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SOME PROBLEMS FOR THE DETERMINATION OF ORGANIC CARBON IN MARINE SEDIMENTS

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ABSTRACT

In the determination of organic carbon in sediments, some problems in the preparation of samples, such as homogenization and drying conditions, have been discussed, as well as the correction of chlorine error.

From the results obtained, the following points were emphasized concerning the preparation of samples: the coarser fraction of the sediments should be removed by a sieve in order to gain a homogenous sample, and the sediments thus obtained should be dried at air temperature to prevent the loss of organic carbon through descomposition.

The positive error of organic carbon caused by the amount of chlorine in sediments can be corrected by the subtraction of $0.0717 \times Cl \frac{100}{1000}$ (%) from the amount obtained of organic carbon (%), and here, Cl is the chlorine content in sediments (mg/g.). In this way, the unwashed sediments containning chlorine can be used for the determintation of organic carbon, and thus the negative error due to the loss of organic carbon during the washing of sediments can be prevented.

RESUMEN

Para la determinación del carbono orgánico en los sedimentos se han discutido algunos problemas en la preparación de las muestras, tales como la homogeneización y las condiciones de desecado, así como también la corrección del error del carbono orgánico debido a la cantidad de cloruros.

De los resultados obtenidos, concernientes a la preparación de las muestras fueron recalcados los siguientes puntos: A saber, la fracción más gruesa de los sedimentos podría separarse haciéndolas pasar a través de un tamiz para obtener unas muestras homogéneas y los sedimentos deben ser desecados a bajas temperaturas para prevenir la pérdida de carbono orgánico durante el desecado al tiempo de colección.

El error positivo de carbono orgánico causado por la cantidad de cloruros en sedimentos puede ser corregido por la sustracción de $0.0717 \times Cl \times \frac{100}{1000}$ de la cantidad de carbono orgánico obtenido (%) y aquí, el Cl es el cloruro obtenido en los sedimentos (mg/g). En esta forma, los sedimentos no lavados que contienen cloruros pueden ser usados para la determinación de carbono orgánico y entonces, el error negativo por la pérdida de carbono orgánico durante el lavado de los sedimentos puede ser prevenido.

INTRODUCTION

The character of sediments may indicate the hydrographic conditions over the bottom, and may occasionally be used as a measure of the enviromental conditions of the benthic organisms. In addition, many problems concerning marine sediments are of immediate significance to phases of geochemistry and geology. From these points of view, many workers have taken interest in the determination of organic materials in sediments as well as inorganic materials and mechanical analyses. Especially, the determination of organic carbon and nitrogen in sediments has been carried out by many workers.

In order to treat many samples within a short time, organic carbon in marine sediments is frequently determined by the combustion method with potassium dichromate, because of its simplicity and rapidity. However, in this method, a relatively high quantity of the chlorine contained in marine sediments is simultaneously oxidized by potassium dichromate under the process of the oxidation of organic materials; as a result, the organic carbon content obtained has a positive

error. In order te remove the interference of chlorine in this method, washed sediments freed from chlorine are often used in the determination of organic carbon(1). However, it may be that the organic materials in sediments are lost in the washing water. Accordingly, the author has developed a method for the elimination of positive error due to the amount of chlorine which does not involve the washing of sediments. In addition, in the present paper, some problems in the preparation of sample such as the homogenization and the drying conditions have been discussed.

Material and analytical method

The five sediments used in this study were collected from around the Island of Margarita (samples A - D) and Laguna Unare (sample E). The determination of organic carbon in sediments was carried out by the wet combustion method with potassium dichromate in following procedure: 0.2 g of dried powdered sediments were weighed and put in the Erlenmeyer flask afterward 10 ml of chromic acid mixture (0.4 N as to potassium dichromate) were added. The sample and the solution were heated at a constant temperature for a period of 7 minutes, and were poured into approximately 150 ml of distilled water. They were then titrated against ferrous ammonium sulfate (0.2 N) using diphenylamine indicator. The calculation of organic carbon was done assuming 1 ml of ferrous ammonium sulfate (0.2 N) corresponding to 0.6 mg. of carbon.

