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. Among these, the gasometric methods are applicable only to the estimation of manganese dioxide and do not include manganous compounds (Johnson, *Hawaii Agric. Expt. Sta.*, 1924. *Bull.* No. 52; Robinson, *Soil. Sci.*, 1929, **27**, 335). The procedure, besides being highly tedious, rarely yields accurate results. The colorimetric methods are based on the acid digestion of the soil followed by the oxidation of the manganous salts in solution to permanganate (Willard and Greathouse, *J. A. C. S.*, 1917, **39**, 2366; Emmert, *Soil. Sci.*, 1931, **31**, 175). Here again, the procedure is tedious and the method is applicable only to small quantities. The volumetric methods have found the greatest favour because of the rapidity with which they can be conducted. They are also fairly accurate. In principle, they are similar to the colorimetric methods, but, more recently, a number of modifications have been introduced with a view to eliminating the need for pre-digesting the soil. The procedure consists in first extracting the soil with suitable reducing agents (ferrous sulphate, hydrogen peroxide and such like), followed by oxidation of the extract to permanganate. Unfortunately, all reducing agents are not equally efficient in extracting manganese: nor is the extracted manganese quantitatively oxidised to permanganate presumably because of the interference from halides and dissolved organic matter. With a view to eliminating these defects and to standardising the conditions for the accurate estimation of manganese in all types of soils, the present enquiry was undertaken.

EXPERIMENTAL.

Some preliminary experiments were carried out with known quantities of manganese dioxide in order to determine the efficiency of the different extractors—ferrous ammonium sulphate (Brewer and Carr, *Soil Sci.*, 1927, **23**, 165), hydrogen peroxide (Schollenberger, *Soil Sci.*, 1930, **29**, 261), zinc and alkali sulphite (chloride-free), all sulphuric acid media. Wherever possible, the extractions were carried out according to the specifications of the authors referred to. Extraction with hydrogen peroxide was conducted on the lines of Schollenberger on the water-bath for 30 minutes. In the other cases, the suspensions of the dioxide in 100 c.c. of 4 N sulphuric acid, were boiled with 10 c.c. of the reducing agent, for 10 minutes, to complete the extractions and then filtered. The filtrates were made upto known volumes and aliquots treated with sodium bismuthate in sufficient excess to produce a permanent pink colour. They were then just raised to boil and filtered, through Gooch, into excess of standard ferrous ammonium sulphate. The unused reagent was estimated, in the usual way, by titration against standard permanganate.

TABLE I.

	Manganese dioxide .... (in mg.) after extraction with				
	Zinc	Ferrous Ammonium sulphate	Hydrogen peroxide (cold)	Hydrogen peroxide (hot)	Sodium sulphite
Taken	149·2	143·6	188·7	139·8	141·5
Found	131·7	143·0	187·1	139·2	141·0

The results (Table I) show that fairly accurate estimates can be obtained in all the cases except that of zinc.

The observations were next extended to the estimation of manganese dioxide in some of the representative specimens of soils. The procedure consisted in treating 10 g. of each soil with the necessary quantity of sulphuric acid and sufficient excess of the appropriate reducing agent. The results have been presented in Table II.

TABLE II.

Description of soil	Manganese (in parts per million) after extraction with			
	Ferrous Ammonium sulphate	Hydrogen peroxide (cold)	Hydrogen peroxide (hot)	Sodium sulphite
Bangalore	231	313	331	363
Dacca Farm—Lowland .	200	225	231	250
N. Bihar—Upland ..	163	150	163	163
Nasik Dt.—Sub-soil ..	413	325	413	525

The above soils contained no chloride.

It may be noted that widely divergent results were obtained by adopting different methods of extraction. The best results were obtained after treatment with sulphite: they were also the most consistent.

The lower results obtained in the other cases may be due to one or more of the following causes:—(1) The difference in behaviour and general extractability of the manganese dioxide of the soil from those of the pure, precipitated chemical; (2) incomplete extraction of manganese compounds other than the dioxide; (3) interference from organic matter which may be extracted to greater extent than in the case of sulphite. Further research on this aspect of the problem is needed before any definite conclusions can be drawn.

It was not clear from the foregoing observations whether even the sulphite had extracted the entire quantity of manganese present in each soil; so, some experiments were carried out comparing the manganese contents as obtained by that method and those after 'Kjeldahl' digestion with sulphuric acid and potassium and copper sulphates and subsequent estimation by oxidation with bismuthate of an aliquot after making the digest to a known volume. The results (Table III) show that very nearly the entire quantity was extracted in each case by treatment with sulphite.

