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AECU-2910

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W.O. 44122

RADIOCHEMICAL METHODS FOR
THE DETERMINATION OF PHOSPHORUS -32

by:

RICHARD B. HAHN & ROBERT L. ANDERSON

DEPARTMENT OF CHEMISTRY

WAYNE UNIVERSITY

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INTRODUCTION

Phosphorus - 32 in the form of the phosphate ion is used extensively as a radioactive tracer in chemical and biological investigations. It is frequently necessary to determine the amount of radioactive phosphorus present in a given sample. This necessitates a radiochemical analysis.

A radiochemical analysis usually involves the following steps: The sample containing the radioactive material is put into solution. A known amount of inactive isotope is added as carrier. A series of precipitations, or extractions are then carried out which separates the radioactive isotope and carrier from other activities or interfering ions. A final precipitation of the carrier and radioactive isotope is then made. This precipitate is dried, weighed and counted. This count is corrected for gravimetric yield, coincidence, and background which then gives a true measure of the total activity present.

The only radiochemical method in the literature for the determination of phosphorus - 32 is that given by Meinke⁽⁴⁾ for the separation and determination of radioactive phosphorus in targets bombarded in the cyclotron. Meinke's procedure involves the precipitation of phosphorus in the form of ammonium phosphomolybdate.

Various precipitates have been used in the gravimetric determination of the non-radioactive phosphate ion. Among these are: magnesium ammonium phosphate,⁽⁶⁾ zirconyl phosphate,⁽⁸⁾ ammonium phosphomolybdate,⁽⁶⁾ silver phosphate,⁽³⁾ benzidine phosphate,⁽⁹⁾ and bismuth phosphate⁽²⁾. In this study all of the above methods were investigated to find if they were suitable for use as a radiochemical method for the determination of phosphorus - 32 in the form of phosphate ion.

EXPERIMENTAL

Preparation of carrier

A carrier solution was prepared by dissolving a known weight of chemically pure potassium dihydrogen phosphate in water. This solution was standardized by

precipitation as magnesium ammonium phosphate followed by ignition and weighing as magnesium pyrophosphate.⁽⁵⁾ This standard solution was used as carrier for the radioactive phosphorus in all the experiments.

Preparation and counting of radioactive tracer

The radioactive phosphorus was obtained from the Oak Ridge National Laboratories in the form of phosphoric acid in nitric acid solution. Radioactive phosphorus (P^{32}) is a beta emitter with a half life of 14.3 days. The solutions used for experimental purposes were prepared by diluting the tracer with 1 M nitric acid. Standards were prepared by evaporating a known volume of this solution to dryness on a watch glass then counting the beta radiation using a Tracerlab TGC-2 mica window G. M. tube and Nuclear Instrument Scaler Model 3. Precipitates containing radioactive phosphorus were counted in the same manner. These results were compared with a standard prepared and counted at the same time, thus no corrections for decay were necessary. All counts given are corrected for background and coincidence. Other random fluctuations in counting were corrected by daily standardization with a standard uranium source. All samples were counted on the second shelf of a lead tower, which gave a geometry of approximately ten per cent.

General procedure

The same procedure was used in all experiments: a known weight of carrier was taken, to which was added a known amount of radioactive phosphorus (in phosphate form). The mixture of carrier and radioactive phosphorus was precipitated by the addition of a given precipitating agent. The final precipitate was dried (or ignited) to constant weight. This was weighed to determine the percent recovery of carrier and finally the radioactivity in the precipitate was counted. If the gravimetric yield was less than one hundred percent a correction was applied to determine the count at one hundred percent recovery. This corrected count was compared with the standard to determine if the method was suitable as a radiochemical method. The results from the various methods are discussed in the following

paragraphs.

Determination

DETERMINATION OF P⁽³²⁾ BY MAGNESIUM PYROPHOSPHATE

The determination of phosphate ion as magnesium pyrophosphate by the official method of the Association of Agricultural Chemists⁽¹⁾ involves an initial precipitation as ammonium phosphomolybdate, filtration, then redissolving the precipitate with ammonium hydroxide. The phosphate ion is finally precipitated as magnesium ammonium phosphate by the addition of "Magnesia Mixture," then filtered and ignited at 900° C. for one hour. This residue of magnesium pyrophosphate is then weighed.

