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Rapid analysis of organic carbon and nitrogen in particulate materials

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Abstract

A method for rapid determination of organic carbon and nitrogen in natural particulate materials is described. The procedure allows the determination of 60 samples per day by a single analyst. It involves the determination of carbon and nitrogen using an automatic CN-analyzer following the partitioning of inorganic and organic carbon phase by acidification with 25% HCl in situ within silver sample cups. The technique eliminates reweighing procedures, losses of organic and inorganic compounds (except carbonates and sulphides) and is free from matrix interferences. Extensive testing and application showed long-term precisions for organic carbon and nitrogen of about 3%. The accuracy is excellent, irrespective of the calcium carbonate content of the sample.

1. Introduction

In order to quantify fluxes of carbon and nitrogen within and exchanges among aquatic systems, biologists, geologists and chemists often determine the spatial and temporal distribution of organic carbon and nitrogen. Rapid, routine analyses of organic carbon and nitrogen are required to better constrain ecological and biogeochemical budgets. Carbon in suspended matter and sediments includes both organic carbon and carbon contained within biogenic and abiogenic carbonate minerals. Measurement of organic carbon in natural particles therefore requires quantitative partitioning between organic and inorganic forms of carbon.

There are three groups of methods in use to determine organic carbon. The first group of methods are based on the direct determination of organic carbon by wet oxidation (e.g. Duursma, 1961; Sims and Haby, 1971). In the second group of methods the organic carbon

content is obtained by the difference in total carbon content before and after dry combustion at high temperature (usually between 400 and 600°C) (e.g. Heath et al., 1977; Krom and Berner, 1983). The third group of methods are based on the removal of inorganic carbon forms by acid leaching before measurement of the carbon content (e.g. Froelich, 1980; Weliky et al., 1983; Hedges and Stern, 1984; van Iperen and Helder, 1985; Verardo et al., 1990; Cutter and Radford-Knoery, 1991).

Many of these methods can be subject to systematic errors for a particular sample. Organic carbon contents determined by wet oxidation can either be too high, if reduced species other than organic carbon (e.g. sulphides) are oxidized, or too low, if refractory organic compounds are not oxidized by the oxidant used (e.g. Duursma, 1961; Froelich, 1980). Organic carbon contents estimated by difference-on-ignition techniques may be biased towards higher values, if some carbonate minerals have decomposed at the applied

temperature (Froelich, 1980; Weliky et al., 1983), or towards lower values, if organic matter is incompletely combusted at the temperature chosen (Gibbs, 1977). For carbonate-rich materials in particular it is difficult to obtain accurate organic carbon measurements by loss-on-ignition techniques. For these samples organic carbon is calculated by subtracting one large number from another, which results in poor statistics for the residual. Organic carbon contents determined after acid treatment of the sample to eliminate inorganic carbon may be too low, because of leaching of soluble organic carbon (Froelich, 1980) and because of weight increase after acidification (Hedges and Stern, 1984; van Iperen and Helder, 1985), or too high, because of leaching of non-carbonate inorganic matter (Hedges and Stern, 1984).

To overcome these problems related to acidification, methods have been developed that (1) include measurement of carbon both in the H_3PO_4 acidified supernatant and in solid residue (Froelich, 1980), (2) determine sequentially and directly the CO_2 yield from inorganic carbon by H_3PO_4 acidification and from organic carbon by wet oxidation (Weliky et al., 1983), (3) dry the HCl acidified slurry to conserve soluble material and correct the sample weight for hygroscopic salt formation (Hedges and Stern, 1984; van Iperen and Helder, 1985), (4) apply a vapour HCl acidification procedure to remove inorganic carbon that does not require reweighing the sample (Hedges and Stern, 1984), and (5) acidify samples in situ with sulfurous acid (Verardo et al., 1990) or hydrochloric acid (Cutter and Radford-Knoery, 1991). These procedures have provided substantial improvement in accuracy. However, the first two methods require relative large (50–200 mg) samples and cannot be easily automated. Moreover, Froelich's procedure demands a dissolved and solid phase carbon analyzer and the Weliky et al. method relies on wet-oxidation and provides no nitrogen data. Vapour phase methods do not have these restrictions, but can fail to

remove all traces of carbonate from calcareous oozes (e.g. Hedges and Stern, 1984). In-situ acidification methods have the advantage that they eliminate reweighing procedures, avoid losses of acid-soluble organic and inorganic materials (except carbonate and sulphidic compounds), and consume only about 10 mg sample per analysis.

