Short Contribution

A Simple Indirect Method for the Determination of Organic-Carbon in Marine Particles

Shinichiro Noriki†, Chizuru Saito† and Shizuo Tsunogai†

Abstract: A simple indirect method for the determination of organic carbon in marine particulate matter is proposed. The recommended procedure is as follows: The dried sample is ashed at 450°C for about 24 hr. The ashed sample is put into a Teflon vessel followed by a mixed solution of nitric acid, perchloric acid and hydrofluoric acid. The vessel is sealed and allowed to stand at 150°C for 5 hr. The concentrations of Si and Al in the digested solution are determined. The organic carbon content (Cal-C, %) is calculated by the following equation:

\[ \text{Cal-C} = 0.52 ([\text{CF}] - 0.10 [\text{Opal}] - 0.03 [\text{A-Si}]) \]

where [CF] is the combustible fraction (%), [Opal] is the biogenic-SiO₂ (%), and [A-Si] is the content of aluminosilicate mineral (%).

1. Introduction

Particulate materials, especially settling particles, are important for explaining the dynamics of chemical substances in the ocean, since particulate materials carry chemical substances from the surface water to the deep ocean. The major components of particulate matter in the ocean are the following (e.g. Honjo, 1980; Tsunogai et al., 1982; Noriki and Tsunogai, 1986):

1. Aluminosilicate mineral
2. Opal
3. Calcium carbonate
4. Organic matter.

In these components, the content of organic matter is usually represented by the organic-carbon content. Organic carbon is generally determined by CHN elemental analysis (e.g. Ducklow et al., 1985; Neilson and Smith, Jr., 1986) or infrared spectrometry (e.g. Strickland and Parsons, 1972). These analyzers are rather exclusive, and the sediment trap samples are usually costly, because the samplings are difficult and expensive. Thus, it is extremely desirable to be able to analyze multicomponents with a small sample size.

An indirect method, which measures the weight loss of a sample by ashing it at 450°C (CF; combustible fraction) has been used for the determination of organic matter contents (Honjo, 1980; Tsunogai et al., 1982; Noriki and Tsunogai, 1986). This method has an advantage that we can determine some inorganic elements and some natural radionuclides from the same samples as are used for determining the organic matter contents. The results obtained by this method, however, sometimes have large errors. Tsunogai and Noriki (1987) have considered these errors to be due to the water of hydrous silicate, which remains after heating at 60°C in a vacuum but escapes after ashing for the determination of dry weight at 450°C. Therefore, they have proposed the following equation for the calculation of the organic carbon contents by examining the data obtained by Honjo (1980) and Wefer et al. (1982):

\[ \text{Org-C} = 0.52 ([\text{CF}] - 0.091 \times [\text{SiO₂}]) \]

where Org-C is the organic-carbon content in % to be obtained by calculation, [CF] is the combustible fraction in % measured at 450°C for 24 hr, and [SiO₂] is the total silicate content in %.

If we can permit the error of 5-10% for the

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organic carbon content, the above equation can be used to determine the organic-carbon content of biogenic materials of various origin. It is, however, desirable to obtain a more accurate equation for various particles, including sediment trap samples.

In this paper, we have examined 60 particle samples and obtained an improved equation for estimating the organic-carbon content of marine particles such as suspended particles and sinking particles.

Table 1. Concentrations of chemical components of settling particles.

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<th>Sample No.</th>
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<th>Total Si %</th>
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* Samples are the same as in Table 1.
2. Experimental

A marine particle sample is placed into a glass ampoule which is preheated at 500°C for 5 hr, and dried at 110°C for 2 hr. After it is cooled to room temperature, its weight is measured. The decrease in weight after ashing at 450°C for 24 hr (CF) is also measured. A chemical analysis of the remaining sample is done by the method of Noriki et al. (1980). The procedure is described briefly as follows: The ashed sample is placed into a Teflon vessel, followed by a mixed solution of nitric acid, perchloric acid, and hydrofluoric acid solutions, and the vessel is sealed and allowed to stand for 5 hr at 150°C. The concentrations of Al, Ca, and Si in the solution in the Teflon vessel are determined together with other components.

The results are listed in Table 1. The results shown in Table 2 were calculated by the following equations:

\[ T\text{-SiO}_2 \text{ (Total silicate)%} = \left(\text{Total Si} \times [60/28]\right) \]

\[ \text{Opal\%} = \left[\left(\text{Total Si} - \left[\text{Al} \times [28/8.1]\right]\right) \times [60/28]\right] \]

\[ \text{A-Si \ (Aluminosilicate\%)} = \left(\text{[Al]} \times [8.1]\right) \times 100 \]

\[ \text{CaCO}_3 \text{\%} = \left[\text{Ca} \times [100/40]\right] \]

where

\[ [60/28] \]: the ratio of molecular weight of \text{SiO}_2 to atomic weight of \text{Si}.

\[ [28/8.1] \]: the average crustal abundance ratio of \text{Si} to \text{Al}.

\[ [100/40] \]: the ratio of molecular weight of \text{CaCO}_3 to atomic weight of \text{Ca}.

Organic-carbon content was directly determined by a CHN elemental analyzer (denoted as CHN-C). Acetanilide was used for a standard material in the analysis. Average concentration and standard deviation of 13 samples of acetanilide were 70.9% (theoretical value: 71.1%) and 1.3%, respectively.

Although the samples of No. 3, No. 6, No. 7, and No. 23 might have been subjected to some accidental errors during analysis, all the data were used.

3. An improved equation

As mentioned above, the difference between the organic-carbon content determined by the direct method and that determined by an indirect method was caused by the hydrous water of silicate, so an improved equation is given as follows:

\[ \text{Cal-C} = 0.52 \left(\text{CF} - \text{A(Opal)} - \text{B[A-Si]}\right) \]

\[ (2) \]

Fig. 1. The observed CHN-C vs the calculated-C in the sample. ● This work, ○ Honjo (1980), ○ Wefer et al. (1982).

where

Cal-C: calculated organic carbon in %,

A: coefficient for opal content,

B: coefficient for aluminosilicate content.

The correction for the calcium-carbonate content was not made, because the calcium carbonate has no water molecules remaining after heating at 110°C for 2 hr.

Coefficients A and B were obtained by the least squares method to minimize the difference between the values on the left side and right side, using the 43 samples listed in Table 2 and the 17 samples reported by Honjo (1980) and Wefer et al. (1982). The most reasonable values were found to be A=0.10 and B=0.03.

In Fig. 1, the calculated organic-carbon contents were plotted against the carbon contents by a CHN-analyzer. The average of the absolute value of the difference between [Cal-C] and the observed [CHN-C] was 1.2%, while it is 1.3% using Eq. (1).

When the silicate and aluminum contents are measured, the proposed equation can be used. If only the silicate content can be measured, Eq. (1) may be used, although the error is somewhat larger.

Acknowledgments

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Analytical Chemistry, Faculty of Fisheries, Hokkaido University for their discussions and help in the sampling.

References