Procedure

Known amounts of carrier containing 100 microliters of radioactive phosphate solution were treated according to the method outlined above. These samples and a standard, prepared by evaporating 100 microliters of radioactive phosphate solution to a dryness in a porcelain crucible of the same size as those used for the ignition, were counted by placing the crucible on a solid slide on the second shelf of the lead tower and centering with a slide in the first shelf.

The results after correction for chemical yield were consistent but uniformly low, as shown in Table I.

TABLE I. MAGNESIUM PYROPHOSPHATE

mg. PO ₄ Carrier	Gravimetric Yield %	Count count/min.	Count Corrected to 100% Count/min.	Standard Count count/min.	Radiometric Yield
19.4	94.85	8309	8760	10,263	85.4
19.4	90.72	7604	8382	10,263	81.7
19.4	92.27	7707	8352	10,263	81.4

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Between eighty-one and eighty-five per cent radiometric yield was obtained using 19.4 mg of carrier. When smaller amounts of carrier were used the results were less consistent, but higher, ranging from eighty-eight to ninety-five per cent radiometric yield. These results do not justify the rather long procedure when compared with several other more direct methods investigated.

PRECIPITATION AS ZIRCONYL PHOSPHATE

A procedure for the determination of phosphate ion as the zirconium salt of phosphoric acid reported by Stumper and Mettlock was investigated.⁽⁸⁾ In this method the phosphate ion is quantitatively precipitated from acid solution as insoluble zirconyl phosphate by the addition of a slight excess of zirconyl chloride. This precipitate is filtered then ignited to zirconium pyrophosphate, which is weighed. It was found, however, that precipitates of constant composition could not be obtained. Gravimetric yields ranged from 75% to 262%. An adaptation in which the count was not corrected for gravimetric yield but compared directly with a radioactive standard in a small porcelain crucible did not give results consistently within the optimum limits of radiochemical yield (Table II).

TABLE II. ZIRCONYL PHOSPHATE

mg. PO_4 = Carrier	Count count/min.	Standard Count count/min.	Radiometric Yield Uncorrected %
4.85	2363	2549	92.7
4.85	2502	2549	98.2
9.7	2415	2549	94.7
9.7	2349	2549	92.2
19.4	2108	2549	82.7
19.4	2051	2549	80.5
4.85	12,940	14,231	90.9
4.85	12,672	14,231	89.0
4.85	12,231	14,231	86.7

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PRECIPITATION AS SILVER PHOSPHATE

In weakly acid solution the phosphate ion is quantitatively precipitated as insoluble silver phosphate, Ag_3PO_4 . Epperson⁽³⁾ devised a procedure in which silver phosphate is precipitated from acid solution, the resulting precipitate dissolved and then titrated with standard thiocyanate solution.

Procedure

Known quantities of phosphate carrier were precipitated by the addition of silver nitrate using the procedure of Epperson. Instead of dissolving and titrating the precipitate as in Epperson's procedure, attempts were made to dry and weigh the precipitate. Erratic results were obtained, however, due to partial decomposition of the precipitate during the drying process. Because of this difficulty this study was not carried further.

PRECIPITATION AS BENZIDINE PHOSPHATE

The precipitation of phosphate ion by benzidine is used in the separation of phosphate ion from sulphate ion. The precipitation is made from weakly acid solution. The separation is based on the insolubility of the precipitated sulphate in 1 N hydrochloric acid and complete solubility of the precipitated phosphate in 1 N hydrochloric acid. In the method reported the dissolved phosphate is determined by titration with standard sodium hydroxide.⁽⁹⁾

An attempt to utilize the benzidine phosphate precipitate itself showed incomplete carrying (Table III). Because of this the method is unsuitable for radio-metric analysis of phosphorus.