In this paper we present an in-situ HCl acidification procedure to determine organic carbon and nitrogen in suspended matter, sediment trap material and sediments. Our in-situ acidification method deviates from previously published techniques (Verardo et al., 1990; Cutter and Radford-Knoery, 1991) in three aspects:

(1) Concentrated HCl rather than sulfurous acid (Verardo et al., 1990) or 1 N HCl (Cutter and Radford-Knoery, 1991) is used to ascertain complete removal of all inorganic carbon from carbonate-rich or dolomite containing samples.

(2) Commercially available silver cups with a height of 12 mm are used rather than laboratory made aluminum containers with a height of about 7–8 mm. Higher container walls will reduce possible sample loss.

(3) Approximately 60, rather than 20, dried and homogenized samples can be processed per day by a single analyst.

The method can be applied to most natural materials and has been tested for carbonate-free samples as well as calcareous oozes and reef sediments. The long-term precision for both organic carbon and nitrogen is about 3% of the measured values. The rapid turn-over time of samples and the high accuracy and precision of this method make it an excellent procedure for routine analysis of organic carbon and nitrogen.

2. Materials and methods

2.1 Materials

The recommended standards for use in carbon and nitrogen analysis are acetanilide (C_8H_9ON), available from Merck, and BCR-71

(C₁₃H₉BrClN₃O₂S), available from the Community Bureau of Reference of the European Communities. The Canadian National Research Council certified estuarine sediment BCSS-1 (Berman, 1987) can be used as a carbon standard more representative of natural particulate materials.

2.2 Sample preparation and removal of inorganic carbon

Samples should be freeze-dried or oven-dried at 60°C, thoroughly ground in an agate mortar mill, and very well homogenized to reduce variability between replicates. Splits of 20 mg of powdered, homogenized samples (10 mg for calcareous samples) are weighed accurately (0.01 mg) into pre-cleaned silver cups (12 × 5 mm). The silver cups are cleaned by a hexane/acetone Soxhlet extraction for 8 h followed by an overnight placement in a 250°C oven to remove any remaining contaminants and solvents. This procedure was chosen to achieve optimal cleaning while preventing the cups from becoming too brittle as a consequence of their exposure to high temperatures (e.g. see also Cutter and Radford-Knoery, 1991). Silver cups, rather than tin or aluminum, are used since they are more resistant to hydrochloric acid than those made of tin that show dissolution phenomena and those made of aluminum that become brittle upon exposure to concentrated hydrochloric acid. The silver cups used (Van Loenen Instruments, D2010) are similar to those distributed by Carlo Erba, except for the side walls which are 50% higher. Sediment spillage during acidification will consequently be lower.

After weighing out one analytical batch of samples, 10 µl 25% HCl are carefully added. It is not necessary to wet the samples before adding acid to prevent sample loss because of the relatively high walls of the silver cups. After completion of the reaction, as evidenced by termination of carbon dioxide escape, 10 to 20 µl 25% HCl are added, the quantity depending on the carbonate content of the sample. If any

effervescence is noted on the second HCl addition, the procedure is repeated. The acidification procedure must be performed very carefully to avoid sample loss and to ascertain the complete saturation of sample with HCl. If any material is lost from the sample cup, the sample is discarded. Hydrochloric acid was chosen to completely remove inorganic carbon from samples, since carbonate phases such as dolomite may be present in suspended matter (e.g. van der Weijden and Middelburg, 1989) and sediments (e.g. Baker and Burns, 1985). Experiments to determine the optimal acid strength showed that the reproducibility was slightly better when using 25% HCl compared with lower acidities.

