

can be exactly related. For this reason sucrose losses cannot always be detected. In view of the high temperature and long time in contact of the liquor at the center of a filter filled as first described, one might expect to find notable losses of sugar at this point. This is especially true when the liquor is of high test and of relatively low pH. An example of invert sugar destruction is shown in Tables VI and VIII; Table IV shows a loss of sucrose by inversion.

Tests have demonstrated, and experience has shown, that the pH of liquor from char filters is a valuable guide in pro-

tecting sucrose from inversion during char filtration. It has been found advisable to lime washed sugar liquor, if necessary, so that it will come off the filters with a pH of 6.8 to 7.0; while second liquor may have a pH as low as 6.5 without apparent loss by inversion. Usually, invert sugar is destroyed as a consequence of keeping liquors near the neutral point; it is a choice, however, of the lesser evil.

In view of the benefits to be derived from proper distribution of char, investigation of a means of securing this would seem worth while.

Colloidal Complications in the Thiocyanate Method of Estimating Soil Acidity¹

By F. O. Anderegg and R. P. Lutz

PURDUE UNIVERSITY, LA FAYETTE, IND

IN THE thiocyanate method of titrating soil acidity² a saturated solution of potassium thiocyanate in 95 per cent alcohol is added to the sample of air-dried soil. A red color is produced if the soil is acid and ferric iron is present. Alcoholic base is then added until the red color is just permanently discharged. This often requires the addition of many increments of base, considerable shaking, and the longer or shorter periods necessary for the soil to settle, before the color can be seen. If this method is to be used successfully, the limitations imposed by the ease of hydrolysis of the indicator and by the colloidal character of some of the soil constituents should be determined.

Hydrolysis of Ferric Thiocyanate

On mixing either aqueous or alcoholic solutions of ferric chloride and potassium thiocyanate, red ferric thiocyanate was formed. In each case immediate passage through parchment paper seemed to indicate that the salt was present in a molecular dispersion at first, but, except in absolute alcohol, the salt soon gave evidence of hydrolysis at rates varying with the amount of water present. Even in 95 per cent alcohol a slow hydrolysis was observed with the aid of an ultramicroscope and by following the development of a Tyndall beam. The moisture present in the air-dried soil, as well as the time required for the titration in a heterogeneous system, may have considerable influence on the acidity determination by breaking down the indicator. The solubility of ferric iron is of considerable importance in this connection. The observation by Johnson³ of its complete pre-

The ease of hydrolysis of ferric thiocyanate even in 95 per cent alcohol complicates the thiocyanate method of soil acidity determination. The ferric hydroxide formed by hydrolysis of the thiocyanate is often adsorbed by the colloidal clay usually present in a soil, resulting in a shifting of the hydrolysis equilibrium and hence of the end point. The time factor is of importance here.

Some of the troubles that may arise from overstepping the end point are pointed out.

The blue or green color developed in handling maniferous soils by this method is probably due to colloidal manganese dioxide.

The decolorization of the ferric thiocyanate, which occurs in soils high in manganese, and has led to the significance of the iron-manganese ratio in soils to be tested by this method, is apparently produced by the mutual adsorption of oppositely charged colloids.

cipitation at pH 4.4 indicates a source of error which may occur under certain conditions.

Adsorption of Ferric Hydroxide by Colloidal Matter in Soil

The hydrolysis of the indicator is assisted by the presence of negatively charged colloids in the soil. These include clay colloids, silicic acid, and the so-called humic acids. All of these are active in adsorbing trivalent ferric ion and in lessening the red color of the indicator. Moreover, the positively

charged ferric hydroxide hydrosol is markedly adsorbed by these colloids with a consequent shifting of the hydrolysis equilibrium. If the soil contains much colloidal material, the results for soil acidity may be seriously affected. In a number of experiments with soils of varying colloid content, the extent of ferric ion and hydroxide hydrosol adsorption was found to depend upon the amount of colloid material, the iron content, the pH, the temperature, the amount of shaking, and the time of standing. These conclusions are in accord with well-known principles, but because of the complicated nature of this colloidal system the data obtained, which can only be qualitative in character, are not given.

