

ture and its action on metals, etc.—are probably due to the hydrobromic acid formed rather than to the ether-bromine compounds.¹

Further work on similar systems at low temperatures is being done in this laboratory.

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[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

METHOXYL IN SOIL ORGANIC MATTER.²

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The fact that the quantity of organic matter in different soils varies has been so well established that it is common knowledge. On the other hand the fact that the organic matter of soils varies widely in kind, that two soils may contain the same quantity of organic matter and this material be made up of quite different organic compounds in each case, while quite easily demonstrated, has not received general recognition.

The prevailing ideas regarding humus and humus formation seem to be based on the assumption that the multitude of organic compounds of many types present in the dead vegetation that contributes to the formation of the organic matter of soils is in some mysterious way reduced in the process of decay to a few compounds of the same type. The first step toward showing that this assumption is unwarranted is taken when it can be shown that soil organic matter varies greatly in the kind or types of organic chemical compounds comprising it. This can be shown in a number of ways, but the methods used can be classed under two general heads: first, the isolation of a number of definite organic compounds of different types; second, the application of group or class reactions that disclose the presence or absence of certain groups of organic compounds.

Under the first head much work has been done and has already been reported.³ In this work the demonstration of the variability in kind of organic matter has been incidental to the broader investigation of the chemical nature of this material.

In the use of type or group reactions the application may be simply a qualitative one, or where the reaction is of a character to permit it, may be quantitative. A reaction that may be used in this way is the formation of methyl iodide when compounds in which there is a methoxyl group, CH_3O , are treated with concentrated hydriodic acid. The method

¹ NOTE.—Carefully dried ether and bromine (75 per cent. Br) had at -30° a resistivity of 1000 ohms; then chemical action commencing the temperature rose and in a few seconds the resistance had fallen to 7 ohms.

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³ *Bulls.* 53 and 74, Bureau of Soils, U. S. Dept. Agr. *THIS JOURNAL*, 30, 1295, 1599 (1908); 31, 116 (1909); 32, 1674 (1910). *J. Biol. Chem.*, 8, 381 (1910).

for the quantitative determination of the methoxyl radical by this reaction was first suggested by Zeisel, and is generally known as the Zeisel¹ method. A number of improvements and modifications of the apparatus used have been suggested,² but the method as originally described is still in general use.

The first and only application of this method to organic material derived from soils is found in a paper on the chemistry and physiological action of the humic acids, in which Robertson, Irvine and Dobson³ reported investigations into the chemical composition and constitution of humic acids. These authors obtained four preparations of humic acid—two natural from peat by treatment with ammonium and potassium hydroxide respectively, and two artificial by boiling sugar with hydrochloric acid and treating portions of the brown amorphous material so obtained with ammonium and potassium hydroxide. They found some difference in composition of the natural preparations that obtained through ammonia containing 54.24 per cent. carbon, while that through potassium hydroxide contained 56.67 per cent. The artificial preparations were almost identical in composition except that the one obtained through ammonia contained 0.76 per cent. nitrogen, while the other was nitrogen-free. In these preparations the authors determined methoxyl, CH_3O , by the Zeisel method, and found such a wide difference between the natural and artificial preparations in this respect, that the only conclusion justified is that there are important differences in constitution, despite the general agreement of properties and composition. In the humic acid from peat 1.71 to 2.47 per cent. CH_3O was found while in that from sugar 6.47 was obtained.

In the application of this method to soils reported here, ten soils of widely different types and organic content, the same used in the pentosan determinations discussed elsewhere,⁴ were used. In making the determination five grams of air-dried soil were used except in cases where the organic content was very low, when ten grams were used. Ten cubic centimeters of hydriodic acid, sp. gr. 1.7, were added and the determination carried out in the manner originally described by Zeisel. The results obtained were calculated to the basis of the soil dried at 105° and the figures given are the mean of closely agreeing duplicates. In the case of the North Carolina peat, No. 4, and the Marshall loam, No. 5,

¹ *Monatsh. Chem.*, 6, 989 (1885); 7, 406 (1886).

² Benedict and Grüssner, *Chem.-Ztg.*, 13, 872 (1889). Ehmann, *Chem.-Ztg.*, 14, 1767 (1890). Benedict and Bamberger, 15, 221 (1891). Perkin, *Proc. Chem. Soc.*, 13, 239 (1903). Herzig, *Monatsh. Chem.*, 9, 554 (1888). Bamberger, *Monatsh. Chem.*, 15, 505 (1894). Gregor, *Monatsh. Chem.*, 19, 116 (1898). Kaufler, *Analyst*, 27, 126 (1902).

³ *Biochem. J.*, 2, 458 (1907).