TABLE III.

Description of Soil	Manganese (in parts per million) after	
	Treatment with sulphite	Kjeldahl digestion
Bangalore	359	357
Anakapalle—Red loam ..	282	281
Cuttack—Upland	228	232
Nasik	522	525

The above soils contained no chloride.

The procedure was next extended to the determination of manganese in some representative specimens of Indian soils.

TABLE IV.

Soil from	Manganese (in p.p m.) as estimated after	
	Sulphite extraction	Kjeldahl digestion
Willingdon Cattle Farm—Sindh	488	389
Baramathi—Alkali soil ..	800	638
Karl soil, Sholapur	913	825
Godavari Delta	888	775

It was found that in some of the cases the estimates were abnormally high. The values obtained for the Kjeldahl digestion showed that the estimates obtained by sulphite extraction were fictitious. This combined with the observation that there was pronounced smell of chlorine on treating the sulphite extract with bismuthate, suggested that the chlorides present in these soils were being oxidised to elementary chlorine, and that the latter was probably responsible for the abnormally high values. This was subsequently verified by direct addition of known quantities of sodium chloride to soils which do not naturally contain any.

TABLE V.

Soil from	Soil alone	Soil + Sodium chloride (1 per cent)					
		1 c.c.	2 c.c.	3 c.c	4 c.c.	5 c.c	6 c.c.
	Manganese as estimated (in p.p.m.)						
Bangalore	351	489	615	753	879	1029	1167
Dharwar—Highland ..	464	628	778	941	1092	1242	1343

With a view to eliminating the interference of chlorides, a number of reagents were tried. Among these, mercury salts were found to be the most satisfactory. A convenient procedure was found to be that of adding mercuric oxide (red or yellow, 1 g.) to the acid extract prior to the addition of bismuthate. The permanganate solution thus obtained was quite free from chlorine and yielded fairly correct estimates of manganese as may be seen from the following table (Table VI).

TABLE VI.

Soil from	Soil alone	Soil + Sodium chloride (1 per cent.)		
		1 c.c.	4 c.c.	6 c.c.
	Manganese (in p.p.m.) as estimated			
Bangalore	351	351	364	351
Dharwar—Highland ..	464	470	464	458

Silver salts were not effective in removing the interfering halides. They tended to form soluble salts on addition of bismuthate and thus passed into filtrate together with the permanganate.

The mechanism of the action of mercury salts is still obscure. It is clear, however, that they form certain halide complexes which are highly resistant to the action of oxidising agents. As observed in a previous enquiry, even boiling chromic acid in fairly concentrated sulphuric acid media (2 : 1 or more) is not effective in releasing chlorine from that complex. (Subrahmanyan, Narayanayya and Bhagvat, *J. Indian Inst. Sci.*, 1934, **17A**, 197; Narayanayya and Subrahmanyan, *Curr. Sci.*, 1935, 3, 423; *J. S. C. I.*, 1935, **54**, 106T; *Proc. Ind. Acad. Sci.*, 1935, 2, 213; Harihara Iyer, R. Rajagopalan and V. Subrahmanyan, *Curr. Sci.*, 1935, **4**, 98; *Proc. Ind. Acad. Sci.*, 1936, 3, 35.)

Manganese contents of some Indian soils.—Applying the above procedure, the manganese contents of a number of representative soils were determined. In some cases, the acid soluble manganese was separately estimated. This would include the water soluble forms as also compounds such as the carbonate, phosphate and sulphide of manganese. Manganese dioxide, being insoluble in dilute acid, would not be included in this estimate but the difference between the total and the acid soluble manganese would be largely represented by that form.

TABLE VII.

Total Manganese Contents of Some Indian Soils.

Locality and Description of Soil	Total Manganese in p.p.m.	Locality and Description of Soil	Total Manganese in p.p.m.
Bangalore — red gravelly type	362	Cuttack — Upland ..	225
Dacca — Lowland ..	250	Willingdon Cattle Farm, Sindh ..	389
North Bihar — Upland ..	163	Baramathi — Bombay Presidency ..	638
Nasik — Subsoil ..	525	Belgaum	313
Anakapalle — Red loam ..	281	*Kalar* soil — Sindh ..	825

TABLE VIII.

Total and Acid Soluble Manganese Contents of Some Indian Soils.