Preparation of sample

Before the discussion of the problems of the preparation of samples, the method of collection (such as the number of stations, the repetition of sampling, the thickness of sediments, etc.) should be considered in order to get correct information about the characteristics of the area sampled. The present paper deals only with the problems of the preparation of sample for analysis.

There are three problems to be considered on the prepa-

ration of samples: first, the homogenization of the samples; secondly, their drying conditions; and thirdly, the effect of washing of sediments.

(1) *Homogenization*

Marine sediments contain shell fragments, gravel, and large organic detritus with fine-grained minerals and fine organic materials. These large-sized materials in sediments frequently interfere in obtaining an homogenious sample. This large fraction of sediments may or may not be a representative characteristic of the area and it must be decided whether the chemical analysis may be made on a total sample including the coarse fraction or only on the fine fraction. By the repetition of sampling, one may be able to confirm whether or not the sample has the representative characteristics of the area. However, for various reasons the repetition of sampling is frequently restricted.

In general, since a relatively small amount of sample (0.2-0.5 g) is used for the determination of organic carbon in sediments, the homogeneity of the sample is very important. For the sake of the comparison of the results obtained, it is desired that the preparation method of samples be standardized. For that purpose, the author attempted the following procedure on preparation of samples for the determination of organic carbon in sediments: the coarser fraction of the original sample was removed through a sieve of 1 mm. in diameter at the time of collection, and after drying the fraction remaining was homogeneously mixed in a porcelain mortar and used for the determination of organic carbon.

The effect of the sieving on the homogeneity of a sample was examined by using three different types of sediments (mud, sand, and muddy sand) and the results obtained are shown in Table 1. Each of the unsieved and sieved samples of sediments were analyzed five times. The sieved samples of the three different sediments showed a somewhat higher organic carbon content than the unsieved samples. This may be attributed to the removal of the coarse fraction, which has a lower content of organic carbon. Although in sediments A (mud)

TABLE 1. EFFECT OF THE SIEVING OF SEDIMENTS ON THE CONTENT OF ORGANIC CARBON

Samples	Organic Carbon %					
	A		B		C	
	Unsieved	Sieved	Unsieved	Sieved	Unsieved	Sieved
1	5.21	5.25	0.913	0.955	0.318	0.333
2	5.22	5.31	0.967	0.912	0.304	0.323
3	5.15	5.38	0.902	0.945	0.301	0.335
4	5.10	5.28	0.896	0.923	0.302	0.328
5	5.20	5.32	0.872	0.944	0.327	0.330
Average	5.18	5.32	0.910	0.936	0.310	0.330
Standard deviation	0.050	0.055	0.035	0.018	0.012	0.005
Type of sediments	Mud		Muddy sand and coral		Sand and coral	

there is not a great difference in the standard deviation between the unsieved and the sieved samples, there are somewhat greater differencs in the sediments B (muddy sand) and C (sand) because of the lower homogeneity of the unsieved samples in muddy sand and sand.

The sediments used in this experiments contain only slight amount of gravel. When the sediments have a large amount of gravel, the values analyzed will be more widly dispersed because of the lesser homogeneity of samples. Thus, it is desirable that the sediments be sieved in order to remove the coarser fraction.

(2) *Drying conditions*

Since the organic materials contained in sediments will decomposed with time, it is best that the determination of organic carbon be carried out on the moist sediments at the time of collection. Correction of humidity is necessary in order to establish the content of organic carbon based on dry sediments. However, since in sandy sediments the correction of humidity can lead to an error, the author decided to use the dried sediments to determine the organic carbon content, and to examine the effect of the drying condition of the sediments on the organic carbon content.

The unsieved and sieved samples were dried at air temperature, 60 °C and 105 °C. Table 2 shows the results obtained, in which the organic carbon content decreases slightly with the increase of the dry temperature. This may indicate an influence of dry temperature on the decomposition of organic materials in sediments. Accordingly, it is preferable that the sediments be dried at a low temperature.

Since these samples were kept moist for a fairly long time after their collection (i. e., two months for sample-D, and six months for sample - E), a considerable decomposition of the organic materials in sediments must have occurred during their storing. Therefore, the fresh sediments may have been more affected by the during process than the older ones.