After acidification, the sample tray is placed on a pre-heated plate at 50°C and the temperature is gradually increased to 120°C. The samples are dry after about 10 min at 120°C. To confirm the complete removal of inorganic carbon, another 20 µl of 25% HCl is added. Incomplete removal is evident from effervescence, and the sample is then acidified again until all of the inorganic carbon is removed as CO₂. The sample tray is dried again, but now at 120°C for 1 h. This drying procedure was chosen to achieve minimal loss of volatile compounds, while removing hydrochloric acids that may otherwise enter the CN-analyzer and accumulate in the combustion tube. It is our experience that this procedure will not lead to loss of volatile compounds in sediments, but that for biota and fresh detritus it is better to dry samples at 70°C to prevent any potential loss of volatile organic compounds. After drying, the silver cups are pinched closed, compacted and formed into a ball. Care must be taken to avoid any sample spillage. These balls are transferred to the autosampler of the CN-analyzer.

2.3 Elemental analysis

The analytical procedure described above was designed specifically for use with a Carlo Erba type NA-1500 elemental analyzer but can easily

be adapted for any other type of elemental analyzer capable of handling micro samples. The operating parameters of the Carlo Erba NA-1500 are very similar to those reported by Froelich (1980), Verardo et al. (1990) and Cutter and Radford-Knoery (1991). The analytical operation of the Carlo Erba NA-1500 has been described in detail by Verardo et al. (1990). Briefly, the sample is oxidized by combustion at 1010°C using an oxidation catalyst containing chromium trioxide (Cr₂O₃) and silvered cobaltous cobaltic oxide (AgCo₃O₄). The combustion products subsequently pass a reduction reactor containing elemental copper at 650°C to transform NO_x compounds into N₂ and to remove excess oxygen which co-elutes with N₂ in the chromatogram. After removal of water, the evolved N₂ and CO₂ are separated by gas chromatography and detected by thermal conductivity. Data acquisition, integration and handling are performed with an on-line PC using the software package EAGER-200 (Carlo Erba Instruments).

At the start of each day of operation the instrument blank is checked and the retention times are determined using acetanilide as a standard. In each analytical batch blanks, standards and samples have fixed positions. Each analytical batch starts with a confirmation of a zero instrument blank for carbon and nitrogen and an empty silver cup to determine the procedure blank. The silver cup has been subject to the same treatments as the others, containing standards or samples, and will be used as the zero standard. The instrument response is determined in duplicate using acetanilide as a standard. The instrument response is subsequently used to calculate the calibration factors, which should fit into a very narrow range. After the analysis of BCR-71, the organic carbon and nitrogen content estimated with these calibration factors are compared with the certified values. If both the calibration factors and the organic carbon and nitrogen values for BCR-71 agree with those usually obtained or certified, respectively, then the analysis can continue. After the analysis

of 12 samples, the calibration factors are determined and compared with those obtained previously. If the new calibration factors are acceptable, then another 12 samples can be analyzed, and so on. The values obtained for both the acetanilide and BCR-71 standards can be used to assess the precision and accuracy of the run.

3. Results and discussion

3.1 Blanks, precision and accuracy

Average short-term ($n = 8$) and long-term ($n = 23$) blank values are 0.00 and 0.00 $\mu\text{g N}$ and 1.67 ± 0.71 and $4.14 \pm 0.85 \mu\text{g C}$, respectively. The carbon blank originates primarily from the silver cups despite our rigorous cleaning procedure. The differences between short- and long-term carbon blank values are probably related to differences in silver cups manufacturing batches. On the basis of these data we estimate a detection limit (3 times standard deviation of the blank) of about 2 $\mu\text{g C}$, which is 0.02% C for a sample of 10 mg. The detection limit for nitrogen (about 0.4 $\mu\text{g N}$) is not determined by the blank, but by the sensitivity of the detector.

Table 1
Replicate analysis of organic carbon and nitrogen in BCSS-1, an estuarine sediment reference material from the Canadian National Research Council (Berman, 1987)

Run	Organic C	Nitrogen
1	2.148	0.212
2	2.083	0.201
3	2.131	0.199
4	2.129	0.201
5	2.111	0.206
6	2.066	0.203
7	2.134	0.206
8	2.126	0.208
9	2.026	0.202
10	2.068	0.208
Average \pm Std. Dev.	2.102 ± 0.039	0.205 ± 0.004
Certified value \pm Std. Dev.	2.19 ± 0.09^a	not available

^a Reported as total carbon.

