it does not seem possible that this plant could have adapted itself to the conditions by precipitation of lime as oxalate. It does seem that the independence of the plant to these soil conditions is due to the regulatory power of the root cells in the absorption of nutrients.

While we believe that ratios of different salts, including lime and magnesia, affect plant growth under certain conditions, it does not seem, with our imperfect means of determining the soil nutrients available to or affecting the plant, that the hypothesis of the lime-magnesia ratio should be considered as applying to all soil conditions. Moreover, work on balanced solutions and the regulatory power of plant cells in the absorption of nutrients would seem to indicate that the whole subject is more complicated than was supposed when Loew formulated his hypothesis.

PORTO RICO AGRICULTURAL EXPERIMENT STATION
MAYAGUEZ

A SIMPLE METHOD FOR PREPARING NEUTRAL AMMONIUM CITRATE SOLUTION

By A. J. PATTEN AND W. C. MARTI

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The necessity of having a strictly neutral solution of ammonium citrate for the determination of available phosphoric acid in fertilizers is recognized by every fertilizer chemist. Methods for preparing such a solution have been discussed by the Association of Official Agricultural Chemists and investigated by many of its referees on phosphoric acid. This subject has also been studied by the Division of Fertilizer Chemists of the American Chemical Society, but to-day there are almost as many methods in use as there are laboratories doing fertilizer work.

Some chemists are still using the corallin method, some the alcoholic calcium chlorid method, some the azolitmin method proposed by Hand¹ and still others use a slight excess of ammonium hydroxid and depend upon the volatilization of the ammonia, upon long standing, to make the solution neutral.

McCandless,² when referee on phosphoric acid for the Association of Official Agricultural Chemists in 1908, compared solutions of ammonium citrate made by different chemists. In nine different solutions the ratio of ammonia to anhydrous citric acid was found, by analysis, to vary from 1 : 3.775 to 1 : 4.189. Doctor McCandless commented upon the unreliability of the methods then in use and closed his report with the following words: "While the referee has a strong conviction that the only proper method of making the solution is by analysis and calculation of the exact quantity of ammonia or citric acid to be added to it, still he hesitates to urge it officially, as no work has yet been done by any other referee along this line, and because the referee is himself no longer an official chemist."

Somewhat later the Fertilizer Division of the American Chemical Society proposed that the ratio of ammonia to citric acid should be 1 : 4.25. Such a solution, however, would be distinctly acid and would give higher results for available phosphoric acid than

a solution having the ratio of the tri-ammonium salt.

More recently a method based upon the change in electrical conductivity of a solution as it changes from an acid to an alkaline reaction was proposed by Hall and Bell³ and later by Patten and Robinson.⁴ This method gives satisfactory results and is not difficult of operation, but owing to the expensive apparatus required or for other reasons it has not been generally adopted. Later Bell and Cowell⁵ proposed two methods for preparing neutral ammonium citrate solutions but they present difficulties of manipulation that will undoubtedly militate against their general acceptance. There is still, therefore, the need of a method that will be simple, easy of manipulation, rapid and accurate and that does not call for unusual or expensive apparatus.

The method to be proposed fulfills these requirements and is based upon the work of Schiff⁶ who found that ammonia unites with formaldehyde to form hexamethylenetetramin according to the following equation:

Schiff also found that the same reaction takes place between salts of ammonia and formaldehyde and that the acid may then be titrated with a standard solution of sodium or potassium hydroxid, using phenolphthalein as indicator. Herstein⁷ made use of this reaction as a means of testing the purity of ammonium salts, and states that it gives satisfactory results with ammonium chlorid, bromid, iodid, fluorid, sulfate, acetate, oxalate, citrate, thiocyanate and molybdate.

The method as adopted by us is called the "titration method" and is essentially as follows: Fifty cc. of a citrate solution are carefully measured into a 250 cc. flask, made up to the mark with water and thoroughly shaken. Five cc. of the diluted solution are then measured (preferably by means of a burette) into a beaker, 4 cc. of a perfectly neutral 40 per cent solution of formaldehyde added and titrated with $N/10$ NaOH, using phenolphthalein as indicator. The pink color should remain after the solution is brought to boiling. The ammonia is determined in 5 cc. of the diluted solution in the usual manner by distilling with magnesia. The difference between the acid and ammonia titration gives the number of cubic centimeters of $N/10$ NH_3 required to neutralize 1 cc. of the acid citrate solution, from which the amount of a stronger solution of NH_4OH required to neutralize any given amount of the acid solution may be easily calculated.

The titration method was first tried out by us on a solution of ammonium citrate made neutral by the conductivity method and the ratio of ammonia to anhydrous citric acid was found to be 1 : 3.765, the same as for triammonium citrate. We then compared the titration method with the conductivity method for preparing neutral solutions. For this purpose a stock solution of citric acid was nearly neutralized

¹ *J. Am. Chem. Soc.*, **33**, 711 (1911).

² *THIS JOURNAL*, **4**, 443 (1912).

³ *J. Am. Chem. Soc.*, **35**, 49 (1913).

⁴ *Liebig's Annalen*, **319**, 76 (1901).

⁵ *Bur. of Chem., U. S. Dept. Agr., Bull.* **150**, 47.

¹ *Bur. of Chem., U. S. Dept. of Agr., Bull.* **132**, 11.

