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The Spectrophotometric Determination of Phosphate in Nuclear Materials

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January 1972

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THE SPECTROPHOTOMETRIC DETERMINATION
OF PHOSPHATE IN NUCLEAR MATERIALS

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ABSTRACT

By extracting molybdophosphoric acid into 1-butyl acetate in the presence of ethylenediaminetetraacetic acid and fluoride, a very simple but selective and sensitive spectrophotometric procedure for phosphate is obtained by measuring the absorbance of the extracted heteropoly acid at 310 nanometers. The optimum acid and reagent concentrations for the method were determined and the effect and tolerance levels of 36 interfering ions, including uranium, thorium, and plutonium, were measured. The method is capable of measuring 0.7 μg of phosphorus and has a molar absorptivity of approximately 25,000. The standard deviation for the method is $\pm 5.4\%$. This procedure has been used to determine the concentration of phosphate in uranium-233 product solutions, to follow the radiolysis of entrained tributyl phosphate and dibutyl phosphate in uranium-233 product solutions, and to determine the phosphate content of nuclear waste solutions.

THE SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE IN NUCLEAR MATERIALS

INTRODUCTION

Phosphorus analyses of uranium and plutonium product solutions are required in order to ensure that the final product will meet the desired specifications. Phosphate analyses may be used to obtain a portion of the total phosphorus content and to monitor the degradation of traces of organic phosphorus extractants such as tributyl phosphate (TBP) which may be entrained in the product solutions during separation. Phosphate analyses are also desired in the characterization of nuclear waste solutions before long-term storage or further processing.

The spectrophotometric determination of phosphates based on the formation and extraction of molybdophosphoric acid has been extensively described in the literature.^[1-5] Studies by Wadelin and Mellon^[5] indicated that 1-butyl acetate was the most selective extractant for molybdophosphoric acid; however because of its poor separation properties, they chose to use a mixture of 1-butyl alcohol and chloroform. For nuclear process applications the phosphate method needed to be highly specific, sensitive, and convenient to use. Because the molar absorptivity of the extracted molybdophosphoric acid at 310 nm is equal to that of the reduced heteropoly blue^[3,4] and because of the high selectivity and density of 1-butyl acetate, it was decided to investigate the application of 1-butyl acetate as an extractant for molybdophosphoric acid in nuclear processing solutions.

SUMMARY AND CONCLUSIONS

A highly selective and sensitive procedure for determining phosphate in nuclear processing solutions was developed. The phosphate was separated from interfering ions by extracting molybdophosphoric acid into 1-butyl acetate in the presence of fluoride and ethylenediaminetetraacetic acid (EDTA). The separated phosphate was then determined by measuring the absorbance of the extracted heteropoly acid at 310 nanometers.

The molybdophosphoric acid was developed and extracted in an acid concentration between 0.64 and 0.9M HCl with a molybdate concentration of at least $3.1 \times 10^{-3}M$ $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The extracted heteropoly acid was then washed with 0.85M acid to remove any entrained molybdate or sample which may absorb in the ultraviolet region. The absorbance of the washed organic was then measured by reading against a reagent blank. The color was stable for at least one hour following separation.

Thirty-six ions were tested for interference in the procedure. Nitrite was found to give a positive interference when over 0.5 mg was introduced into the procedure. Zirconium(IV), plutonium(IV), and titanium(IV) were found to give negative interference at the 0.1 mg level when EDTA and fluoride were not used as complexing agents. Tungstate at the 1 mg level gave an uncharacteristic spectrum. However, at the 0.1 mg level no interference from tungstate was observed. All interferences were compared at the 2 μ g phosphorus level. By using EDTA and fluoride as complexing agents to free complexed phosphate, the determination for phosphate was made very specific.