⁴ THIS JOURNAL, 32, 1680 (1910).

in the table, there was a slight darkening of the silver iodide precipitate due, no doubt, to the evolution of hydrogen sulfide by the action of the acid on the soil, and the consequent formation of silver sulfide. Separation of the silver sulfide gave quantities too small to weigh, and while the figures for these soils may be high the error can be but slight.

The results obtained and calculations made therefrom are presented in the following table.

METHOXYL IN SOILS.

	Per cent. total carbon.	Per cent. CH ₃ O.	Per cent. methoxyl carbon.	Methoxyl carbon per 100 total carbon.
1 Elkton silt loam.....	0.522	none
2 Sassafras silt loam.....	0.315	0.003	0.001	0.317
3 Chester silt loam.....	1.510	0.004	0.001	0.066
4 N. Carolina peat.....	27.102	1.114	0.431	1.590
5 Marshall loam.....	6.971	0.131	0.050	0.717
6 Cal. peaty soil.....	11.478	0.027	0.010	0.087
7 Norfolk fine sandy loam.....	0.822	none
8 Santa Paula Cal. loam.....	1.308	0.004	0.001	0.076
9 Portsmouth loam.....	3.854	0.006	0.002	0.051
10 Susquehanna clay loam.....	1.048	0.002	0.0007	0.066

It will be noted that two soils contain no methoxyl; that soils Nos. 3, 8, 9 and 10 gave figures for the ratio methoxyl carbon to total carbon approximately the same, while soils Nos. 2, 4, 5 and 6 gave a much higher ratio. The Elkton silt loam and the Sassafras silt loam soils Nos. 1 and 2 are geologically of the same origin, of the same mechanical and mineral composition, and contain approximately the same quantities of total organic matter, but the former contains no methoxyl while the latter stands third in the ratio of methoxyl carbon to total carbon. On the whole the figures are sufficient to warrant the conclusion that the quantity of methoxyl bears no constant relation to the total organic matter. In other words the soil organic matter varies with respect to the compound or compounds containing the methoxyl radical.

The methoxy group, CH₃O, is found in a large number of organic compounds of very diverse origin. Many alkaloids contain this radical and its determination by the Zeisel method has aided materially in establishing the constitution of some of these compounds. Among the more important alkaloids quinine¹ and codeine² contain one and brucine³ two methoxyl groups.

A number of essential oils contain the methoxyl radical usually in a methyl ester of a substituted phenol. Thus anise oil contains anethole,

¹ Hesse, *Ann.*, 205, 314 (1880). Lipmann and Fleissner, *Monatsh. Chem.*, 16, 34 (1895).

² Herzig and Meyer, *Monatsh. Chem.*, 15, 613 (1894).

³ Zeisel, *Monatsh. Chem.*, 6, 989 (1885). Shenstone, *J. Chem. Soc.*, 43, 101 (1883).

$C_3H_5, C_6H_4OCH_3$, oil of cloves, eugenol, $C_3H_5C_6H_3(OCH_3)OH$, and oil of parsley, apiole, $C_3H_5C_6H(OCH_3)_2: O_2: CH_2$.

From the point of view of the origin of this radical in soil organic matter its occurrence in woody tissue is most important. Benedict and Bamberger¹ determined the methoxyl in a large number of woods and found it to be fairly constant, the methoxyl calculated as CH_3 was usually between two and three per cent., the extremes being 1.99 and 3.21 per cent., and they suggested this determination as a method of arriving at the quantity of wood cellulose in a mixture such as paper. It has been found that methoxyl is always a constituent of the lignocellulose or so-called compound cellulose of higher plants but the quantity in grasses, shrubs, etc., varies much more than in woods.

With these three sources of methoxyl compounds in mind it is clear that in the death and decay of vegetation all soils are having added to them organic material containing this radical. The fact that the quantity of methoxyl in soils varies and bears no relation to the total organic matter is no doubt due in part to variation in the composition of the vegetation that is the source of the organic matter, but the fact that it persists or forms in one soil and disappears in another of the same general type indicates that the processes of decay are quite different in different soils.

The methoxyl group then constituting but a small, and perhaps unimportant, part of the soil organic matter, by its presence or absence, or when present, by its proportion to the total organic matter, demonstrates one form of variation of soil organic matter. This or any other variation when found in soils of the same type and supplied with organic material from the same general source must be regarded as proof of some fundamental difference in the chemical, physical or biological factors that decide in what way a complex organic compound shall break down or decay when added to a soil.

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GLYCERIDES OF FATTY ACID IN SOILS.²

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The oils, fats and waxes are widely distributed in plants and animals and it follows that considerable quantities of these materials get into the soil and form the material from which soil organic matter is made. From the evidence at hand in the form of substances isolated from soils, it is clear that in some soils, at least, these compounds persist unchanged.

¹ *Monatsh. Chem.*, **II**, 260 (1890).

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