

SUMMARY.

Experimental results indicate that the precipitation method for estimation of per cent of oil in lemon extracts is accurate, providing the height of the column of oil is considered instead of the actual volume.

The polarimetric method is the less accurate of the two, due to a number of factors, *i. e.*, the variation in rotation of various lemon oils and the effect of the aging of an extract upon its rotation. In the past most of the experimental work has been performed upon extracts of recent manufacture. The present A. O. A. C. method is readily adaptable for such extracts. The fact that the rotation of extracts increases upon standing introduces a source of considerable error, and after scrutinizing the results in Table VI, one wonders if, after all, it is not advisable to increase the factor 3.2 (66.6) to make the method applicable to the older extracts.

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THE ASSAY OF PHOSPHORIC ACID.*

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Most methods of determining phosphoric acid gravimetrically are troublesome and time consuming, and since much manipulation is necessary it is correspondingly inexact. Perhaps the most common gravimetric analysis of phosphoric acid is carried out by precipitation as ammonium phosphomolybdate.

Baxter (*Am. Ch. Jr.*, vol. 28, p. 298) has made a thorough study of the composition of ammonium phosphomolybdate and found the precipitate quite useful and efficient when weighed directly as a means of determining phosphoric acid. Although Baxter's method has been found to give satisfactory results in my hands, and is perhaps the shortest gravimetric method developed, it is obviously quite desirable to have a reliable method of determining phosphoric acid by titration with volumetric solutions.

Of all the volumetric methods which have been developed for this assay, perhaps three have stood out as the most reliable and each of these methods experienced a vogue at different periods. Unfortunately, neither of these methods show any marked advantage over the others and seem to have superseded each other only as a matter of course in the trend of time.

First we had Pemberton's volumetric method of solution of the ammonium phosphomolybdate in standard potassium hydroxide and titration with standard acid. This was subject to the errors due to the loss of ammonia, and to the uncertainty of the end-point with phenolphthalein in the presence of ammonium salts.

Next came the method of direct neutralization with standard potassium hydroxide, which at one time was used in the U. S. P. A weighed quantity of the acid was diluted with water and sufficient pure sodium chloride was added to saturate the solution. Methyl orange was then used as the indicator, and titration with normal potassium hydroxide begun and continued until the red color changed

* Scientific Section, A. P. H. A., St. Louis meeting, 1927.

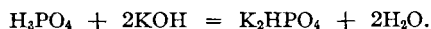
to yellow, indicating the formation of the monobasic phosphate. Sodium chloride was used in this assay to decrease the ionization of the acid salts produced in the reaction. However, the end-point in this reaction is too uncertain, and the color change of the indicator is so gradual that the exact end-point becomes merely a matter of judgment varying with each operator.

The neutralization method for assay of phosphoric acid was discarded in the U. S. P. IX and precipitation with standard silver nitrate recommended and adopted. An excess of the silver nitrate solution is added to the neutralized phosphoric acid and the residual silver nitrate solution titrated with standard sulphocyanate. This method of assay has been retained in the U. S. P. X, and since the method which is proposed in this paper is merely a slight modification of the official assay, the U. S. P. method will be stated in full.

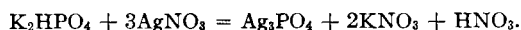
The procedure is as follows: An accurately weighed quantity of acid (about 0.1 Gm.) is diluted with 10 cc. of distilled water, in a 100-cc. flask. One drop of phenolphthalein T. S. is added and the solution neutralized with special potassium hydroxide solution, *i. e.*, one free from chlorides.

Fifty cc. of tenth-normal silver nitrate are now added and the mixture agitated, gradually adding zinc oxide in small portions until the liquid is neutral to litmus paper. Sufficient distilled water is added to make the liquid measure 100 cc., again thoroughly agitated, and filtered through a dry filter, collecting 50 cc. of the filtrate. To this 50 cc. of filtrate is added 2 cc. of nitric acid and 2 cc. of ferric alum T. S., and then titrated with tenth-normal potassium sulphocyanate to the production of a permanent red color.

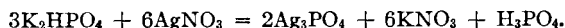
The neutralization of phosphoric acid, using phenolphthalein as the indicator is represented by the equation,



The reaction of silver nitrate on the dibasic phosphate may be represented by the following equation,



It is also claimed by some that free phosphoric acid is formed,



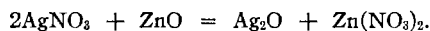
Silver phosphate (Ag_3PO_4) is soluble in phosphoric and nitric acids and the zinc oxide is added in this assay to neutralize any of these acids formed in the interaction.

But even this method of analysis is not reliable, and if the value of the assay is judged by the number of results that can be duplicated the method is as unreliable as any of the previous methods which have been discarded.

The following table shows some of the results obtained in this laboratory from assays of the same sample of phosphoric acid by different operators, using the U. S. P. X method of assay.