This procedure was used to determine phosphate in uranium-233 product solutions and to follow the degradation of entrained TBP in product solutions to phosphate; it was also used to determine phosphate in nuclear waste solutions. The method has a standard deviation of $\pm 5.4\%$ at the 2 μ g level

of phosphorus. Even though the procedure does not have excellent precision, its sensitivity, speed, and selectivity make it applicable for determining phosphate in many nuclear processing solutions.

EXPERIMENTAL

REAGENTS

Molybdate: acid molybdate (0.047M) was prepared by dissolving 58.4 grams of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 200 ml of concentrated (12M) HCl, and diluting to 1 liter with deionized H_2O . The ammonium molybdate must be dissolved in 12M HCl before adding water, or the molybdophosphoric acid will not develop. Since this reagent appears to degrade, causing low recoveries, it was stored in polyethylene and refrigerated. The reagent should be checked frequently by analyzing phosphate standards.

Extraction HCl: 0.70M HCl in deionized water stored in polyethylene.

Wash HCl: 0.85M HCl in deionized H_2O and stored in polyethylene.

Fluoride: ≈ 10 g/liter F^- made from reagent grade NaF dissolved in deionized H_2O .

EDTA: ≈ 10 g/liter made from the sodium salt and dissolved in deionized H_2O at pH 11.

Phosphate Standard:* prepare a 10 $\mu\text{g}/\text{ml}$ standard by dissolving 0.04382 g of oven-dried KH_2PO_4 into 1 liter of deionized H_2O and store in polyethylene.

* Throughout the discussion, standard phosphate additions will be referred to in terms of phosphorus. The amount of phosphate may be computed by multiplying the $\mu\text{g P}$ by 3.07.

APPARATUS

Plastic vials and Teflon[†]-coated stir bars were used for all experiments.

One-cm silica absorption cells and a Beckman DK-2A with a deuterium lamp were used for spectrophotometric measurements.

GENERAL PROCEDURE

The sample is pipeted into 10 ml of 0.7M HCl and stirred briefly. One milliliter of the molybdate reagent is then added to the vial and the contents are stirred for two to three minutes. Exactly 5 ml of 1-butyl acetate is then added and the contents are stirred thoroughly to an emulsion for two to three minutes. The phases are then allowed to separate and as much of the organic as possible is transferred to a second vial containing 5 ml of 0.85M HCl. The contents of this vial are then stirred for one to two minutes and the phases separated for three minutes. The organic is then transferred to a 1-cm spectrophotometer cell and the absorbance measured against a reagent blank at 310 nm. If Ti, Zr, or Pu are present, then 500 μ l of 10 g/liter fluoride and 1 ml of EDTA should be added to the first vial before adding the sample. After adding the sample, the contents of the vial should be thoroughly stirred for three to five minutes to ensure that any phosphate complexes of Ti, Zr, and Pu are broken up. Other stirring times should be increased to improve the kinetics when Ti, Zr, and Pu are present.

The method is calibrated by using the same procedure over a range of 0.5 to 5.0 μ g phosphorus.

[†] Trade name of E. I. du Pont de Nemours and Company.

RESULTS AND DISCUSSION

ACID CONCENTRATION

The optimum acid condition was determined by measuring the absorbance of a 5 μ g phosphorus spike after extracting and washing the heteropoly acid with varying acid concentrations. Five hundred μ l of an 0.01 g/liter phosphorus standard and 1 ml of the molybdate reagent were used with 10 ml of a particular HCl concentration. The extracted molybdophosphoric acid was washed with 5 ml of the same acid concentration used for the extraction. Since the molybdate reagent contains HCl, a final acid concentration has been tabulated in Table I. The results are plotted in Figure 1.