The amount of iron taken up by three different types of soil is given in the figure, varying amounts of aqueous or alcoholic ferric chloride being added to a 10-gram sample of soil. After shaking for 4 hours end over end in glass-stoppered cylinders at $22 \pm 2^\circ \text{C}$., the soil was allowed to settle. The unadsorbed iron was determined in the water solution by titrating with dichromate. In the alcohol solutions most satisfactory results were obtained by iodometry. The results given are typical of several other soils studied. The three soils used were of different character: the first from Webster Co., Kentucky, known as "dark brown clay loam (bottom),"⁴ was a light clay, very acid soil, washed down from sandstone hills. The second soil was a slightly acid soil residual from

¹ Presented under the title "Some Colloidal Aspects of the Thiocyanate Titration of Soil Acidity" as a part of the Symposium on Soils, Fertilizers, and Crops, before the joint session of the Divisions of Agricultural and Food Chemistry and Fertilizer Chemistry at the 68th Meeting of the American Chemical Society, Ithaca, N. Y., September 8 to 13, 1924. Revised manuscript received August 3, 1925.

² Carr, *THIS JOURNAL*, **13**, 931 (1921).

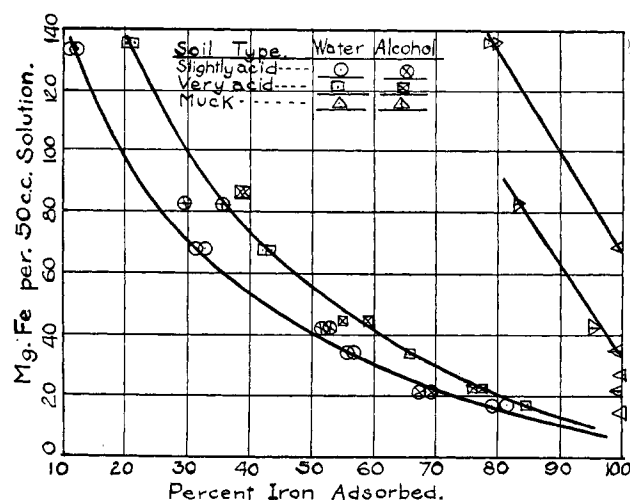
³ *Hawaiian Agr. Expt. Sta., Bull.* **52**.

⁴ Webster County Soil Survey Bulletin.

limestone, called "Decater silt loam,"⁶ and coming from the Princeton Experimental Fields. The muck soil, obtained near La Fayette, contained 65 per cent volatile matter and was intermediate in acidity between the two Kentucky soils.

The two Kentucky soils show a marked similarity in the amount of iron removed from both aqueous and alcoholic solutions. The muck is still more effective in removing iron from solution. To remedy this removal of iron in a titration, alcoholic ferric chloride may be added. If 10 grams of muck will remove 25 mg. of iron from solution, a 25-gram sample of this muck soil used in a titration should take up 62.5 mg. If this had to be added as ferric chloride the acid liberated would require 33.6 cc. of 0.1 *N* alkali. While this particular estimate is probably excessive, it emphasizes a potentially harmful factor in the thiocyanate method.

The tendency of many soils to promote hydrolysis and adsorption of iron is also shown by the not infrequent fading



of the red color of ferric thiocyanate from alcohol solutions on standing in contact with soils. Such a fading is noteworthy in soils of lesser acidity and has bearing on the recommendation of Gustafson⁶ for the comparison of an unknown with a known soil. A colleague, P. H. Brewer, called this to the writers' attention and, to confirm its existence, they have tried fifteen soils, and found that four of them faded completely and three others showed a perceptible decrease in color, though the remaining eight did not yield any noticeable effect.

A very finely divided soil settles out so slowly that considerable hydrolysis may take place while waiting for the alcohol to become sufficiently clear to determine the color. When this is repeated several times during the repeated addition of small increments of base, the cumulative effect may introduce a considerable error through removal of the indicator.⁷ On the other hand, it is undesirable to pass the end point because of further complications. Excess base peptizes more of the clay, and before the colored compound is formed again, especially when working with soils of high colloid content, much more than the equivalent amount of acid must be

⁶ Jones, extension specialist in soils; personal communication.

