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## DETERMINATION OF MANGANESE IN SOILS.

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During recent years, a number of methods have been proposed for the estimation of manganese in soils. Most of them consist of three steps.—(1) extraction from soil; (2) conversion into one of the better known forms, generally the permanganate and (3) the quantitative estimation of the final products. The major part of the manganese of soils being either in the form of insoluble manganous salts or higher oxides, chiefly manganese dioxide, the extraction is best carried out after treatment with suitable reducing agents such as zinc dust, reduced iron, ferrous sulphate, oxalic acid or hydrogen peroxide in media containing sulphuric or hydrochloric acid. After extraction, the manganese in solution (which will be exclusively in the manganous condition) is oxidised to either manganese dioxide or permanganate, preferably the latter, by one of the more powerful oxidising agents—persulphate, periodate, perchlorate or bismuthate. Among these, the bismuthate is perhaps the most rapid and, at the same time, the most convenient to handle. The estimation of the resulting permanganate is carried out by one of the usual methods, preferably by absorption in excess of ferrous ammonium sulphate followed by back-titration against standard permanganate.

The various methods that have been so far proposed differ from each other in regard to efficiency of extraction. The subsequent oxidation does not also proceed quantitatively unless the conditions are properly standardised. There is also interference from the halides which may be present either in the soil or in the reagents employed. In view of these defects a systematic enquiry was undertaken with the object of evolving a rapid and quantitative method for the estimation of manganese in soil.

**Extraction.**—Preliminary experiments with known quantities of manganese dioxide, either as such or after addition to soil, showed that while most of the reagents were more or less efficient in bringing manganese dioxide alone into solution, they were not so effective when it was admixed with soil. The results obtained for the soil itself were generally variable, so that it was not possible to decide as to which of the reagents previously mentioned was the most efficient. Some new reagents were accordingly tried and it was found that alkali sulphite in acid medium was not only more rapid but also more efficient than any of the

other reagents so far tried. The final estimates obtained with soil were also higher than those secured by other methods.

**Oxidation to Permanganate.**—Attempts were first made to convert the manganese in solution to manganese dioxide which could be subsequently estimated iodometrically. Among the various reagents tried for this purpose, hydrogen peroxide in alkaline medium was the most efficient. The reaction was almost instantantaneous. The subsequent estimation of the precipitated manganese dioxide was also very rapid, but, unfortunately, the method is not suitable for soil extracts, which invariably contain iron. The resulting ferric oxide also releases iodine from potassium iodide so that exaggerated estimates of manganese are obtained. In view of this defect, the oxidation was carried to the permanganate stage in subsequent trials.

As already mentioned, treatment with bismuthate in acid medium is the most elegant method of converting manganous salts into permanganate. The reducing inorganic substances, if any, as also such small quantities of organic matter as may have passed into the extract are readily oxidised by the bismuthate.

**Elimination of Errors due to halides.**—It has been shown by Subrahmanyam, Narayanayya and Bhagvat (2. *Indian Inst. Sci.*, 1934, 17A, 197) that mercury salts prevent the formation of free halogen from halides even in presence of hot, sulphurochromic acid mixture. Some experiments were accordingly carried out, adding known quantities of sodium chloride to manganous salts treated with mercuric oxide to determine whether any chlorine was formed on addition of bismuthate. It was found that there was not a trace of chlorine even after prolonged boiling.

**Blank for Bismuthate.**—Another source of error which many workers seem to have overlooked is the blank for bismuthate itself. The error is generally positive and is proportional to the quantity of bismuthate added. The correction to be applied is, however, quite small being of the order of about 0.1 c. c. N/10 for each gram of the reagent.

The procedure developed by Harihara Iyer and Rajagopalan in these laboratories may be outlined as follows.—The soil (10-15 g.) is treated with pure sodium sulphite (chloride-free; 5 g.) and dilute sulphuric acid (4N; 100 c. c.) If the sulphite has been partly oxidised to sulphate, a larger quantity than 5 g. will be required. It will be desirable therefore

to check the purity from time to time. The mixture is well shaken and raised to boil. The boiling can be done in the open laboratory. The major part of the sulphite is taken up in the reduction, so that the quantity of sulphur dioxide actually given off is very small. After a few minutes, the entire quantity of manganese is brought into solution and the unused sulphur dioxide driven off. The suspension is then filtered through a Buchner and the clear filtrate transferred to a conical flask (capacity about 250 c. c.) It is then treated with mercuric oxide (red or yellow variety, 2-3 g.) and sodium bismuthate, the latter being added in small quantities at a time. Suspension is momentarily raised to boil, fresh quantities of bismuthate being added until the colour of permanganate is permanently established. It is then filtered through a Gooch or Jena glass filter, the filtrate being received in acidified, ferrous ammonium sulphate (N/25). The unused portion of the latter is then titrated against standard permanganate (N/25) in the usual way.

A preliminary experiment carried out with known quantities of bismuthate alone will give an idea of the error due to that reagent. As already explained, the error is very small and the necessary correction can be easily applied by adding known quantities of bismuthate for each experiment.

**Advantages of the modified procedure.**—(1) The extraction is rapid and quantitative. (2) The use of excess of reducing agent and consequent wastage of the expensive bismuthate is avoided. (3) The error due to halides is obviated.

**Applications.**—The method has been successfully applied not only for estimation of total manganese but also for studying the transformations of manganese attendant on the decomposition of organic matter in the soil. It is also capable of extension to a number of other enquiries relating to the role of manganese in plant nutrition.