TABLE I

DETERMINATION OF OPTIMUM ACID FOR EXTRACTION
OF MOLYBDOPHOSPHORIC ACID IN 1-BUTYL ACETATE

<u>M HCl</u> <u>Extraction</u>	<u>M HCl</u> <u>Wash</u>	<u>M HCl</u> <u>Corrected For</u> <u>HCl in Molybdate</u>	<u>Absorbance</u>
0.10	0.10	0.30	0.589
0.25	0.25	0.43	0.860
0.50	0.50	0.64	0.922
0.75	0.75	0.86	0.940
1.00	1.00	1.08	0.899
1.25	1.25	1.30	0.467
1.50	1.50	1.51	0.111
2.00	2.00	1.95	0.003
4.00	4.00	3.69	0.000

Between the acid values of 0.6 and 0.95M HCl the absorbance varied by about $\pm 2\%$ from the maximum. These final acid concentrations were chosen for the upper and lower acid limits for the method. By using 0.7M HCl for extracting the heteropoly acid and 0.85M HCl for washing the organic, the optimum acid conditions may be maintained.

FIGURE 1

EFFECT OF ACID ON THE FORMATION AND
EXTRACTION OF MOLYBDOPHOSPHORIC ACID

Sample sizes may be chosen for samples whose acid concentrations are less than 0.64M and greater than 0.95M by using the following formulas:

$$9.4 \text{ meq} + x \text{ spl size } (N \text{ of spl}) = (12.5 \text{ ml} + x \text{ spl size}) \\ (0.95N) \text{ upper limit}$$

$$9.4 \text{ meq} + x \text{ spl size } (N \text{ of spl}) = (12.5 \text{ ml} + x \text{ spl size}) \\ (0.64N) \text{ lower limit}$$

$$9.4 \text{ meq} = 10 \text{ ml } (0.70N) + 1 \text{ ml } (2.4N \text{ HCl molybdate reagent acid})$$

where

x = sample size

N = normality of sample

spl = sample

meq = milliequivalents

12.5 + x = total ml (10 ml, 0.70M HCl, 1 ml molybdate, + x ml of sample)

0.95 and 0.64 = final normality limits for optimum extraction

For neutral solutions the sample size should not exceed 2 ml. Unusual sample sizes should be tested on standards before applying to samples since the absorbance is also a function of molybdate concentration.

MOLYBDATE CONCENTRATION

The optimum molybdate concentration was determined by maintaining a constant volume, by varying the amount of molybdate reagent added, and by controlling the acid so that optimum acid conditions were maintained. A 4.64 µg phosphorus spike was added to each molybdate concentration and the change in absorbance recorded as shown in Figure 2. The maximum absorbance

FIGURE 2
EFFECT OF MOLYBDATE CONCENTRATION ON THE
FORMATION AND EXTRACTION OF
MOLYBDOPHOSPHORIC ACID IN 1-BUTYL ACETATE

is obtained at $3.05 \times 10^{-3}M$ molybdate which corresponds to 750 μ l of the molybdate reagent (0.047M) in 11.5 ml total volume. In order to ensure that an excess of molybdate was present, a 1-ml quantity or 0.047 millimoles of the molybdate reagent was chosen for the procedure.

INTERFERING IONS

Varying quantities of interfering ions were added to 1.86 μ g of phosphorus spike. Fluoride and EDTA were not used in the initial studies. The percent recovery of spike was determined for each ion. If the percent recovery was outside the limit of $100 \pm 10\%$, the ion was considered to interfere. Results of these initial studies are presented in Table II, which shows that Pu(IV), Zr(IV), and Ti(IV) were the ions most often found in nuclear processing solutions which would interfere with the method. Tungsten, tantalum, and nitrites are not normally present in high enough concentrations in nuclear process solutions to interfere. In addition, nitrite and tungsten interferences could be recognized by their non-characteristic spectra as shown in Figure 3.

Because plutonium was of special interest, it was decided to attempt to remove its interference by reducing to Pu(III) with hydroxylamine or oxidizing to Pu(VI) with dichromate. The hydroxylamine gave improved performance but the results were inconsistent and low. The large amount of dichromate used to oxidize Pu to the 6 valence state resulted in some dichromate remaining in the butyl acetate phase causing high results. These tests may merit further investigation with special attention to the quantities of reducing and oxidizing agents used and the time, heat, and other kinetic factors needed to cause the necessary valence change.

