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THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDATE-MAGNESIA METHOD.

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FOR the investigation of the official molybdate method as used by the American Association of Official Agricultural Chemists for 1894, three samples were sent to various agricultural and commercial chemists with instructions for analysis.

No. 1 was a mixture of cottonseed-meal and castor pomace, containing about two and one-half per cent. P_2O_5.

No. 2 was an acid phosphate with about seventeen per cent. P_2O_5.

No. 3 was a phosphate solution containing ten grams C. P. disodium hydrogen phosphate ($Na_2HPO_4 + 12H_2O$) to the liter, the theoretical percentage of P_2O_5 in this salt being 9.826.

The discussion, which will be made here, of this work will be confined to the results obtained on solution No. 3, as it was the only sample whose content of P_2O_5 was definitely known. Twenty-eight chemists reported thirty-four determinations on No. 3, the highest of which was 20.67 per cent., and the lowest 19.74 per cent., the latter being 0.086 of one per cent. below the theory, and the former 0.844 per cent. above. The average of all results was 20.09 per cent., or 0.264 of one per cent. above the theory; the variation between highest and lowest results was 0.93 of one per cent.; the variation below the theory was 0.086 and above the theory 0.844 of one per cent. Eighteen per cent. of the determinations were within 0.05 of one per cent. of the theory, thirty-six per cent. within one-tenth, and forty-four per cent. within two-tenths. In the work on this sample a few analysts have gotten results reasonably close to the theory, a great many have varied widely from it, and nearly all have gotten high results, which brings me to the point to which I desire to draw especial attention, and that is the tendency of the molybdate-magnesia method to give high results, even when the greatest care is exercised as is reasonable to suppose was the case in this test work. I might add here that nearly all the chemists taking part in this work had had some years experience with the method, and those who had not, worked under good supervision.

The tendency of the method then, it seems, is for high results, and it is in order to ask where the trouble lies.

The phosphate solution sent out was precipitated directly with magnesia mixture by four chemists, when they obtained (1) 19.92, (2) 19.93 and 19.94, (3) 19.91 and 19.85, and (4) 20.03 and 20.05 per cent. P_2O_5, against (1) 19.93 and 19.87, (2) 19.93 and 19.91, and (3) 19.93 and 20.06 by precipitating with molybdic solution first.

The results here by both methods of procedure, while slightly high, most of them, are practically the same whether precipitation was made direct with magnesia mixture, or previously with molybdic solution. This argues that the trouble is not in the molybdate precipitate or precipitation. The magnesium ammonium phosphate precipitate obtained from this sample in the usual way was, after washing, dissolved by one chemist in hydrochloric acid and reprecipitated with ammonia, when he obtained 19.80 and 19.81 per cent. P_2O_5, while another added one gram citric acid to the alkaline solution in which the "white precipitate" is formed and obtained 19.83 and 19.83 per cent. P_2O_5 against 20.06 and 19.93 by the regular method.

The results by the last two methods of procedure are, while few, close to the theory and indicate that in the regular molybdate-magnesia method that either some of the magnesium of the magnesia mixture is thrown down as hydroxide and contaminates the precipitate, or else the magnesium ammonium phosphate formed under the conditions of precipitation, contains more than a normal amount of magnesium, and that by dissolving the "white precipitate" in hydrochloric acid and reprecipitating, and also by the presence of citric acid in the solution where the "white precipitate" is formed, the trouble is prevented.

H. Neubauer[1] has shown that magnesium ammonium phosphate formed in solutions containing an excess of both ammonia and magnesium salt, which is the condition of precipitation in the method under discussion, contains more than a normal amount of magnesium. The writer has had magnesium of the magnesia mixture to deposit as hydroxide and contaminate precipitates where very large excesses of the magnesia mixture were used in strongly alkaline solution and on long standing, though little or no error is thought to be introduced by this latter cause where the prescribed amount of magnesia mixture is used and too long standing not allowed. It is to the excess of magnesium in the magnesium ammonium phosphate, we consider, that the high results by the molybdate-magnesia method are due.

The results upon which the foregoing discussion is based will appear in the proceedings of the A. O. A. C. in the "Report on Phosphoric Acid" made by the writer to that association at its recent meeting.

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ON THE GUNNING METHOD FOR TOTAL NITROGEN IN FERTILIZERS.

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COMPARED to the Scovell-Kjeldahl nitrogen method, that of Gunning, modified to include nitrates, does not seem to have met with the favor that its cleanliness and simplicity would warrant. It is believed that this is, in the main, due to the lower results consequent upon the use of the latter process; hence the following record of an investigation of its merits.

The work was commenced by running parallel analyses on fertilizers of unknown composition, containing sodium nitrate, by both of the methods named. In each case the manipulation, adopted by the Association of Official Agricultural Chemists,

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[1] Abstract *J. Chem. Soc.*, of London, October *1893*, 489.