Table 2
Applicability to carbonate-rich samples and estimation of organic carbon by difference

Type of sample	Organic C (wt%)	N (wt%)	CaCO ₃ ^a (wt%)	Total C ^b (wt%)	Organic C ^c (wt%)
Land van Saafinghe, The Netherlands, estuarine salt-marsh sediments (n = 6)					
30296	3.39 ± 0.12	0.28 ± 0.01	13.66 ± 0.08	4.93 ± 0.11	3.29 ± 0.11
30297	3.46 ± 0.10	0.28 ± 0.006	13.00 ± 0.08	5.11 ± 0.06	3.55 ± 0.06
30298	3.47 ± 0.05	0.29 ± 0.006	13.92 ± 0.24	5.17 ± 0.24	3.50 ± 0.24
30299	3.44 ± 0.10	0.28 ± 0.009	13.66 ± 0.08	5.27 ± 0.06	3.63 ± 0.06
30300	3.36 ± 0.17	0.28 ± 0.01	13.58 ± 0.32	5.05 ± 0.06	3.42 ± 0.04
30378	3.45 ± 0.09	0.29 ± 0.008	13.17 ± 0.32	5.29 ± 0.22	3.71 ± 0.22
30379	3.91 ± 0.10	0.34 ± 0.006	13.58 ± 0.32	5.61 ± 0.15	3.98 ± 0.16
30380	3.82 ± 0.09	0.34 ± 0.005	13.00 ± 0.08	5.30 ± 0.13	3.74 ± 0.13
30381	4.21 ± 0.16	0.38 ± 0.017	12.00 ± 0.58	5.63 ± 0.08	4.19 ± 0.11
30382	3.41 ± 0.06	0.30 ± 0.008	12.67 ± 0.24	4.99 ± 0.07	3.47 ± 0.08
Spermonde Archipelago, Indonesia, seagrass-covered sediments (n = 5)					
43260	0.30 ± 0.03	0.04 ± 0.00	96.9 ± 1.9	11.75 ± 0.02	0.13 ± 0.23
43261	0.50 ± 0.03	0.04 ± 0.00	3.20 ± 0.3	0.92 ± 0.07	0.54 ± 0.08
43262	1.87 ± 0.04	0.07 ± 0.001	33.5 ± 0.4	5.85 ± 0.06	1.84 ± 0.08
43263	0.24 ± 0.03	0.04 ± 0.006	95.2 ± 4.3	11.44 ± 0.03	0.03 ± 0.52
43264	0.36 ± 0.05	0.05 ± 0.004	94.1 ± 2.7	12.20 ± 0.20	0.92 ± 0.38
43265	0.32 ± 0.02	0.03 ± 0.005	97.4 ± 4.6	12.25 ± 0.08	0.57 ± 0.56
43266	0.36 ± 0.06	0.05 ± 0.00	99.6 ± 3.0	12.20 ± 0.04	0.26 ± 0.36
43268	0.66 ± 0.03	0.05 ± 0.005	11.9 ± 0.2	1.99 ± 0.05	0.57 ± 0.06
43269	1.91 ± 0.07	0.07 ± 0.00	48.2 ± 0.3	7.60 ± 0.06	1.82 ± 0.07
Madeira Abyssal Plain, Atlantic Ocean, turbiditic deep-sea sediments (n = 2)					
632	0.17 ± 0.00	0.045 ± 0.007	45.0 ± 0.14	5.60 ± 0.04	0.20 ± 0.04
634	0.23 ± 0.007	0.045 ± 0.007	49.2 ± 0.28	5.71 ± 0.01	0.00 ± 0.04
636	1.02 ± 0.00	0.10 ± 0.00	50.8 ± 0.98	6.80 ± 0.04	0.71 ± 0.12
637	1.02 ± 0.007	0.105 ± 0.007	49.4 ± 0.99	6.81 ± 0.00	0.88 ± 0.12
647	1.01 ± 0.00	0.10 ± 0.00	47.0 ± 5.30	6.79 ± 0.04	1.15 ± 0.64
Eastern Mediterranean, sapropel containing hemipelagic deep-sea sediments (n = 2)					
1074	0.11 ± 0.007	0.04 ± 0.00	46.1 ± 3.6	5.57 ± 0.01	0.16 ± 0.31
1080	2.12 ± 0.03	0.165 ± 0.007	34.1 ± 1.8	6.02 ± 0.01	1.93 ± 0.22
1081	1.83 ± 0.04	0.15 ± 0.00	25.5 ± 1.4	4.77 ± 0.01	1.71 ± 0.17
1082	0.18 ± 0.00	0.045 ± 0.007	40.3 ± 1.4	4.94 ± 0.04	0.11 ± 0.17
1090	1.32 ± 0.02	0.115 ± 0.007	22.5 ± 0.49	3.95 ± 0.01	1.26 ± 0.06
Punta Piccola Formation, Pliocene sedimentary rocks from Southern Sicily, Italy (n = 2)					
005	0.15 ± 0.00	0.055 ± 0.007	55.95 ± 1.77	6.94 ± 0.01	0.24 ± 0.21
015	1.00 ± 0.01	0.125 ± 0.007	34.75 ± 1.06	5.22 ± 0.01	1.05 ± 0.13
020	0.94 ± 0.01	0.13 ± 0.00	35.30 ± 0.28	5.21 ± 0.02	0.97 ± 0.04
025	0.77 ± 0.01	0.12 ± 0.00	46.15 ± 0.64	6.40 ± 0.01	0.86 ± 0.08
030	0.20 ± 0.00	0.085 ± 0.007	53.50 ± 0.99	6.68 ± 0.04	0.26 ± 0.13
034	0.25 ± 0.00	0.11 ± 0.00	48.35 ± 1.06	5.83 ± 0.04	0.03 ± 0.14
042	0.21 ± 0.00	0.08 ± 0.01	45.65 ± 1.34	5.60 ± 0.05	0.12 ± 0.17
21	0.10 ± 0.00	0.135 ± 0.007	68.65 ± 1.48	8.42 ± 0.02	0.19 ± 0.18
47	0.20 ± 0.03	0.115 ± 0.02	71.10 ± 1.13	8.65 ± 0.04	0.12 ± 0.14