Since the use of oxidizing and reducing agents did not look extremely promising, it was decided to investigate the

TABLE II

THE EFFECT OF VARIOUS IONS ON THE DETERMINATION
OF PHOSPHATES BY 1-BUTYL ACETATE EXTRACTION
OF MOLYBDOPHOSPHORIC ACID
(No Fluoride or EDTA Added)

Ion	Level	Results
Si [silicate]	1. mg	No interference
Fe(III)	1. mg	No interference
Sr(II)	1. mg	No interference
Al(III)	1. mg	No interference
Mn(II)	1. mg	No interference
Zr(IV)	1. mg	10% recovery
	0.1 mg	30% recovery
Cd(II)	1. mg	No interference
Pb(II)	1. mg	No interference
Pu(IV)	1. mg	10% recovery
	0.1 mg	44% recovery
La(III)	1. mg	No interference
U(VI)	1. mg	No interference
W(VI) [tungstate]	1. mg	Non-characteristic spectra
	0.1 mg	No interference
Cs(I)	1. mg	No interference
Ti(IV)	1. mg	39% recovery
	0.5 mg	59% recovery
	0.1 mg	77% recovery
	0.05 mg	78% recovery
	0.025 mg	87% recovery
	0.01 mg	No interference
Ta(V)	1. mg	44% recovery
	0.1 mg	72% recovery
Cr(VI)	1. mg	No interference
Nd(III)	1. mg	No interference
Y(III)	1. mg	No interference
Ba(II)	1. mg	No interference
Th(IV)	1. mg	No interference
Co(II)	1. mg	No interference
Hg(II)	1. mg	No interference
Pd(II)	1. mg	No interference
Ni(II)	1. mg	No interference
Zn(II)	1. mg	No interference
Ru(III)	1. mg	No interference
Cu(II)	1. mg	No interference
Sn(IV)	1. mg	No interference
Sb(III)	1. mg	No interference
As(III)	1. mg	No interference
SO ₄ ⁼	1. mg	No interference
NO ₃ ⁻	1. mg	No interference
F ⁻	1. mg	No interference
	2.5 mg	No interference
	5.0 mg	No interference
	10. mg	9.4% recovery
NO ₂ ⁻	1. mg	125% recovery
	0.5 mg	No interference
Citrate	500 µl-0.5M citrate	30.6% recovery
	100 µl-0.5M Citrate	No interference
EDTA	1. mg	No interference
	2.5 mg	No interference
	5.0 mg	No interference
	10.0 mg	No interference

FIGURE 3
ABSORPTION SPECTRA OF
MOLYBDOPHOSPHORIC ACID IN 1-BUTYL ACETATE

use of complexing agents to release any phosphates that may be tied up as Zr, Pu, or Ti complexes. The tolerance levels for fluoride, citrate, and EDTA are given in Table II. One hundred microliters of 0.5M citrate were added to the extraction vial after the interfering element and a 1.86 μ g P spike had been thoroughly mixed. Citrate failed to improve the results of Zr, Pu, or Ti. However the use of 5 mg of fluoride or 10 mg of EDTA improved the results for Zr, Pu, and Ti, as illustrated in Tables III, IV, and V. Plutonium and zirconium phosphate complexes were broken up with either fluoride or EDTA. However, only fluoride is capable of destroying the titanium phosphate complex. For the most selective procedure both fluoride and EDTA should be utilized and an appropriate calibration prepared using these complexing agents. Fluctuations such as that noted between 0.5 and 1.0 mg Ti percent recoveries may be due to the kinetics involved in destroying phosphate complexes. For systems involving large amounts of

TABLE III

EFFECT OF FLUROIDE AND EDTA ON THE FORMATION AND EXTRACTION OF MOLYBDOPHOSPHORIC ACID IN 1-BUTYL ACETATE FROM PLUTONIUM NITRATE

