°.

Fig. 3 shows differential thermal analysis patterns of several of the lake sediments. Sediments 19, 29 and 45 are noncalcareous and gave thermal patterns similar to those obtained for peat horizons (Fig. 1). Exothermic reactions characteristic of the oxidation of organic matter were complete by 600° and no further thermal reactions occurred. For the calcareous sediments 1, 9, 12, 26, 40 and 42, organic matter oxidation was complete essentially by 600° and the endothermic peak for CO_2 liberation from carbonates was initiated at temperatures in excess of 670° (Fig. 3). Calcite was added to two sediment samples to further verify the position of the carbonate endotherm. The effect of added carbonate on the endothermic reactions of sediments 26 and 29 is shown in Fig. 4. In sediment 26, which is calcareous, addition of calcite resulted in a more intense endotherm; however, the temperature was not shifted significantly and no additional peaks resulted. In the noncalcareous sediment (No. 29), an endotherm initiated at 680° resulted from the addition of calcite. Thus, C-determinations by the microcombustion procedure at a maximum temperature of 650° represent only C arising from organic components of the lake sediment sample (Table 1).

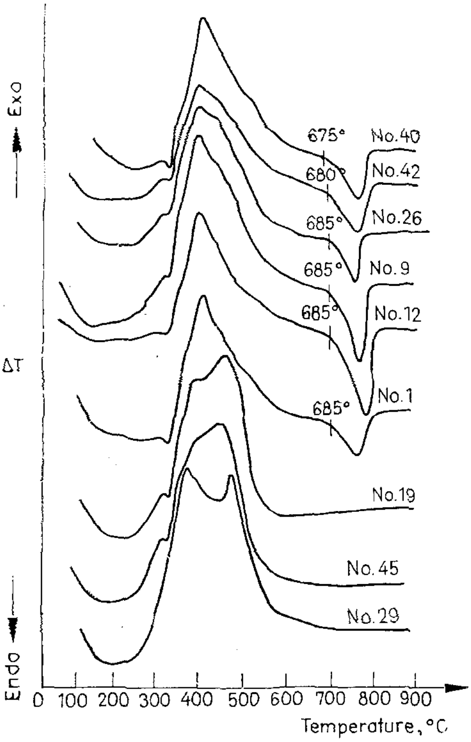

Fig. 3. DTA curves in air of several freshwater lake sediments

Total-C was obtained by combustion of the sediment samples at 950° and carbonate-C was taken as the difference between total- and organic-C (Table 2). The average variation between total- and organic-C for noncalcareous sediments was 1.9%. This value indicates that essentially all the organic-C was removed at 650° and the average variation was almost identical with the relative error obtained between replicates at 650° (approximately 2%). Carbonate-C contents of the sediments were determined by the gasometric method of Leo [6] (Table 2). Carbonate-C values obtained by difference using the microcombustion procedure were, in general, slightly higher than obtained by the gasometric method. The average difference was 3.3%, which is within acceptable experimental error for results obtained by a difference method. From the close agreement of carbonate-C values by the two procedures, it was concluded that carbonate-C could be obtained accurately from the difference between the total- and organic-C values obtained using the microcombustion procedure.

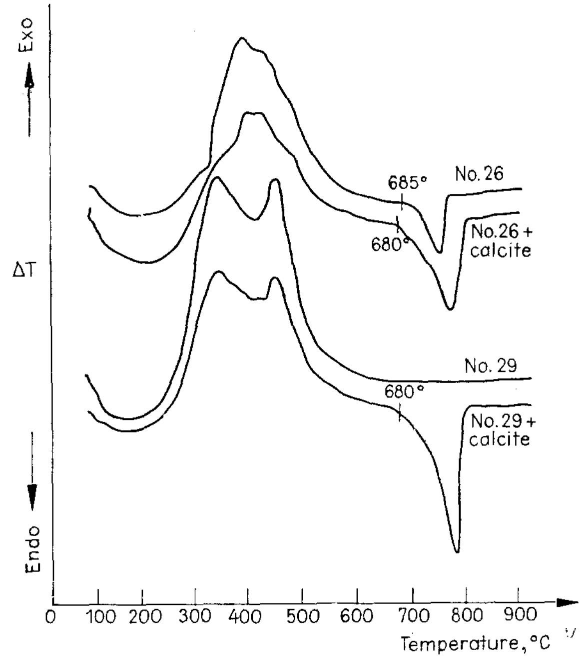

Fig. 4. DTA curves in air of a calcareous and a noncalcareous lake sediment before and after addition of calcite

Separation of the several carbonate minerals was not possible by differential thermal analysis in air (Fig. 2). However, thermal decomposition of carbonate minerals in an atmosphere of CO_2 provided patterns showing that decomposition of calcite and aragonite are suppressed with endothermic peaks occurring at 950° (Fig. 5). Dolomite decomposition occurs in two steps, namely, 1) $MgCO_3$ decomposition at 810° and 2) $CaCO_3$ decomposition at 930° [10, 11]. Although mixtures of the carbonates resulted in slight shifting of the endotherms, dolomite can be clearly identified in a mixture of other carbonate minerals. Thus, it appears that differential thermal analysis of lake sediments using a CO_2 atmosphere can be used to distinguish dolomite from calcite and aragonite. Calcite and aragonite cannot be separated on the basis of differential thermal analysis; presumably under the conditions used in this investigation, aragonite is transformed to calcite at about 550° without observable thermal reactions [12]. Dolomite could not be identified positively in the sediments; however, differential thermograms of several lake sediments under CO_2 showed a small endotherm at 810°, but no endotherm at 930°. The conditions for the formation of dolomite by calcite dia-

