

METHOD FOR THE RAPID DETERMINATION OF TOTAL PHOSPHORUS IN PHOSPHORUS PASTES.*

BY FREDERICK J. AUSTIN.

It is a matter of general information that Phosphorus Pastes, of one type or another, find extensive use as vermin-eradicators. Such pastes are merely dilutions of the element Phosphorus, which is present in a minute state of subdivision in some sort of vehicle intended to effectively mask it from contact with the air and to thus prevent oxidation and consequent loss in strength. The average preparation of this nature, aside from the Phosphorus present, is composed essentially of organic matter and water, not more than traces of inorganic salts being present as incidental impurities. The assay method here described, which includes no novel reactions but merely outlines details of manipulation, is intended for application to pastes in which the vehicle is made up of organic matter and water.

In view of the fact that these products must comply with certain regulations as set forth in the Insecticide and Fungicide Act of 1910, a method for the rapid determination of their Phosphorus content, which yields fairly accurate results, is desirable. Such method should be simple as well as rapid for results must be promptly available that delay in subdividing the batch into trade packages and consequent hold-up of production may be avoided. In addition such method, to be acceptable, must necessarily guard against undue losses during the oxidation of the Phosphorus to phosphate and the attendant destruction of organic matter.

On account of the viscous nature of these pastes, it has been found advisable to take samples for examination from each lot as soon as manufactured by filling two or more collapsible tubes which are sealed at once with the screw caps in place.

Being ready to proceed with the determination and having ascertained that the exteriors of the tubes which contain the samples are clean and dry, a tube is placed on the balance pan and carefully weighed.

A medium-sized Kjeldahl flask, containing 10 Gm. of powdered, or granular, Sodium Nitrate of reagent grade, is held in a vertical position by means of a ringstand and clamp and a sample, equivalent to about 0.045 Gm. of Phosphorus, is introduced into the flask by pressing on the inverted collapsible tube, the open top of which projects downward into the upper part of its neck. Care should be taken that much of the sample falls on the Sodium Nitrate and that, if possible, none of it comes in contact with the interior of the neck of the flask. That portion which clings to the outlet is either drawn back into the tube or it may be detached by means of a suitable crystal of pure Sodium Nitrate and added, with the crystal, to the contents of the flask, without messing the thread. The screw cap is replaced without delay and the tube with contents again weighed when convenient, the loss in weight representing the sample taken for the determination. The paste in the flask is at once overlaid with about 5 Gm. more of the Sodium Nitrate which is immediately followed by 25 cc of concentrated Sulphuric Acid. A small glass funnel is inserted into the neck of the flask and its contents slowly warmed over the water-bath or hot plate. During this gradual heating, which requires only 5 to 10 minutes, the contents of the flask are given an occasional swirling motion that the mass may be kept beneath the surface of the acid liquor as undue exposure is certain to result in too rapid reaction. As the temperature rises the paste softens, loses shape and eventually, with the exception of the Nitrate of Sodium, the mixture becomes homogeneous. The temperature is then further increased, the frequent rotation of the flask being continued until active oxidation starts, which is indicated by the liberation of brownish fumes of Nitrogen Peroxide. Having ascertained that the reaction is

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proceeding uniformly throughout the mixture, the flask is placed on a ringstand in the fume chamber at the usual inclination, the base resting on a wire gauze having a thin asbestos center and the heating continued until Nitrogen Peroxide ceases to be evolved. During this stage of the operation the liquid froths actively and should be shaken occasionally.

The liquor is allowed to cool nearly to room temperature and successive small amounts of distilled water are added through the funnel in such a manner that it runs down the neck of the inclined flask into the liquid which is given a swirling motion coincident with each addition. More Nitrogen Peroxide may be liberated at this time. About 40 cc of distilled water are thus used, the final addition being followed by vigorous shaking. The liquor is brought to boiling over the Bunsen flame, the heating being continued until the contents of the flask are colorless or nearly so.

The liquor is cooled, transferred completely to a 500-cc beaker, diluted and carefully rendered slightly alkaline with filtered stronger Ammonia Water and then made faintly acid with Hydrochloric Acid.

Magnesia mixture, which has been filtered clear, is then added to the cold solution using approximately 10 cc for each 0.15 Gm. P_2O_5 present, followed by filtered 10% Ammonia Water until alkaline. After allowing the mixture to stand one hour, stirring occasionally, being careful to touch the stirring rod against the sides of the beaker as little as possible, it is made strongly alkaline by means of filtered 28% Ammonia Water and allowed to stand two hours, or, if need be, over night.

After testing the supernatant liquor and ascertaining that sufficient Magnesia mixture has been used, the precipitate of Magnesium Ammonium Phosphate is transferred to an ignited and weighed Gooch filter, washed with weak Ammonia Water until free from Chloride, dried, ignited, weighed as Magnesium Pyrophosphate and the percentage of Phosphorus calculated therefrom. $Mg_2P_2O_7$ is converted to Phosphorus by means of the factor 0.27873.

The following points should be noted:

During the transfer of the sample to the Kjeldahl flask some fumes of oxides of Phosphorus may escape but on account of the nature of the vehicle there is, if proper care be exercised, little likelihood of measurable loss of Phosphorus at this time.

The increase in temperature which governs the rate of oxidation must be carefully controlled or consequent loss of active ingredient is unavoidable.

The initial liberation of Nitrogen Peroxide must not be preceded by dense whitish fumes of oxides of Phosphorus readily recognizable by the familiar odor of Phosphorus as their appearance invariably accompanies those losses which result from improperly conducted oxidation.

A large excess of the reagents Sodium Nitrate and Sulphuric Acid are used, the former to weight down the paste by adhering to it and the latter to furnish sufficient liquid to easily cover the mass at all times.

Results obtained by the method described represent total Phosphorus content of the paste and include, of course, the small amount of oxides formed during manufacture.

Fairly satisfactory duplicate results are promptly available by the method outlined, the error rarely being greater than 0.1% and frequently as small as 0.025%.

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