^a Scheibler method.

^b Carlo Erba CN-analyzer.

^c Obtained by difference.

The short-term precision of organic carbon and nitrogen was determined from replicate analyses of BCSS-1 (Table 1; $n = 10$), an estuarine sediment reference material (Berman, 1987), and various samples (Table 2). Short-term reproducibilities for organic carbon and nitrogen average ± 2.78 and $\pm 2.80\%$ of the measured values, respectively. The long-term precision was determined from the results obtained for standard BCR-71 over the period from January 1992 to March 1993. The long-term precisions are very similar to the short-term precisions, namely $\pm 2.89\%$ for organic carbon and $\pm 3.67\%$ for nitrogen ($n = 210$).

The accuracy of the method is excellent as indicated by the correspondence between the recommended and measured value of BCSS-1 (Table 1) and the excellent agreement between certified values of organic carbon $40.39 \pm 0.8\%$ and nitrogen $10.85 \pm 0.8\%$ in BCR-71 and the long-term average ($n = 210$) of measured values, $40.45 \pm 1.17\%$ for organic carbon and $10.64 \pm 0.39\%$ for nitrogen.

3.2 Applicability of the method to natural particles

Many biogeochemical studies are based on the spatial and temporal distribution of organic carbon and nitrogen in a variety of materials. These studies require a method with not only high precision and accuracy, but also free of matrix interferences, i.e. the accuracy is independent of the carbonate content of the sample. The most direct test to determine the accuracy of organic carbon measurements in carbonate-rich samples is to analyze appropriate certified reference materials; unfortunately these are not available. The method proposed here has been applied to more than 2000 samples varying from carbonate-free mangrove sediments to carbonate-rich reef and deep-sea sediments (e.g. Table 2). So far, there are no indications of any systematic error related to the partitioning of organic and inorganic carbon phases.

Sediment samples from a variety of environ-

ments, covering a range of carbonate contents, were analyzed not only for organic carbon, but also for total carbon using the Carlo Erba elemental analyzer and for carbonate carbon by the method of Scheibler (Table 2). For these samples, organic carbon can also be estimated by subtracting carbonate carbon from the total carbon content. The organic carbon contents obtained by difference and those measured directly following in-situ acidification to remove inorganic carbon, are very well correlated ($r^2 = 0.986$, $n = 38$) with a slope (1.02 ± 0.02) and intercept (-0.03 ± 0.17) not significantly different from one and zero, respectively (Fig. 1).

