

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

DETERMINATION OF SULPHURIC ACID IN SOILS.

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SULPHUR generally occurs in the soil in the form of sulphates and has been heretofore estimated by slightly acidifying the soil solution with hydrochloric acid, boiling and then precipitating by slowly adding barium chloride with constant stirring. After standing a few hours, the precipitate is filtered, washed, dried and weighed as barium sulphate and calculated to sulphur trioxide.

There are three difficulties generally encountered in determining sulphuric acid in soils: (1) The small quantity of the constituent usually present; (2) the solubility of some of the barium sulphate precipitate in the ferric chloride or aluminum chloride or both, which are almost invariably present; (3) as well as on the other hand the strong liability of the precipitate becoming contaminated by iron, especially if the soil is of a ferruginous character and the soil solution is not strongly acid.

Lunge¹ found that in determining sulphur in pyrites unless the solution is strongly acidulated with hydrochloric acid, considerable iron is carried down with the barium sulphate and is not removed by washing; on the other hand he found that the barium sulphate is dissolved by the solution if too strongly acid. Experiments by Jannasch and Richards² show that if sulphuric acid is precipitated in the presence of iron, a double barium iron sulphate is formed which, when ignited, sets free sulphur trioxide. They, in the light of their work, stated that to obtain correct results the iron had to be removed before precipitation with barium chloride.

The conditions and difficulties cited above are similar to those that frequently obtain when we come to determine sulphur in soils, for not infrequently soils contain as much as 5 to 15 per cent of ferric oxide. Now if Lunge found it difficult to estimate sulphur with any degree of accuracy in the presence of iron in pyrites, then may we not expect to encounter difficulty when we attempt to estimate it in soils where the relative proportion of iron

¹ *Ztschr. anal. Chem.*, **19**, 419-431.

² *J. prakt. Chem.*, **39**, 321.

to sulphur is vastly greater and the sulphur usually in such minute quantities as to require the greatest precision without unfavorable conditions?

The writer in analyzing soils during the past year noticed that if iron and alumina were first removed by precipitation with ammonia, the results were considerably higher in almost all instances than if the acid was precipitated direct as directed in the methods prescribed by the Association of Official Agricultural Chemists. It was also observed that the precipitate was coarse-grained and did not tend to run through the filter as it did if precipitated in the presence of iron and alumina.

In the following table are recorded comparative results obtained by the two methods, or rather two modifications of the same method. Those under "official" are obtained by the method prescribed by the Association of Official Agricultural Chemists, while those under "modified" are results obtained by first removing the iron and alumina before precipitating the barium sulphate.

Soil No.	Per cent. sulphur trioxide.		Difference.
	Official method.	Modified method.	
58	0.013	0.040	0.027
59	0.019	0.037	0.018
60	0.022	0.034	0.012
61	0.015	0.036	0.021
62	0.012	0.031	0.019
63	0.039*	0.039
64	0.020	0.040	0.020
65	0.015	0.032	0.017
66	0.011	0.030	0.019
67	0.050	0.061	0.011
68	0.013	0.029	0.016
70	0.057	0.065	0.008
71	0.027	0.041	0.014
72	0.026	0.031	0.005
73	0.017	0.027	0.010
74	0.022	0.038	0.016
75	0.021	0.031	0.010
76	0.026	0.041	0.015
77	0.034*	0.034
78	0.110*	0.106
79	0.021*	0.031
80	0.103	0.123	0.020
81	0.087*	0.106
82	0.027	0.055	0.028
83	0.058*	0.050

* Barium sulphate colored brown by the presence of iron.

Soil No.	Per cent. sulphur trioxide.		Difference.
	Official method.	Modified method.	
84	0.065	0.098	0.033
85	0.034	0.087	0.053
86	0.007	0.082	0.075
87	0.003	0.045	0.042
88	0.024	0.057	0.033
89	0.000	0.050	0.050
90	0.082	0.093	0.011
91	0.017	0.046	0.029
92	0.041	0.058	0.017
93	0.027	0.034	0.007

In the first eleven results by both methods, 4 grams of soil were taken for the determinations, in the next twelve, 2 grams for the "official" and 1 gram for the "modified," and in the last twelve 1 gram for the "official" and 2 grams for the "modified" methods. It is seen that the differences generally with the last twelve soils by the two methods are much greater than in the preceding twenty-three. The explanation for this greater divergence seems to lie in the amount of soil taken for analysis, as all other conditions were identical and it is noticed that when only 1 gram of soil is used with the "official" method the sulphuric acid is precipitated in such a finely divided condition that a little will pass the most retentive filter-paper (No. 589, S & S, blue ribbon) unobserved, unless the filtrate is examined very closely by transmitted light.

Whatever else may be said, the results in the table point very clearly to the fact that when sulphuric acid is precipitated in the presence of iron and alumina some of the barium sulphate is dissolved by either the ferric chloride or aluminum chloride or by both, and that it can only be determined accurately in soil solutions in which these two bases have been eliminated. If the results by the "modified" method are correct, and it can not be seen why they are not, as the ferric and aluminum hydroxides were in all instances washed at least ten times, using about 20 cc. at each washing, then the "official" method lacks over 35 per cent. of getting out all the sulphur trioxide in the above thirty-five samples.

In an experiment to test the solubility of barium sulphate in ferric chloride, it was found that when a solution was taken containing 0.110398 gram ferric chloride and 0.001288 gram of sulphuric acid (the averages of both sulphur trioxide and ferric chloride in the thirty-five samples experimented with when 2 grams of

soil are taken), that 17 per cent. of the sulphur trioxide was dissolved, results being obtained in closely agreeing duplicates. In a preliminary experiment it was observed that if the solution was only slightly acid (0.2 cc. excess of concentrated hydrochloric acid) iron in some form, probably an oxychloride, was frequently deposited on the bottom of the beaker in boiling prior to the addition of barium chloride, and stuck so tenaciously as to be removed only by the addition of considerably more hydrochloric acid. This same phenomenon was often observed in working with soils containing a moderately high percentage of iron with only a slight acidity of the soil solution.

In the experiment above to ascertain the solubility of barium sulphate in ferric chloride, 3 cc. excess of hydrochloric acid were present, as this was sufficient to prevent the deposition of iron and was found in a preliminary trial to exert an inappreciable, if any, dissolving effect.

Although the determination of sulphuric acid is not at present considered by soil chemists of the highest importance, because it generally exists in most soils in sufficient quantity for the complete development of crops for years to come, yet its importance as an essential constituent of plant food and its probable deficiency in many instances has prompted the writer to submit the above results and observations.

THE INTERACTION OF SULPHURETTED HYDROGEN AND ARSENIC ACID.¹

BY L. W. McCAY.

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FROM solutions of arsenic acid which have been treated with sulphuretted hydrogen I have been able to separate large amounts of monosulphoxyarsenic acid in the form of its tertiary sodium salt, and small amounts of disulphoxyarsenic acid, also in the form of its tertiary sodium salt. In addition to the above-mentioned acids the solutions appear to contain some trisulphoxyarsenic acid. Thus far, however, all attempts to isolate this compound have failed. If we assume its existence in the solutions, and a number of facts warrant us in making the assumption, the action of

¹ The facts given in the first part of this article have been taken from a paper which appeared in the *Ztschr. anorg. Chem.*, 29, 36 (1901).