Locality and Description of Soil	Manganese in p.p.m.		Locality and Description of Soil	Manganese in p.p.m.	
	Acid soluble	Total		Acid soluble	Total
Jaffna—Ceylon	275	690	Jacobabad	186	366
Godavari Delta—Alluvial	204	775	Ahmedabad—Surface soil	59	96
Sholapur—*Kaal* soil	257	1177	Mandalay—Rice soil	276	402
Tellichery—Red, sandy loam	95	131	Sukkur—Surface soil	275	438
Nilgiris—Estate soil	601	997	Ratnagiri	212	907
Tindivanam—Alkali soil	140	186	Tanjore—Alluvial	186	294
Hagari—Black cotton	436	888	Nandyal	203	925
Dharwar—Highland	465	1340	Galle	311	943
N. Bihar—Calcareous	263	366	Tarsal	690	1249
Kandy, Ceylon	348	510	Gorakhpur—Upland	262	574
Poona—Light, cane soil	423	1269	Ranchi—Upland	277	1032

It may be seen from the above that the manganese contents of soils show considerable variation, from under 100 to over 1300 p.p.m. The distribution does not follow any well-defined geographical order, but speaking generally, it would appear that the black cotton tracts of Deccan and the neighbouring areas are richer in regard to both acid soluble and total manganese than the others.

In many of the soils, the major part of the manganese is present in acid insoluble form, while in some others, the acid soluble forms account for a large part of the total manganese.

The significance of manganese supply and its relation to plant growth and crop yield from Indian soils is still awaiting elucidation. It may be expected that the availability of manganese in soil has also some bearing on animal nutrition.

Procedure to be adopted in presence of excess of soluble organic matter.—The extracts from the commoner types of soils contain very little organic matter and generally offer no difficulty in the estimation. There are, nevertheless, some (such as those from freshly manured soils), which contain fairly large quantities of organic matter and take up considerable amounts of bismuthate before developing the pink colour of permanganate. In such cases, it has been found advisable to take smaller aliquots than usual. The bismuthate should be added in small instalments at a time until the pink colour makes its appearance. The mixture is then just raised to boil, allowed to cool to some extent and treated with a further quantity of bismuthate. The resulting suspension is quickly filtered into standard ferrous ammonium sulphate and the back titration carried out in the usual way.

If the bismuthate-treated extract is allowed to stand for some time, then the pink colour slowly fades out, owing to interaction with some of the organic matter still present in the extract. The addition of the extra quantity of the bismuthate followed by quicker filtration eliminates this error and yields accurate estimates of manganese.

Blank for bismuthate.—Some of the commercial brands of alkali bismuthate contain chlorides. The error due to this, as also any halide that may be present in the material to be examined, can be removed by treatment with mercuric oxide in the manner described above. In addition to this, some error may be introduced by certain other soluble constituents associated with the bismuthate itself. It has been found that when a known weight of sodium bismuthate is treated with excess of 4 N normal acid and the acid suspension just raised to boil and then filtered, the filtrate takes up a small quantity of standard ferrous ammonium sulphate. This has been found to be proportionate to the weight taken. For one brand of bismuthate used in this laboratory, the correction was equivalent to 0.5 c.c. of N/50 ferrous ammonium sulphate for 1 gm. of bismuthate; for another brand, it was 1.1 c.c.

The above correction, though small, may be quite necessary when dealing with materials containing very small quantities of manganese.

Distribution of manganese in the soil.—It appeared probable that, in addition to acid soluble forms described in an earlier section, there may be also water soluble ones which may be of some importance in plant nutrition. It is also desirable to ascertain whether varying quantities of manganese can be brought into solution by different strengths of acid. With a view to determining these and to evolving a general procedure for the study of the distribution of manganese in soils, the following experiments were carried out with representative specimens from different parts of India. In one series, the samples were extracted successively with water, diluted (4 N) acid, alone and as combined with sulphite. The residues left after the extractions were subjected to Kjeldahl digestion (as for Nitrogen estimation) and the manganese in the digests estimated in the usual way. In another series, parallel samples were extracted with different strengths of sulphuric acid and the amounts of manganese so extracted compared. The results have been presented in Tables IX and X.

TABLE IX.

Distribution of Manganese in Some Indian Soils.