Another way to check for systematic errors in organic carbon data from calcareous sediments is to compare the results of our method with those of other methods. This comparison is made for sediment samples for which organic carbon results are available, from de Lange (1992), Van Os et al. (submitted) and van Santvoort and de Lange (pers. commun., 1993). Their organic carbon data were obtained by dry combustion at 900°C following wet acidification with 1 N HCl, rinsing, removal of the supernatants, drying and reweighing. It should be mentioned that this procedure may result in loss of soluble organic matter (Froelich, 1980). Fig. 2 shows that the organic carbon results of the two methods are excellently correlated ($r^2 = 0.988$;

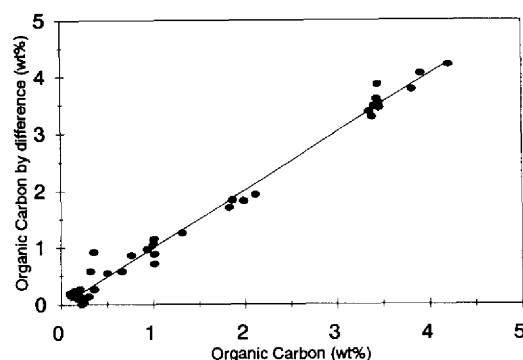


Fig. 1. Agreement between organic carbon results by our method and those obtained by difference. The solid line represents the best fit ($r^2 = 0.986$, $n = 38$). OC difference = (1.02 ± 0.02) OC - (0.03 ± 0.17) .

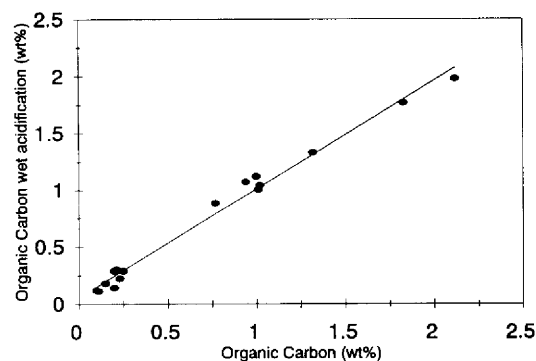


Fig. 2. Agreement between organic carbon results by our method and those obtained by dry combustion at 900°C following wet acidification with 1 N HCl. The solid line represents the best fit ($r^2 = 0.988$, $n = 16$). OC wet acidification = (0.95 ± 0.03) OC + (0.06 ± 0.07) .

$n = 16$) with a slope and intercept of 0.95 ± 0.03 and 0.06 ± 0.07 , respectively.

Although organic carbon data by our method and those by two other methods (Figs. 1 and 2) are correlated excellently, it should be realized that the line-fitting parameters are biased toward the better agreeing higher values. A more close inspection of data presented in Table 2 reveals that the in-situ acidification method yields better reproducible and more consistent results for calcium carbonate-rich samples. Samples 636, 637 and 647 should have identical organic carbon concentrations since they originate from a single homogeneous turbidite unit from the Madeira Abyssal Plain (de Lange, 1992). The organic carbon data obtained by our method indeed reflect this homogeneity, whereas those obtained by the reference difference method show significant variability. Moreover, the average relative standard deviation for sediments from the Madeira Abyssal Plain is 0.7% for our method, whereas the relative standard deviations for the reference difference method are all higher than 13%. Similarly, average relative standard deviations of organic carbon determinations for carbonate-rich reef sediments (carbonate contents > 90 wt%) are 11.9 and 438% for our and the reference difference method, respectively.

Finally, the reproducibility of the in-situ acidifi-

cation method depends on the homogeneity, e.g. grain size, of the sediments being analyzed, since only small aliquots are actually used. For instance, organic carbon data for heterogeneous, relative coarse-grained, estuarine salt-marsh and seagrass-covered sediments have average relative standard deviations of 2.9 and 8.4%, whereas those for homogeneous fine-grained deep-sea sediments from the Madeira Abyssal Plain, Eastern Mediterranean and Sicily have average relative standard deviations of 0.7, 2.3 and 1.3%, respectively.

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