<u>Pu</u> <u>mg</u>	<u>Complexing</u> <u>Agent</u> <u>mg</u>	<u>% Recovery</u>
0.10	0.5 F ⁻	97.3
0.25	5.0 F ⁻	69.0
0.50	5.0 F ⁻	90.7
1.00	5.0 F ⁻	88.5
0.10	1.0 EDTA	71.1
0.25	10.0 EDTA	92.4
0.50	10.0 EDTA	92.8
1.00	10.0 EDTA	83.0

TABLE IV

EFFECT OF FLUORIDE AND EDTA ON THE FORMATION AND
EXTRACTION OF MOLYBDOPHOSPHORIC ACID
IN 1-BUTYL ACETATE FROM ZIRCONIUM NITRATE

<u>Zr</u> <u>mg</u>	<u>Complexing</u> <u>Agent</u> <u>mg</u>	<u>% Recovery</u>
0.10	0.5 F ⁻	96.0
0.25	5.0 F ⁻	102.8
0.50	5.0 F ⁻	95.4
1.00	5.0 F ⁻	103.8
0.10	1.0 EDTA	98.0
0.25	10.0 EDTA	91.9
0.50	10.0 EDTA	100.0
1.00	10.0 EDTA	99.7

TABLE V

EFFECT OF FLUORIDE AND EDTA ON THE FORMATION AND
EXTRACTION OF MOLYBDOPHOSPHORIC ACID
IN 1-BUTYL ACETATE FROM TITANIUM

<u>Ti</u> <u>mg</u>	<u>Complexing</u> <u>Agent</u> <u>mg</u>	<u>% Recovery</u>
0.10	5 F ⁻	96.4
0.25	5 F ⁻	99.4
0.50	5 F ⁻	78.3
1.00	5 F ⁻	85.0
0.10	10 EDTA	49.0
0.25	10 EDTA	37.2
0.50	10 EDTA	26.3
1.00	10 EDTA	29.5

Ti, Zr. or Pu, heating, longer stirring times, or other measures to improve the kinetics of the reaction may be required. The effect of EDTA and fluoride on Ta and W was not studied. By using EDTA and fluoride as complexing agents, the procedure can be extended to the analysis of phosphates in Zr, Ti, and Pu solutions at moderately high levels.

PRECISION AND ACCURACY

Precision and accuracy measurements were made without the addition of fluoride or EDTA using standard phosphorus solutions. The accuracy and precision at the 95% confidence level for a single determination on a 1.86 μg phosphorus spike is $100.4 \pm 12.9\%$ based on 10 analyses. The accuracy and precision at the 95% confidence level for 4.65 μg of phosphorus is $99.3 \pm 11.3\%$ based on 10 analyses. The precision of the method for these analyses plus the results for the 1.86 μg phosphorus spike on all ions which did not interfere was $97.9 \pm 10.6\%$ at the 95% confidence level based on 50 analyses. The accuracy and precision of the points used for each calibration were $100.1 \pm 2.2\%$. Since the precision between the calibration data and standard results are considerably different, it was believed that something was happening to the molybdate reagent causing small changes in the calibration. In order to minimize this possible effect, the molybdate reagent was stored in the refrigerator and a new calibration run with fresh molybdate whenever standard recoveries began to decrease. Another possible cause for the poor precision may be from 1-butyl acetate which is very difficult to separate from the aqueous phase. Attempts to use mixtures of 75 vol% butyl acetate with 25 vol% cyclohexane, xylene, and chloroform resulted in a 20% decrease in absorbance. Fifty percent mixtures of these same organics resulted in no absorbance. Since no suitable replacement solvent was found, the 1-butyl acetate is thoroughly centrifuged and then

carefully transferred to the spectrophotometric cell by allowing the organic to run down the inside wall of the cell to prevent any residual aqueous phase from clouding the organic. The cell should then be carefully inspected for the slightest cloudiness. Since the sample is analyzed in the ultraviolet region, it is especially sensitive to any entrained H_2O or dirty cells. By carefully monitoring these points, a reasonably accurate and precise procedure may be obtained.