TABLE III. BENZIDINE PHOSPHATE

mg. PO ₄ = Carrier	Count count/min.	Standard count/min.	Radiometric Yield %
4.85	127	802	15.9
4.85	19	802	2.4
9.7	92	802	11.5
9.7	160	802	20.0
19.4	166	802	21.0
19.4	197	802	24.6

PRECIPITATION AS AMMONIUM PHOSPHOMOLYBDATE

Meinke⁽⁴⁾ previously investigated the radiochemical determination of phosphorus by precipitation as ammonium phosphomolybdate. This method was reinvestigated in order to compare it with the other methods.

Procedure

Known amounts of carrier and radioactive tracer were precipitated from nitric acid solution by the addition of ammonium molybdate using the procedure outlined by Scott⁽⁶⁾. The precipitates were filtered, dried, weighed, then counted. Difficulties were encountered in filtering the precipitate through filter paper disks in a Hirsch funnel. The precipitate is finely divided and partially passes through the filter paper. This resulted in low gravimetric yields and erratic results.

Better results were obtained by filtering through Pyrex sintered glass crucibles. Counting was done by placing the entire crucible and precipitate on a stand inside the lead tower and adjusting the height so that the precipitate was at the level of the second shelf. The sides of the crucible were cut down to a height of one half inch above the sintered glass surface. This reduced the columating effect of the crucible walls on the beta particles. Radiometric standards were

prepared by evaporating known amounts of phosphorus tracer on a small watch glass then placing this on the sintered glass surface of the same type of crucible.

The sintered glass crucibles can be decontaminated by washing with 30 ml of 6 M ammonium hydroxide and rinsing with 100 ml of distilled water. After this treatment no residual activity was found on any crucible.

The results of various determinations are given in Table V.

TABLE V
AMMONIUM PHOSPHOMOLYBDATE ON SINTERED GLASS

mg PO_4 Carrier	Gravimetric yield %	Count counts/min.	Count corrected to 100% counts/min.	Standard counts/min.	Radiometric yield
4.85	99.0	1717	1734	1787	97.0
4.85	77.9	5546	7120	7235	98.4
9.7	85.6	4583	5354	5696	94.0
9.7	74.2	3661	4934	5696	86.6
19.4	91.2	9253	10,146	11,925	85.1
19.4	90.2	9042	10,024	11,925	84.0

These data show that more accurate results are obtained using small amounts of carrier. Variation in the composition of the precipitate and self absorption cause the low results with larger amounts of carrier.

PRECIPITATION AS MAGNESIUM AMMONIUM PHOSPHATE

The double precipitation of the phosphate ion as insoluble magnesium ammonium phosphate is one of the most widely used methods for its determination.⁽⁵⁾ Since chemical yields of exactly one hundred per cent are unnecessary in radiochemical

determinations, an adaptation of this method involving only one precipitation was studied.

Procedure

Solutions containing known amounts of carrier and tracer were treated with "Magnesia Mixture". The solutions were then made basic by the addition of 15 M ammonium hydroxide. After standing for one hour the precipitates were filtered and washed with dilute ammonium hydroxide. The precipitates were then dried by washing with thirty milliliter portions of absolute ethyl alcohol and ether; after this air was drawn through for twenty minutes. The precipitate was allowed to stand in a desiccator finally for at least twenty minutes.

While a single precipitation gives consistently high chemical yields, when the precipitate is collected on filter paper disks in a small Hirsch funnel the radiometric yields were consistent and within instrumental error of one hundred per cent yields (Table VII).

TABLE VII

MAGNESIUM AMMONIUM PHOSPHATE ON FILTER PAPER DISKS

mg. PO_4^{3-} Carrier	Gravimetric Yield %	Count count/min.	Standard Count count/min.	Radiometric Yield Uncorrected %
9.7	110.4	5316	5288	100.5
9.7	103.1	5196	5288	98.3
9.7	102.1	5145	5288	97.3
9.7	103.1	4138	4223	98.0
9.7	103.1	4131	4223	97.8
9.7	103.1	4165	4223	98.6

Thus a single precipitation as magnesium ammonium phosphate, collection on filter paper disks, alcohol, ether, air drying was shown to be an accurate method for

determining P^{32} in the phosphate ion form. The slightly high gravimetric yields were probably caused by small amounts of moisture retained by the precipitate. The dried precipitate is assumed to have the composition, $MgNH_4PO_4$.