Description of Soil	Manganese per cent.			
	Water soluble	Acid (4N) soluble	Extracted by acid and sulphite	In the digested residue
Sholapur—*Kali* soil	Traces	257 (21·8)	920 (78·2)	Nil
Godavari Dt.—Alluvial soil	,,	293 (16·7)	812 (83·3)	,,
Tellichery—Red sandy loam	,,	95 (72·5)	36 (27·5)	,,
Nilgiris—Estate soil	,,	601 (60·3)	396 (39·7)	,,
Tindivanam—Alkali soil	,,	140 (75·3)	46 (24·7)	,,
Hagari—Black cotton	,,	436 (49·1)	452 (50·9)	,,

The bracketed figures represent the corresponding percentages of total manganese.

TABLE X.

Dissolution of Manganese in Different Strengths of Acid.

Soil from	Manganese (per cent.) as dissolved by			
	N. H_2SO_4	2N. H_2SO_4	4N. H_2SO_4	8N. H_2SO_4
Dharwar—Highland	465	458	472	472
N. Bihar—Calcareous	257	257	250	263
Parbhani, Deccan, Surface soil	420	413	413	420
Punjab	125	112	125	125
Kalavathi	165	165	172	179

It may be seen from the above that, at any rate in the air-dried soil, there is practically no water soluble manganese. The acid soluble forms represent a considerable part of the total manganese. In some cases, it is less than the sulphite-extracted manganese (mostly manganese dioxide), whereas in others it greatly exceeds the other forms.

The absence of any manganese in the residue used for digestion shows that extraction with sodium sulphite and acid brings all the manganese into solution. The results in Table X would show that the amount of manganese extracted by acid does not depend on its concentration to any extent. However, for practical purposes, 2 to 4 N acid may be employed.

General procedure for the estimation of total manganese in soils.—The soil (dry or wet, equivalent to about 10 g.) is suspended in dilute sulphuric acid (4 Normal, 100 c.c.) and treated with 5 to 10 g. of pure (chloride-free) sodium sulphite. The suspension is then boiled for 10 minutes so as to facilitate complete dissolution of manganese and to drive off the unused sulphur dioxide. It is then filtered and the filtrate made upto a known volume. An aliquot (25 to 50 c.c.) is taken, enough sulphuric acid added to bring the normality to 4 N and then treated with mercuric oxide (red or yellow, 2 g.) followed by sodium bismuthate (0.5 g.) and the mixture shaken. If the pink colour develops quickly, and remains more or less permanent, then the suspension is just raised to boil to complete the oxidation. If the pink colour does not develop with the first addition of bismuthate or the colour fades out on heating, a little more (0.5 g.) of the reagent may be added, and the operation repeated. When the colour is finally established on boiling for 2 to 3 minutes, the suspension is allowed to cool somewhat and a small instalment (0.1 g.) of bismuthate added. It is then filtered rapidly into standard ferrous ammonium sulphate. The unused reagent is then estimated in the usual way.

Extension of technique.—The above procedure offers possibilities of extension to other types of biological materials, especially those of plant or animal origin. The present methods of digestion with sulphuric and nitric acids are tedious and time-consuming. By direct extraction with sulphite and acid, a large part of the interfering, insoluble organic matter is eliminated. Subsequent treatment with bismuthate is sufficient to oxidise the interfering organic matter and to convert all the manganese in solution to permanganate. Further work is now in progress with a view to standardising the conditions so as to make it applicable to all types of biological materials in general.

SUMMARY.

1. Among the various reagents that were tried, alkali sulphite (in acid medium) was found to be the most efficient in extracting manganese from soils. The results thus obtained agreed closely with those after digestion with concentrated sulphuric acid.

2. Soils containing chlorides yield fictitiously high estimates of manganese. This has been traced to the formation of free chloride through oxidation by bismuthate.

3. The interfering chlorides can be removed and correct estimates of manganese obtained by treating the extract with mercuric oxide (red or yellow) prior to addition of bismuthate.

4. Interference from organic matter in solution can be eliminated by taking small quantities of the extract and adding sufficient excess of bismuthate to give a permanent pink colour on boiling. A further quantity of bismuthate is then added after cooling and the suspension filtered rapidly into standard ferrous ammonium sulphate.

5. Attention has been drawn to the presence of a water soluble, colourless constituent in the commoner samples of bismuthate which reacts with ferrous ammonium sulphate. The correction to be applied for this is comparatively small and proportional to the weight of the bismuthate added.

6. It has been shown that successive extraction with water, dilute acid and sulphite may be adopted for the study of the distribution of manganese in soils.

7. A general procedure for the estimation of total manganese in soils has been described. The technique has been applied to the determination of manganese in a number of representative specimens of Indian soils. Extension of the method to the estimation of manganese in other types of biological materials has also been indicated.

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