⁷ *Soil Sci.*, **18**, 1 (1924).

⁸ R. H. Carr, in a private communication, states he has titrated one hundred twenty soils collected at three depths and in no case has had to wait more than 2 minutes before being able to tell the color. However, in connection with the study of the self-corrosion of lead cable sheath [Purdue University Eng. Expt. Sta., *Bull.* **18**, 9 (1924)] a number of soils collected in Indiana and Illinois were titrated by the thiocyanate method, which was chosen because so many of the soils were calcareous. Of the thirty samples titrated, nearly half gave considerable trouble because of their slow rate of settling.

added. Several soils have given trouble of this sort in varying degrees, but a highly calcareous, colloidal, glacial till soil served as an extreme illustration. Following the standard thiocyanate method, 76.6 cc. of 0.1 *N* acid were required to produce a permanent end color. Then 2 cc. of 0.1 *N* alcoholic base were added and before the red color appeared again 29.0 cc. of alcoholic acid were required. This was repeated with six similar increments of base, requiring 5.9, 3.9, 2.7, 2.8, and 5.4 cc. of acid, respectively, to restore the red color. Such a treatment, the alternate addition of acid and base, is used by ceramists to increase the dispersion of clay. In this particular case the slowness of the reaction between alcoholic acid and small lumps of calcareous matter was probably partly responsible for the results obtained.

Manganese Dioxide Hydrolysis

Hydrated manganese, which is easily obtained in colloid condition, shows properties which indicate it to act as a manganous acid.⁸ Judging from these acidic properties and from the fact that it is precipitated by positively charged ions, its charge must be negative.⁹ The ease with which divalent manganese absorbs oxygen in an alkaline solution serves as a basis for the Winkler method of oxygen determination and gives a ready explanation for the results of Carr and Brewer.¹⁰ They were the first to observe a blue or green color on adding a slight excess of base to manganiferous soils. This is apparently due to the development of colloidal manganese dioxide, as indicated by its production experimentally, as follows: On shaking a very dilute alkaline solution of a manganese salt, either aqueous or alcoholic, in the presence of oxygen, a pale blue color usually develops, which on standing tends to change to a dark green. Carr and Brewer obtained the same result by the action of very dilute permanganate on thiocyanate. That the color is not characteristic of any definite compound but is structural—that is, is due to the scattering of light from particles of special size rather than of definite composition—is inferred from the fact that the solutions so produced give a strong Tyndall cone and show numerous particles of colloidal magnitude under the ultra-microscope.

Manganese-Iron Color Relationship

Carr and Brewer, on noting Comber's¹¹ failure to get a red color in two particular acid soils, concluded that the color production depended upon the relative amounts of manganese and iron in the soil. When the iron was present in excess they always obtained a red color which could be removed by adding an excess of manganese as permanganate. A plausible explanation for these observations lies in the mutual precipitation of oppositely charged colloids, in this case the adsorption of the positive ferric ion by the negative manganese dioxide. If this is the correct explanation, then a similar decolorizing action should be produced by other negatively charged colloids. Such was actually found to be the case. Decolorization analogous to that produced by the addition of permanganate was obtained with three colloidal materials—a glacial till soil, a sample of fuller's earth, and a suspension of Putnam clay.¹² Since the charge on these soils depends upon the pH, the point of greatest (mutual) coagulation should be shifted by adding acid or alkali. This was found to be true, although on prolonged standing the precipitate often became so compact that hysteresis in responding to changes in pH was observed.

⁸ Mellor, "Modern Inorganic Chemistry," **1912**, p. 477. Longmans, Green & Company.

⁹ Ganguly and Dahr, *J. Phys. Chem.*, **26**, 703 (1922).

¹⁰ *THIS JOURNAL*, **15**, 634 (1923).

¹¹ *J. Agr. Sci.*, **10**, 420 (1920).

¹² Kindly supplied by Dr. Bradfield.