PRECIPITATION AS BISMUTH PHOSPHATE

The precipitation of bismuth phosphate with excess ammonium phosphate has been used for the determination of bismuth. The procedure reported by Blasdale and Parle⁽²⁾ was investigated to determine its adaptability to the radiochemical analysis of phosphorus.

Sulphate and chloride ion interfere in this procedure and lead and cadmium cause high results when present. Moderate amounts of sodium, potassium, magnesium, zinc, copper, and calcium ions have no effect.⁽²⁾ The chloride ion can be easily removed by evaporation with nitric acid. The other interfering ions, are unlikely to be present in substances analyzed for radioactive phosphorus.

Procedure

A solution of 0.03M bismuth nitrate was prepared by dissolving 14.5 g of $Bi(NO_3)_3 \cdot 5H_2O$ in 100 ml of 6M nitric acid then diluting to one liter. This solution was used as precipitant.

The solution containing the radioactive phosphorus is diluted to 40 ml and enough nitric acid added to make the final solution approximately 0.1-0.2N in nitric acid. A known amount of potassium hydrogen phosphate carrier solution is added so that about 50 mg of $PO_4^{=}$ ion are present in the solution. This solution is heated to boiling and 20 ml of the above bismuth nitrate solution is then added. A precipitate of insoluble bismuth phosphate forms immediately. The precipitate and solution is heated to about 80° C. for one hour. The solution is then filtered by suction using a Hirsch funnel fitted with a small disk of filter paper. The precipitate is washed with 100 ml of 0.1N nitric acid, dried at 110° C. for one hour and weighed as $BiPO_4$. The precipitate and filter disk is placed on a watch glass

and counted. The results are shown in Table VIII.

TABLE VIII
BISMUTH PHOSPHATE

mg. PO_4^{3-} Carrier	Gravimetric Yield %	Count count/min.	Count Corrected to 100% count/min.	Standard count/min.	Radiometric Yield %
48.5	94.9.	6203	6540	6773	95.56
48.5	96.9	6331	6533	6773	96.46
48.5	94.0	6153	6544	6773	96.62
19.4	94.3	7118	7546	6773	111.4
19.4	94.3	7276	7713	6773	113.9
19.4	94.3	7052	7476	6773	110.9

The corrected radiometric yields (average 98.7%) are within instrumental error of one hundred per cent yields.

Summary:

(1) Official A.O.A.C. Method (initial precipitation as $(\text{NH}_4)_3\text{PO}_4 \cdot 12 \text{M}_2\text{O}_3$ followed by reprecipitation as MgNH_4PO_4 which is ignited, weighed and counted as $\text{Mg}_2\text{P}_2\text{O}_7$): The method is long and gives low results. This method would be useful only in samples containing large amounts of interfering cations such as calcium, iron, etc.

(2) Zirconyl Phosphate: The method is rapid but not too accurate due to variation in the composition of the precipitate.

(3) Silver Phosphate: Not suitable due to decomposition of the silver phosphate precipitate.

(4) Benzidine Phosphate: Not suitable because of incomplete carrying, and indefinite composition of the precipitate.

(5) Ammonium phosphomolybdate: Good results are obtained under proper conditions. The precipitate is finely divided and is difficult to filter. Erratic results may result due to variation in the composition of the precipitate.

(6) Magnesium Ammonium Phosphate: A quick accurate method. The only drawback of this method is the fact that all soluble cations other than sodium, potassium and ammonium interfere by forming insoluble phosphates which contaminate the precipitate of MgNH_4PO_4 .

(7) Bismuth Phosphate: A quick accurate method. Sulfate, lead, and cadmium ions interfere.

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