

Organic Matter in Littoral Deposits

DURING a general study of the fauna of the Manx intertidal zone, I have been trying to determine, among other environmental factors, the amount of organic matter in littoral deposits. Several methods of determining the organic content of deposits have been tried, but those involving the reduction of chromic acid have been found to be the most useful because of their rapidity. There are many variations of the chromic acid method¹⁻³; but Allison's⁴ modification of Schollenberger's⁵ technique has been used on account of its reasonable accuracy^{4,6}, and because it was supposed to distinguish true organic matter from coal and other 'inert carbons'^{4,7}. The deposit is heated with excess potassium dichromate and concentrated sulphuric acid, rapidly cooled and diluted, and the excess dichromate titrated against standard ferrous ammonium sulphate^{4,5}. The result is expressed as a percentage of organic carbon, but the theoretical value (1.000 gm. carbon \equiv 16.345 gm. potassium dichromate) has to be adjusted to allow for incomplete oxidation of the carbon⁴. Unfortunately, I have now found that coal does react with chromic acid under these conditions, and as coal and other reducing substances in addition to true organic matter may be present in littoral deposits, it seems desirable to direct the attention of other shore ecologists to this fact.

Littoral deposits may contain considerable amounts of coal: in the Isle of Man, at one beach near which colliers are unloaded, the coal content may approach 10 per cent at certain times and levels. Determinations on core samples taken at mid-tide level from this beach have shown the 'organic carbon' content to increase from 0.6 per cent (dry-weight basis) at the surface to 7.8 per cent at 20 cm. deep, and physical analysis showed a corresponding increase in the coal content. Tests made with coal from this beach resulted in an 'organic carbon' content varying from 37 per cent in the case of small pieces (which disintegrated in the process) to 85 per cent with finely ground material.

Littoral deposits usually also contain a certain amount of iron, and where there is shelter from wave action much of it may be present as ferrous sulphide⁸. In the Isle of Man, the beaches may contain as much as 1.5 per cent total iron (estimated as Fe_2O_3), and in sheltered places one-third of this has been found in the ferrous condition. If all the iron was present in the ferrous state its reducing power, ignoring the sulphide ion, would be equivalent to approximately 0.05 per cent 'organic carbon': this value is quite significant when compared with values of total reducing power equivalent to 0.10 per cent organic carbon found at the surface of certain Manx beaches.

Thus, in its present form, the chromic acid method is unsuitable for deposits in the vicinity of coal-mining areas, large ports, and ports of discharge of colliers, and also for sheltered beaches containing ferrous iron. There is no reason why the method should not be used for deposits outside these categories; but it is suggested that before analysis a careful, if necessary microscopic, search be made for particles of coal in the deposit (this also applies to combustion-train determinations and to all methods involving chromic acid). If coal is absent, then tests should be made for ferrous iron. If coal is not present and only small amounts of ferrous iron are found, the method should be capable of giving reliable results, provided that silver sulphate is added to prevent the reaction

of chlorides with the chromic acid⁹. For full accuracy it will be necessary to calibrate the technique against either combustion-train determinations on the same material or tests with substances of known carbon content. Where ferrous iron is present in large amounts the method can be used in conjunction with colorimetric determinations of the iron, although where time permits a wet-combustion process would be better; where coal is present there does not seem to be any suitable method of analysis, nor a way of separating the coal without also separating the organic matter.

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- ¹ Adeney, W. E., and Dawson, B. B., *Sci. Proc. Roy. Dublin Soc.*, **18**, 199 (1926).
- ² Alexander, L. T., and Byers, H. G., *U.S. Dep. Agric. Tech. Bull.* **317** (1932).
- ³ Walkley, A., and Black, I. A., *Soil Sci.*, **37**, 29 (1934).
- ⁴ Allison, L. E., *Soil Sci.*, **40**, 311 (1935).
- ⁵ Schollenberger, C. J., *Soil Sci.*, **29**, 239 (1927).
- ⁶ Waksman, S. A., and Hutchings, I. J., *Soil Sci.*, **40**, 347 (1935).
- ⁷ Mare, M. F., *J. Mar. Biol. Assoc.*, **25**, 517 (1942).
- ⁸ Bruce, J. R., *J. Mar. Biol. Assoc.*, **15**, 553 (1928).
- ⁹ Anderson, D. Q., *J. Mar. Res.*, **2**, 225 (1939).
- ¹⁰ Mills, E. V., *J. Soc. Chem. Indust.*, **51**, 205 (1932).

Polarographic Determination of Fluoride

Willard and Dean¹ have described a polarographic method for the determination of aluminium, based on the measurement of the polarographic step produced by the reduction of 'Solochrome Violet R.S.' (sodium salt of 5-sulpho-2 hydroxy- α -benzene azo-2 naphthol), which is known as 'Pontachrome violet S.W.' in the United States. This compound produces a step of half-wave potential about 0.3 V. vs. the saturated calomel electrode in an acetate buffer solution of pH 4.6. Addition of aluminium to a solution of this dye causes this polarographic step to be reduced in height and a second step to appear at a point about 0.2 V. more negative. The sum of the height of these two steps is equal to the height of the original step, and the size of the second step is proportional to the concentration of aluminium present.

We have investigated the statement by Willard and Dean that this modification of the dye reduction step is inhibited by fluoride and have shown that this inhibition is quantitative. On this basis a method for the determination of microgram quantities of fluoride has been developed, involving the addition of excess aluminium to a solution containing fluoride, followed by the polarographic determination of the aluminium which remains uncombined. The following brief details of the calibration procedure serve as an illustration.

2 ml. of a solution containing 0.025 mgm. per ml. of aluminium in dilute perchloric acid is neutralized to methyl red with sodium hydroxide and treated with 1 ml. of 5 N perchloric acid and 5 ml. of 2 N ammonium acetate. Up to 15 ml. of a standard solution of sodium fluoride is then added, followed by 20 ml. of a 0.05 per cent aqueous solution of the dye. The solution is heated for 5 min. at 70° C., cooled, made up to 50 ml. and polarographed. It is only necessary to record the second polarographic step. A typical series of results is shown plotted on the accompanying graph, from which it is seen that