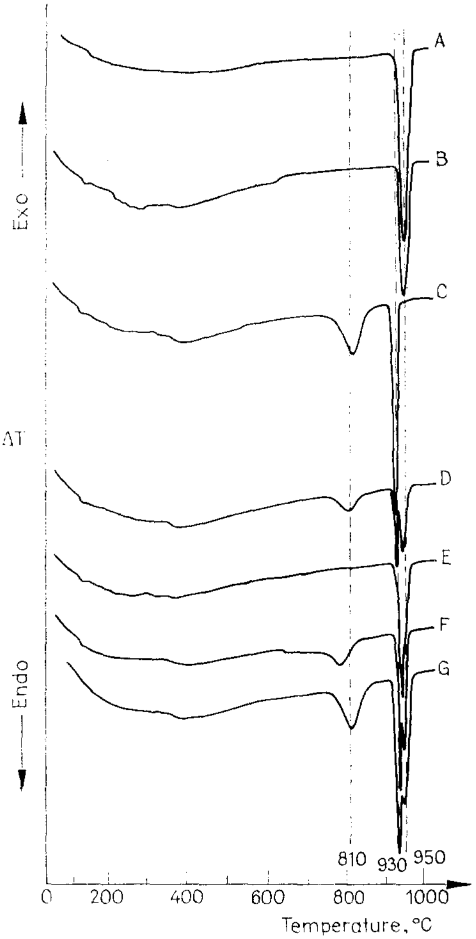

Fig. 5. DTA curves in CO_2 of carbonate minerals. A — aragonite; B — calcite; — C — dolomite; D — calcite + dolomite; E — calcite + aragonite; F — dolomite + aragonite; G — calcite + aragonite + dolomite

Table 2

Total- and carbonate-C contents of Wisconsin lake sediments

Sediment No.	Total-C (%)	Carbonate-C (%) by Gasometry (a)	Carbonate-C (%) by Microcombustion (b)	Difference $\left(\frac{b-a}{b}\right)100$, %
1	12.8	5.6	5.8	3.5
2	14.0	6.0	6.1	1.6
3	14.3	6.3	6.5	3.1
4	15.9	6.7	7.0	4.3
5	15.9	7.3	7.2	—1.4
6	14.7	6.5	6.5	0.0
7	13.9	7.3	7.7	5.2
9	11.0	3.9	4.1	4.9
11	11.2	2.5	2.4	4.2
12	12.4	7.5	7.2	—4.2
13	13.6	6.5	6.7	3.0
14	12.5	5.6	5.7	1.8
15	12.9	6.4	6.7	4.5
16	8.6	0.0	0.2	(—)
19	25.8	0.0	0.4	(—)
20	24.1	0.0	0.1	(—)
22	3.1	0.2	0.2	(—)
23	21.3	0.1	0.4	(—)
24	20.1	0.0	0.3	(—)
25	18.0	0.3	0.1	(—)
26	11.1	3.2	3.4	5.9
29	12.6	0.0	0.2	(—)
40	13.0	4.9	5.2	5.8
41	13.5	6.1	6.0	—1.8
42	8.8	3.3	3.4	2.9
43	9.4	3.7	3.8	2.6
45	13.1	0.3	0.1	(—)
46	16.3	0.2	0.3	(—)

(—) Samples essentially carbonate-free.

genesis, i.e., high Mg : Ca ratios caused by evaporation, do not exist in these lakes [13] and any dolomite identified in lake sediments is not formed *in situ*, but is derived from erosion of the surrounding watershed.

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RÉSUMÉ — On décrit une méthode spécifique de microcombustion pour déterminer la teneur en carbone total, organique et carbonate dans des sédiments des lacs à eau froide. On reçoit le C organique par combustion à 650°, le C total par combustion à 950° et le carbone à l'état de carbonate, par la différence. On a évalué le procédé par ATD des sédiments représentatifs et de minérais de carbonate connus. On a décrit une méthode pour identifier le dolomite dans les sédiments des lacs, par ATD sous CO_2.

ZUSAMMENFASSUNG — Es wurde über ein zur Bestimmung des Gesamt-, Karbonat- und organischen Kohlenstoffgehaltes von Süßwasserrückständen geeigneten Mikroverbrennungsverfahren berichtet. Durch Verbrennen bei 650° erhält man den organischen Kohlenstoff, durch Verbrennen bei 950° den Gesamtkohlenstoff. Der Karbonatkohlenstoff ergibt sich aus der Differenz. Die Methode wurde durch differentialthermoanalytische Prüfung von charakteristischen Sedimenten und bekannten Karbonatmineralien getestet. Ein Verfahren zur Identifizierung von Dolomit in Seesedimenten durch Differentialthermoanalyse unter CO_2 wurde ebenfalls beschrieben.

Резюме — Описана методика микросожжения, являющаяся специфической для определения общего, органического и карбонатного С в осадках озерной пресной воды. По методике органический и общий С определяли сожжением образца при температурах 650° и 950°С, соответственно, а карбонатный С рассчитывали по разнице. Методика основана на дифференциальном термическом анализе характерных осадков и известных минералов карбонатов. Описана также методика отождествления доломита, находящегося в озерных осадках, посредством дифференциального термического анализа в присутствии CO_2.