had been effected with an acid prepared in a similar manner. It might seem, on a superficial examination, that the facts now given throw a doubt on the validity of that synthesis. On examining the account of the work it will be seen, however, that in that synthesis bromisocaproic ester was used instead of the chlorisocaproic ester employed in the later work; further, that the trimethyladipic acid used was not purified, but was mixed with lime and distilled in its crude form. In the subsequent purification of the ketone and its oxime the products derived from the methylisopropylglutaric acid, which was doubtless present, were separated and the pure oxime of trimethylcyclopentanone was obtained. The comparison of the oxime with that obtained from camphor, and especially the fact that mixtures of the two had the same melting-point as either alone, placed the fact of their identity beyond question.

It seems probable, too, that the dimethylcyancarboxethylcyclopentanone[1] and the dimethyldicarboxethylcyclopentanone,[2] described by one of us, have the structure which has been assigned to them. It is difficult otherwise to account for the products formed by their saponification.

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PHOSPHORIC ACID DETERMINATIONS BY THE METHOD OF IGNITION WITH MAGNESIUM NITRATE AND BY THAT OF DIGESTION WITH ACIDS.

By B. L. Hartwell, A. W. Bosworth and J. W. Kellogg.

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The method described by A. Neumann[3] provides for the destruction of the organic matter by digesting the material in a Kjeldahl flask with a mixture of equal volumes of concentrated

claim to priority and promised to correct the statement in his full paper, which was to appear later. When the full account of his work was published (*J. Chem. Soc.* (London) **85**, 128 (1904)) the erroneous statement referred to was omitted but no correction of the earlier statement was made. After further correspondence Professor Perkin has agreed that I shall publish the correction myself. W. A. Noyes.

[1] *Am. Chem. J.*, **22**, 260.

[2] This Journal, **23**, 326.

[3] *Archiv. of Anat. u. Physiol. Abth.*, 159 (1900); *Ztschr. physiol. Chem.*, **37**. 115 (1902-1903); *Ibid*, **43**, 32 (1904). See also E. Poher : *An. d. l. science Agronomique*, 2d ser. 8, T. 2, 441 (1902-1903).

sulphuric and nitric acids, adding small amounts of the acid mixture from time to time until the destruction of the organic matter is completed. Fifty grams of ammonium nitrate are then added to the cooled, diluted solution, the temperature is increased to 70° or 80°, and the molybdic mixture added. After fifteen to twenty minutes' standing, the solution is filtered and the phosphoric acid determined volumetrically in the precipitate.

The method seemed to offer some advantages over the older methods, and it was decided to give it a trial in determining phosphoric acid in the oat plant and in turnips, using the method exactly as outlined, except that the ammonium phosphomolybdate was dissolved in ammonium hydroxide, and the phosphoric acid determined gravimetrically in magnesium pyrophosphate, instead of using the volumetric method. A sample of oats which yielded 0.0377 gram of magnesium pyrophosphate by the magnesium nitrate method of the Association of Official Agricultural Chemists yielded by the Neumann method, with fifteen to twenty minutes' digestion, only 0.0309 gram. In the case of turnip roots, 0.0331 gram of magnesium pyrophosphate was obtained by the magnesium nitrate method and 0.0326 gram by the Neumann method. Upon further digestion of the filtrate from the yellow precipitate (ammonium phosphomolybdate) obtained by the Neumann method, more precipitate was obtained, indicating the advisability of a longer digestion. Other determinations were next made in the same material by digesting for one hour at 65°. The oats yielded 0.0321 gram and the turnip roots 0.0319 gram, as against 0.0377 and 0.0331 gram respectively by the magnesium nitrate method. There seemed to be some difficulty in obtaining all of the phosphoric acid by precipitating with molybdic mixture according to the conditions as outlined in the method, and even upon continuing the digestion for one hour at 65°. The method, as finally modified and used, was to neutralize the acid, after digestion, with ammonium hydroxide. The details of the method, as used in securing the results recorded on succeeding pages, referred to herein as the acid method, are as follows: Five grams of the substance are digested in a Kjeldahl flask. A low heat and small amount of the acid mixture are used at the beginning, the heat being gradually raised and subsequent small portions of the acid mixture added, in the manner described by Neumann, until the least amount of acid has been used which is necessary for the destruction of the organic matter, perhaps 40 cc. in all. After diluting and cooling, the solution is made ammoniacal, acidified with nitric acid, and treated with the molybdic mixture[1] of the Association of Official Agricultural Chemists to which 15 grams of ammonium nitrate per 50 cc. of solution have been added. Some difficulty was experienced at first in securing a complete precipitation of the ammonium phosphomolydate, due perhaps to the large amount of ammonium sulphate present. A large volume of solution, considerable excess of molybdic mixture, an extra amount of ammonium nitrate and digestion at 65° for a few hours were the conditions finally adopted.