² *Ibid.*, **122**, 147.

with ammonium hydroxid, being careful to keep the specific gravity above 1.09. By the conductivity method it was found that 25.9 cc. of a 5 per cent solution of ammonium hydroxid were required to neutralize 1000 cc. of the solution and by the titration method 25.95 cc. were required. With another citrate solution 35.4 cc. of a 5 per cent solution of ammonium hydroxid were required per liter by the conductivity method and 35.6 cc. by the titration method.

We next determined by the titration method the amount of citric acid and ammonia contained in one liter of a strictly neutral solution of ammonium citrate, of exactly 1.09 specific gravity, with the following results:

- 1 cc. citrate sol. gave 26.34 cc. $N/10$ NH_3 ,
- 1 cc. citrate sol. gave 26.33 cc. $N/10$ $C_6H_8O_7$,
equivalent to 44.76 grams NH_3 per liter
equivalent to 168.57 grams $C_6H_8O_7$ per liter
Ratio of NH_3 to $C_6H_8O_7$ = 1 : 3.766.

The three solutions claimed to be neutral by McCandless contained 44.3 grams NH_3 and 168.76 grams $C_6H_8O_7$ per liter, the ratio being 1 : 3.809. The results obtained by us conclusively prove that such a solution would be slightly acid, which fact is further substantiated by the ratio of ammonia to anhydrous citric acid being too wide.

SUMMARY

The titration method of preparing neutral ammonium citrate solutions is accurate and easy of manipulation.

It establishes beyond a doubt that the ratio of ammonia to anhydrous citric acid in the neutral solution should be 1 : 3.765 and that one liter of 1.09 specific gravity should contain 44.76 grams NH_3 and 168.57 grams $C_6H_8O_7$.

The titration method affords a simple means of comparing ammonium citrate solutions made in different laboratories.

MICHIGAN EXPERIMENT STATION
EAST LANSING

THE FLUIDITY OF BUTTER FAT AND ITS SUBSTITUTES

By GEORGE F. WHITE AND RALPH H. TWINING

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The study of the viscosities of butter fat and oleomargarine as a problem of more or less interest, has already been taken up by several investigators with different methods of approach and different types of viscosimeters. Wender¹ worked with an instrument of the Ostwald class, modified so that, according to his statement, it could be cleaned with greater speed and ease. The Reichert-Meissl number of each sample was taken as a measure of purity. The fats were dissolved in chloroform, the viscosity of the solvent being taken into consideration. Wender found that the viscosity of oleomargarine was always greater than that of butter and with both decreased with rise in temperature, but did not change on standing for a considerable length of time. Further, although the viscosities of the butter fats were fairly constant, there were appreciable differences in the margarines from different sources. The amount of mar-

garine added could be approximately determined.

Killing² contributed nothing new in his study of the viscosities of butter and other fats, and his apparatus was so crude that no advance was made.

Raffo and Foresti,³ in an article on a "New Method for the Determination of Margarine in Butter," describe results obtained by an Ostwald instrument. They used butter from two sources and took the viscosities at 50° C. of the fats obtained by melting and filtering from curd and water. The time of flow was found to increase as the percentage of oleo fat increased, different samples giving concordant results. Their data indicate roughly that the viscosity is some function of the composition, but what particular function is not stated.

It is evident that any connection between the viscosity and the composition of butter fats, if it exists, has not been clearly and definitely established. A study of this important relation should therefore reveal by the use of accurate methods of analysis, results of especial value and interest. It is our purpose in this article to present the results of a series of viscosity measurements of various butter and oleomargarine samples, and of mixtures of these of known composition. By utilizing a viscosimeter which enabled us to express viscosities in absolute units, a definite standard of comparison may be adopted. Such measurements are entirely independent of the apparatus employed, and the "times of flow," which are recorded in so many works of this nature and which mean nothing to anyone else than the observer and his particular viscosimeter, do not need to be considered.

We prepared our samples, obtained from various sources, by melting at the lowest possible temperature and allowing to stand for two or three hours in that condition. The curd and water settled to the bottom leaving the clear supernatant fat which was decanted through a filter. The following constants were taken: the iodine number which shows the amount of unsaturated acids present, the saponification number, the percentage of soluble and insoluble acids, the volatile acids, the densities at 40°, 65°, and 90° C., and the viscosities at intervals of 10° from 40° to 90° C. These constants, while by no means representing a complete analysis, give a very definite idea of the purity and the composition of the fat examined.

The iodine number was obtained by treating about one-half a gram of fat with 50 cc. of Hübl's solution (mercuric chloride and iodine in alcohol), and titrating the remaining iodine with sodium thiosulfate solution after three hours' standing to ensure complete absorption. The number is expressed in the percentage of iodine absorbed, *i. e.*, the number of grams of iodine taken up by 100 grams of fat.

The saponification was carried out with an alcoholic potassium hydroxide solution, the mixture being heated on the water bath with a reflux condenser for thirty minutes, and the excess alkali then titrated with half-normal hydrochloric acid. The saponification (Koettstorfer) number is expressed as milligrams

¹ *J. Am. Chem. Soc.*, **17**, 719 (1895).

² *Z. angew. Chem.*, **1894**, 643; **1895**, 102. *J. Soc. Chem. Ind.*, **1895**, 198.

³ *Gazz. chim. ital.*, **39**, 441 (1911).