Analyst.	(1.)	(2.)	(3.)
"A"	53.08%	51.30%	52.96%
"B"	50.00%	48.52%	49.85%
"C"	67.09%	52.76%	64.68%

A glance at the above figures shows quite a discrepancy in the results obtained, and, in the opinion of the author, the whole trouble in this method of analysis lies in the fact that zinc oxide is not the best reagent to use for neutralizing the acids liberated, as explained above. I have found that small quantities of zinc oxide do not react completely to bring the mixture to neutrality, and large quantities are objectionable since zinc oxide will then react with silver nitrate, precipitating Ag_2O ,



Furthermore, zinc oxide being insoluble, materially changes the volume capacity of a 100-cc. flask, especially if a large quantity of the salt is used, thus introducing another source of error.

Zinc oxide obviously is changed to zinc hydroxide, in which form it reacts with the acids to neutralize them. The idea naturally occurred to use the hydroxide instead of the oxide. Samples of phosphoric acid were assayed by the U. S. P. method, introducing the above change, and it was found that absolute duplicates of results could be obtained. The zinc hydroxide used in this assay was best prepared as follows: [Shake very finely powdered zinc carbonate with twice as much potassium hydroxide, in 10% solution, as is necessary theoretically for the decomposition of the carbonate; formation of crystals of zinc hydroxide begins at once and is complete after twenty to thirty minutes. The salt can then be washed free from alkali, either by decantation or on a filter. The salt is then best kept, ready for use, by making a suspension in water.]

The method of procedure is similar to the U. S. P. method. After adding the silver nitrate solution add four or five drops of litmus T. S. Introduce into the flask about 1 cc. of the suspension of zinc hydroxide, drop by drop, from a pipette, shaking the flask after adding each drop until the color changes from red to blue. The procedure is then continued as directed in the U. S. P.

EXPERIMENTAL WORK.

For the purpose of this investigation a sample of U. S. P. phosphoric acid was analyzed gravimetrically by precipitation with molybdate solution and final determination as the pyrophosphate. ("Select Methods in Chemical Analysis"—W. Crookes.) The following results were obtained:

TABLE I.

	Wt. of sample.	Wt. of pyrophosphate.	H_3PO_4 .
(1)	0.1514 Gm.	0.1478 Gm.	85.62%
(2)	0.1630 Gm.	0.1584 Gm.	85.57%
(3)	0.1776 Gm.	0.1728 Gm.	85.67%
(4)	0.1558 Gm.	0.1514 Gm.	85.61%

This same sample of phosphoric acid was then used throughout the remainder of the investigation.

TABLE II.

	Wt. of sample.	N/1 NaOH.	H_3PO_4 .
(1)	1.1267 Gm.	20.1 cc.	87.47%
(2)	1.0552 Gm.	18.7 cc.	86.91%
(3)	1.0388 Gm.	18.5 cc.	87.32%

Another analysis was made by dissolving the acid in a saturated solution of sodium chloride and titrating with normal sodium hydroxide, using phenolphthalein. Results are shown in Table II.

Next the acid was assayed by titration with normal sodium hydroxide as above adding an excess of salt to the solution before titrating—Table III.

TABLE III.

	Weight of sample.	N/1 NaOH.	H ₃ PO ₄ .
(1)	1.0718 Gm.	19.9 cc.	91.03%
(2)	0.9991 Gm.	18.9 cc.	92.75%
(3)	1.0034 Gm.	18.85 cc.	92.22%

The acid was then assayed by the U. S. P. X method, using zinc oxide for neutralization. The weighed sample was diluted to 100 cc., and 10 cc. of the dilution taken for titration—Table IV.

TABLE IV.

	Weight of sample.	N/10 AgNO ₃	N/10 KCNS.	H ₃ PO ₄ .
(1)	1.0263	50 cc.	14.47 cc.	67.09%
(2)	1.1692	50 cc.	15.55 cc.	52.76%
(3)	1.0440	50 cc.	14.67 cc.	64.68%

The same dilution as made above was used in the next experiment. Ten cc. of this dilution was again assayed by the U. S. P. method with the exception that neutralization with ZnO was eliminated—Table V.

TABLE V.

	Weight of sample.	N/10 AgNO ₃ .	N/10 KCNS.	H ₃ PO ₄ .
(1)	1.0263 Gm.	50 cc.	15.5 cc.	60.53%
(2)	1.1692 Gm.	50 cc.	14.07 cc.	61.12%
(3)	1.0440 Gm.	50 cc.	15.28 cc.	60.86%

Finally, the acid was assayed by the U. S. P. method, using zinc hydroxide instead of zinc oxide for neutralization, and using the same dilution that was employed in the later two experiments. Ten cc. of the dilution was again taken for titration.—Table VI.

TABLE VI.

	Wt. of sample.	N/10 AgNO ₃ .	N/10 KCNS.	H ₃ PO ₄ .
(1)	1.0263 Gm.	50 cc.	11.93 cc.	85.57%
(2)	1.1692 Gm.	50 cc.	9.7 cc.	85.62%
(3)	1.0440 Gm.	50 cc.	11.33 cc.	85.60%

CONCLUSIONS.

It can readily be seen from a comparison of Table I and Table VI that we have here a reliable method of determining phosphoric acid. It must be clear from this that the accuracy and rapidity with which phosphoric acid can be determined by this method warrants its consideration for a place among the standard analytical processes. Zinc hydroxide has been used for assaying phosphoric acid in this laboratory for more than one year, during which time a large number of samples were assayed by different operators, and invariably good results were obtained.