(3) *Effect of wash*

To remove chlorine from marine sediments, they are so-

TABLE 2. EFFECT OF THE DRYING CONDITIONS OF SEDIMENTS ON THE CONTENT OF ORGANIC CARBON

Treatment of samples	Drying conditions	Organic Carbon %					
		Sample D			Sample E		
		Uncorrected	Corrected *	Diff. **	Uncorrected	Corrected *	Diff. **
Unsieved and Unwashed	Airdried	4.90	4.44	0.46	4.18	3.66	0.52
	60° C	4.85	4.38	0.47	4.14	3.62	0.52
	105° C	4.83	4.35	0.48	4.11	3.60	0.51
Sieved and Unwashed	Airdried	4.92	4.42	0.50	4.07	3.53	0.54
	60° C	4.87	4.38	0.49	4.05	3.51	0.53
	105° C	4.88	4.35	0.52	4.03	3.49	0.54

* Values were corrected on the chlorine error by means of the method described in this paper

** Corresponding to the chlorine error

metimes washed with fresh water; however, there may be a loss of organic carbon in sediments washed in this manner. To prove this point, a portion of sediments was repeatedly washed with distilled water by means of decantation and of filtration until the filtrate no longer indicated the precipitation of the silver chloride with silver nitrate solution. After washing, the amounts of chlorine in the sediments were 0.034 mg/g (sample - D) and 0.067 mg/g (sample -E), respectively. It was found that the amounts of chlorine in these samples had no significant effect on the organic carbon contents. The organic carbon of the washed sediments as well as that of the unwashed sediments was determined. The corrected values in Table 3 were obtained by the correction of chlorine error by means of the method described below. There was found a difference in organic carbon content between the uncorrected values of the unwashed and washed sediments (0.73% for sample - D and 0.75 % for sample - E). However, although the chlorine error of these samples were 0.52 % and 0.54 %, respectively, the difference (0.21%) between the uncorrected values and the chlorine errors (namely, between the corrected values of unwashed and washed samples), may be attributed to a loss of organic carbon during the washing of sediments. As mentioned before, there is no doubt that a certain amount of organic matter in these samples had been lost during the long storage by its decomposition, and if fresh sediments were used in this experiment, some organic carbon might furthermore be lost during washing.

Relation between the consumption of potassium dichromate and amount of chlorine.

Even if washing has only a small effect on the loss of organic carbon in sediments, owing to the time it takes for washing it is desirable to look for an easier method to eliminate chlorine error in sediments. Therefore, the author made the following experiment on the relation between consumption of potassium dichromate and the amount of chlorine in sediments.

Two groups of samples were prepared; the first group

TABLE 3. EFFECT OF THE WASHING OF SEDIMENTS ON THE CONTENT OF ORGANIC CARBON

Samples	Organic Carbon %					
	D			E		
	Unwashed	Washed	Difference	Unwashed	Washed	Differense
Uncorrected	4.88	4.15	0.73	4.03	3.28	0.75
Corrected	4.36	4.15	0.21	7.49	3.28	0.21
Chlorine error	0.52	0.00	0.52	0.54	0.00	0.54
Chlorinity mg/g	69.85	0.034	—	74.71	0.067	

* Values were corrected on the chlorine error by means of the method described in this paper.

consisted of 10 ml of chromic acid mixture and 1 ml of a sodium chloride solution having diverse concentrations of chlorine (from 0 to 50 Cl-mg/ml). The second group consisted of the same solutions and 0.200 g of dried washed sediments. The second group containing sediments and a sodium chloride solution was prepared to secure the effect of the presence of sediments on the consumption of potassium dichromate by chlorine. Then, in accordance with the above-mentioned procedure, potassium dichromate in samples of these two groups was titrated against ferrous ammonium. In order ascertain the amount of consumption of potassium dichromate by chlorine only in the second group, the burette reading in the sample containing only chlorine free sediments was subtracted from that of the samples of which contained sediments and chlorine.

For convenience sake in correction of the chlorine error, the equivalent values of organic carbon were calculated from the consumption of potassium dichromate by chlorine, assuming 1 ml of ferrorus ammonium sulfate solution (0.2 N) corresponds to 0.6 mg of carbon.

