

The Determination of Organic Carbon in Marine Muds

By

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IN the study of the productivity of shallow waters a knowledge of the organic-carbon content of muds is of considerable value. The determination of organic carbon may be carried out by the method of VAN SLYKE or titrimetrically by wet oxidation with chromic acid. VAN SLYKE's method has two disadvantages, firstly that carbonates must be absent or determined separately, and secondly that it requires special apparatus. The wet oxidation method is not affected by carbonates, but other reducing substances interfere. Most earlier workers have employed the method devised by SCHOLLENBERGER for the analysis of soils, in which the sample is heated for 90 seconds at 175°C. with excess chromium trioxide in concentrated sulphuric acid, and the chromic acid remaining after the reaction is determined volumetrically with ferrous ammonium sulphate solution. ALLISON has examined SCHOLLENBERGER's method and reports that the results obtained by this method must be multiplied by 1.15 in order to bring them into line with those obtained by dry combustion. WALKLEY has carried out a critical study of the determination of organic carbon in soils by chromic acid oxidation and has concluded that the greatest single cause of error is the variable nature of the organic material present.

When attempts were made to apply SCHOLLENBERGER's method to the analysis of muds, two difficulties were encountered. Firstly, the end point of the titration — a change from blue to green — was difficult to observe in the presence of suspended silt. Substitution of the ferrous-o-phenanthroline complex for the diphenylamine indicator gave an end point which was more readily seen. Secondly, samples of mud which had been ignited at 400°C., and which contained no detectable organic carbon, gave quite appreciable values for organic carbon owing to the reaction of chromic acid with the ferrous minerals present. Furthermore, the reproducibility of the method was poor (coefficient of variation ca. 20%).

Table 1
Analysis of carbonate-free muds

Sample No.	% "Carbon" found					Mean (A)	% carbon by combustion (B)	Factor B/A
27 G	0.22	0.23	0.21	0.20	0.22	0.22	0.25	1.14
31 G	0.32	0.29	0.31	0.34	0.34	0.32	0.36	1.13
61 G	0.45	0.44	0.41	0.40	0.42	0.43	0.48	1.12
23 G	0.46	0.50	0.50	—	—	0.49	0.59	1.20
63 G	0.69	0.61	0.72	—	—	0.67	0.81	1.21
12 G	1.24	1.33	1.35	—	—	1.31	1.53	1.17
22 G	4.40	4.28	4.15	4.10	—	4.34	4.59	1.06

In order to reduce interference from ferrous iron, experiments were carried out with the use of much milder and more reproducible oxidation conditions. It was found that consistent results for organic carbon in muds were obtained if the oxidation was carried out at 100°C. for 15 minutes.

Since the amount of chromic acid consumed depends on the completeness of oxidation and on the type of carbon linkages oxidized, the observed results must be multiplied by an empirical factor to bring them into agreement with the actual carbon content. To evaluate this factor a number of muds of salt-water origin were treated with dilute acid to remove carbonates, and after washing and drying, were analysed for carbon by combustion. The same carbonate-free samples were also analysed by the proposed method.

In Table 1 are shown the percentages of carbon determined by dry combustion and by chromic acid oxidation (assuming that 1 ml. of 0.2 N ferrous ammonium sulphate is equivalent to 0.6 mg. of carbon), together with the empirical factor which is their ratio. Its average value (1.15) is comparable with that found by ALLISON for soils under more drastic conditions. It may be seen that there is satisfactory agreement between replicate determinations. The variation of the factor is due in part to the error of the dry combustion method (standard deviation 0.03% of carbon). It is considered that the proposed method will determine organic carbon in muds with a coefficient variation of ca. 7% with 1% of carbon.

The same method may be used for the approximate analysis of plankton samples, in which case it is preferable to extend the heating period to 2½ hours at 100°C. Under these conditions a correction factor of 1.05 should be employed.

Procedure

Reagents

Chromic acid. Dissolve 13 g. of chromium trioxide A.R. in a minimum amount of water. Add about 900 ml. of concentrated sulphuric acid and when cold, dilute to 1 l. with concentrated sulphuric acid.

Ferrous ammonium sulphate (0.2 N). Dissolve 39.3 g. of the reagent grade salt in 400 ml. of water containing 10 ml. of concentrated sulphuric acid. Dilute to 500 ml.

Ferrous-phenanthroline indicator. (0.025 M). Dissolve 0.337 g. of o-phenanthroline monohydrate in 25 ml. of 0.695% ferrous sulphate solution.

Preparation of samples

In order to remove salts, marine muds should be carefully washed with distilled water on a sintered glass funnel (Porosity 4), or on a Buchner funnel fitted with a fine-texture, hardened filter paper. After drying at 105°C. the sample should be ground to pass a 100-mesh sieve.

Method

Weigh out 0.3–0.15 g. of the prepared sample into a boiling tube (15 × 2.5 cm.). Add 10 ml. of chromic acid from a wide-tipped pipette. Gently shake the tube and fit it with a loosely fitting bulb stopper. Heat in a bath of boiling water for 15 minutes. Cool, and pour the contents of the tube into 200 ml. of water. Add 1 drop of ferrous-phenanthroline indicator and titrate with 0.2 N ferrous ammonium sulphate solution until a pink colour just persists. Carry out a blank determination in the same manner but omitting the sample. 1 ml. of 0.2 N ferrous ammonium sulphate \equiv 1.15 × 0.6 mg. of carbon.

For the analysis of plankton samples, 10 mg. should be taken and the heating period extended to 2½ hrs. at 100°C. In this case 1 ml. of 0.2 N ferrous ammonium sulphate \equiv 1.05 × 0.6 mg. of carbon.

Interferences

The most likely sources of interference in the proposed method are halide derived from sea water, ferrous minerals and ferrous salts. Coal and coke lost overboard from ships are sometimes found in mud samples from inshore waters and present possibilities of interference.

Since chlorides react with chromic acid in sulphuric acid with the formation of readily volatile chromyl chloride, their presence in the determination leads to high results for carbon. Thus, 0.15 g. of an organic carbon-free mud sample, to which 7.5 mg. of sodium chloride had been added, gave a titre equivalent to 0.41 mg. of carbon, i. e., to 0.27% of carbon in the mud sample. It is important therefore that before analysis the chloride content of muds should be reduced to less than 0.5% by washing with water.

In order to investigate the errors due to ferrous minerals, a chloritic schist containing 10.7% FeO and no organic carbon, which had been ground to pass a 100-mesh sieve, was examined. With 1 g. samples an average titre corresponding to 0.06 ± 0.01% of carbon was found; the interference of ferrous minerals is therefore only slight. When the iron is present in a more soluble form, as in blue muds derived from a reducing environment, the error may be serious, in which case the soluble ferrous iron should be estimated and correction made for its presence.

The reactions of coal and coke were both tested for their reaction under the proposed conditions. It was found that 5–6 mg. of coal and 0.5 g. of

coke (both ground to pass 100-mesh) gave titres corresponding to 42% and 0.44% of carbon in the samples respectively. The interference of the amounts of coke likely to be found in marine muds is negligible, but the presence of coal will cause serious errors. Mud specimens which come from areas where coal is likely to be present should therefore be examined microscopically, and any coal found removed before analysis.

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Summary

A method is described for the analysis of marine muds for organic carbon, it is based on oxidation with chromic acid and titrimetric determination of the oxidant consumed. An empirical correction factor has been evaluated to correlate the carbon content found with that obtained by combustion. When ca. 1% of carbon is present, a coefficient of variation of about 7% is found. The method can also be used with slight modification for the approximate analysis of plankton.

References

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