In order to compare the results obtained by the above method with those by a well-known method with which we were familiar, the following was selected. To 5 grams of substance in a porcelain dish were added 10 cc. of the official magnesium nitrate solution[2] and sufficient water to allow the entire mass to be moistened. The contents of the dish were dried and ignited. The residue was treated with hydrochloric acid and, after evaporating and drying at about 120° to avoid any possibility of the results being influenced by soluble silica, the mass was digested with hydrochloric acid. The filtered solution was neutralized with ammonium hydroxide, about 30 grams of ammonium nitrate, 40 cc. of half-strength nitric acid and 50 cc. of molybdic solution added, and the digestion conducted at 65° for an hour or more. The two methods were alike after this point, the phosphoric acid being determined in magnesium pyrophosphate as usual. The addition of the nitric acid was found necessary under our conditions, to prevent the separation of molybdenum compounds other than ammonium phosphomolybdate, which otherwise were thrown down and interfered with clear filtration and washing. The evaporation to remove silica was perhaps an unnecessary precaution, as is indicated by the following results upon different samples of oat plants. The results marked *a* were secured when evaporation and drying to render all silica insoluble was resorted to, and those marked *b* were from separate portions of the same samples when these precautions to render the silica insoluble, were not taken.

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[1] U. S. Dept. of Agr., Bureau of Chemistry, Bull. 46, rev. ed., p. 11.

[2] *Loc. cit.*, p. 12.

Grams of $Mg_2P_2O_7$ Obtained from 5 Grams of Oats.

a	0.0398	0.0453	0.0425	0.0398	0.0377	0.0333	0.0435	0.0373	0.0390
b	0.0394	0.0456	0.0430	0.0414	0.0377	0.0328	0.0434	0.0370	0.0390

The following results represent the grams of magnesium pyrophosphate, obtained by the acid and magnesium nitrate methods previously described, from separate 5-gram portions of different samples. It may be seen that from one to three independent determinations were made in a given sample by the two methods, results upon each sample being arranged vertically:

Flat Turnip Roots.

No. of sample	*51*	*53*	*55*	*57*	*58*	*59*
Acid Method	0.0496	0.0644	0.0561	0.0630	0.0576	0.0553
	0.0516	0.0644	0.0535	0.0684	0.0620	0.0556
	0.0532			0.0656	0.0621	
Magnesium Nitrate Method	0.0493	0.0613	0.0534	0.0630	0.0560	0.0539
	0.0502	0.0613	0.0520	0.0640	0.0592	0.0555
		0.0611	0.0534		0.0584	0.0541
No. of sample	*60*	*61*	*63*	*65*	*67*	*69*
Acid Method	0.0533	0.0392	0.0340	0.0320	0.0321	0.0486
	0.0532		0.0344			0.0493
Magnesium Nitrate Method	0.0511	0.0389	0.0323	0.0320	0.0320	0.0476
	0.0530		0.0339			0.0475

Oat Plant (Aerial portion).

No. of sample	*51*	*53*	*55*	*57*	*59*
Acid Method	0.0424	0.0477	0.0404	0.0419	0.0425
Magnesium Nitrate Method	0.0398	0.0456	0.0404	0.0430	0.0414
	0.0394	0.0453	0.0376	0.0425	0.0398
					0.0390
No. of sample	*61*	*63*	*65*	*67*	*69*
Acid Method	0.0379	0.0354	0.0450	0.0368	0.0388
Magnesium Nitrate Method	0.0377	0.0328	0.0434	0.0370	0.0390
	0.0377	0.0333	0.0435	0.0373	0.0390

The average amount of magnesium pyrophosphate obtained per 5 grams of material in the case of the turnip roots, was 0.0493 gram by the acid method, and 0.0480 gram by the magnesium nitrate method, which are respectively equivalent to 0.629 and 0.612 per cent. of phosphorus pentoxide. Similarly, with the oat plant, 0.0409 gram of magnesium pyrophosphate was obtained by the acid method and 0.0397 gram by the magnesium nitrate method which are respectively equivalent to 0.522 and 0.506 per cent. of phosphorus pentoxide.

The results by the acid method are on an average about 3 per cent. higher than those by the magnesium nitrate method. It is not believed, however, that the magnesium nitrate method failed to secure all of the phosphoric acid present in the crop, but rather that there were impurities present in the magnesium pyrophosphate obtained by the acid method; it frequently was of an abnormal color and had a reddish tint, in which case a quite strong reaction for iron was obtained. Furthermore, in a number of instances the magnesium pyrophosphate obtained by each method was dissolved in nitric acid and, upon reprecipitation and ignition, the results by the two methods were more nearly alike.

By a comparison of the results with turnip roots, in which case more than one determination was frequently made by each of the methods, it may be seen that there was more difficulty in obtaining parallel results with the acid method than with the other.

It should be said in explanation of the frequent wide differences in the determinations by a given method, that it was thought advisable to include all of the results as affording an indication of the capabilities of the two methods as followed in the routine analysis of a considerable number of samples, where the time element would preclude reprecipitation for the purpose of increasing the purity of the final product.

It is recognized that a wider experience with the acid method would probably lead to desirable modifications, but for the interest of those who might wish to use the method, the results are presented at this time.

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[CONTRIBUTION FROM THE INSECTICIDE AND WATER LABORATORY,
BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

COMPOSITION OF THE LIME, SULPHUR AND SALT WASH.[1]

BY J. K. HAYWOOD.

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SOME two years ago the author received a sample of the lime-sulphur-salt wash, prepared in the usual way from commercial chemicals, from the Division of Entomology, United States Department of Agriculture, with the request that it be subjected

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[1] Credit is due Mr. B. H. Smith who assisted in the analytical work in this paper and to Mr. C. L. Marlatt for suggesting the advisability of the investigation.