In Fig. 1, the amounts of organic carbon thus obtained, were plotted as ordinates against the amounts of chlorine as abscissae. As will be seen in Fig. 1, both groups showed almost the same amount of organic carbon compared to the amount of chlorine, and the amount of organic carbon increased proportionally with the amount of chlorine. From the relationship between the amounts of chlorine and of organic carbon, the following empirical formula was obtained by the method of least squares.

$$\text{Organic carbon (mg)} = 0.0717 \times \text{Cl}$$

Accordingly, it may be possible to correct the positive error of organic carbon content due to the amount of chlorine in sediments, and to omit the time and trouble of washing sediments as well as the possible error washing involves.

Procedure of correction

The corrected values of organic carbon in sediments may

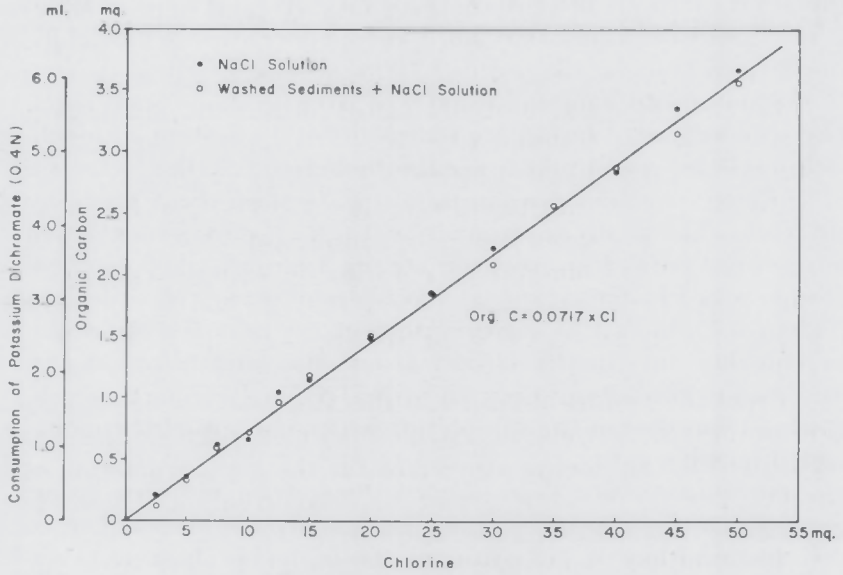

Fig. 1. Relation between the consumption of potassium dichromate and the amount of chlorine.

be obtained by the following procedure. If the amount of chlorine (Cl) is shown in the unit of mg/g, the amount of chlorine in the sample (S g) is shown as Cl x S mg. From the above empirical formula, therefore, the positive error of organic carbon caused by Cl x S mg in the sample becomes 0.0717 Cl x S mg.

The positive error thus obtained will be converted for the unit in per cent (%) by multiplication of $\frac{100}{S \times 1000}$ for 0.0717 x Cl x S mg. Then, the correction of organic carbon in per cent (%) is obtained as follows:

$$\text{Correction of organic carbon (\%)} = 0.0717 \times Cl \times \frac{100}{1000}$$

As a whole the amount of corrected organic carbon is obtained from the following formula.

$$\text{Organic carbon (\%)} = \left(\frac{0.6 \times F \times (T - t)}{S} - 0.0717 \times Cl\right) \times \frac{100}{1000}$$

Here, F: the normal factor of ferrous ammonium solution (0.2 N)
T: blank titrater
t: titration of sample
S: dried weigth of sample (g)
Cl: amount of chlorine in sample (mg/g)

CONCLUSIONS

From the results obtained in this study on the determination of organic carbon in marine sediments, the author has advocated the following procedure for the standardization of the preparation of samples and for the correction of positive error caused by the amount of chlorine.

The wet sediments are passed through a sieve of 1 mm in diameter at the time of collection, and the finer fraction is mixed homogeneously, and then dried at ambient temperature. The air - dried sediments are ground to powder, and a portion is used to determine the organic carbon. Another portion of this powder is dried at 105 °C to determine the moisture of air - dried sediments. A portion of the dried sample is used for the determination of the amount of chlorine.

A correction for moisture is made in the amounts of organic carbon in the air - dried sediments, as well as the correction of positive error due to the amount of chlorine in them.

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