APPLICATIONS

This procedure was first used to check phosphorus results from the emission spectrograph on uranium-233 product solutions. The method failed to provide the same result as the emission spectrograph due to entrained tributyl phosphate (TBP) and dibutyl phosphate (DBP) in the product solutions. However it was possible to follow the degradation of TBP and DBP to orthophosphates from day to day by measuring the increase in the phosphate ion being generated. Attempts to obtain a total phosphorus analysis by speeding up the degradation by heating an aliquot of the sample in concentrated nitric acid failed. The reason for the failure was believed to be the formation of a nitrated product of the TBP solvent NPH (natural paraffin hydrocarbon) which was extracted into the 1-butyl acetate resulting in a high absorbance in the ultraviolet region of the spectrum. Other ways to break the TBP and DBP down to the phosphate ion were not attempted.

The method has also been used to determine phosphates in stored nuclear waste solutions. These solutions are normally caustic with a high salt concentration and contain waste from both past and present nuclear processes. This approach has proven to be valuable for these determinations since the contents of these waste tanks vary considerably and thus require a highly specific procedure. Because of its

simplicity, sensitivity, and specificity, the method should find applications in other fields such as environmental analyses.

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APPENDIX

APPENDIX

DETAILS FOR THE SPECTROPHOTOMETRIC DETERMINATION
OF PHOSPHATE BY THE EXTRACTION OF MOLYBDOPHOSPHORIC
ACID INTO 1-BUTYL ACETATE

Procedure	Comments
1. Into a 15-ml plastic vial, pipet or dispense 10 ml of 0.70M HCl. Prepare a second vial containing 5 ml of 0.85M HCl. Start a reagent blank.	Vials are pre-rinsed with deionized H ₂ O.
2. Pipet the sample into the first vial containing 0.70M HCl and rinse the pipet.	Sample should contain 2 to 17 µg of PO ₄ ⁼ and meet the acid limitations described in this report.
3. Add 1 ml of 10 g/liter EDTA and 500 µl of 10 g/liter to the first vial and stir for 3 to 5 minutes.	The kinetics for destroying Pu, Zr, and Ti phosphate complexes have not been completely evaluated; therefore stirring times may vary depending on the matrix. Heating may aid for difficult matrices.
4. Pipet 1 ml of the molybdate reagent into the first vial and stir for 3 minutes.	
5. Pipet exactly 5 ml of 1-butyl acetate into the first vial and stir the mixture to an emulsion for 3 minutes.	A visible yellow color will form in the organic at the higher phosphate ion concentration range.
6. Allow the phases to separate by standing or centrifuging and transfer as much organic as possible to the second vial containing 0.85M HCl.	This step is added to remove any excess molybdate or entrained colored ion that may absorb at 310 nm.
7. Emulsify by stirring for 3 minutes and then separate phases by centrifuging for 3 to 5 minutes.	<ol style="list-style-type: none">1. Centrifuging is required in this step to ensure that the two phases are completely separated.2. Entrained aqueous in the organic may begin to separate and become cloudy, causing erroneous results.3. Once the phases have been separated, the operator should be careful not to jar or shake the vials.

Procedure	Comments
8. Transfer the organic phase to a clean, 1-cm absorption cell, stopper, and measure the absorbance at 310 nm against a reagent blank.	1. When transferring, place the tip of the pipet against the inside wall of the cell and slowly dispense. Direct pipetting into the bottom of the cell has resulted in entrained water being freed, causing cloudiness. 2. Inspect the cells closely for cloudiness; and if cloudy, recentrifuge. 3. Cells should be washed with reagent grade ethyl alcohol and thoroughly dried. The cell surfaces should be free of any lint or smudge marks since measurements in this wavelength region appear to be especially sensitive to dirty cells.

The method is calibrated by substituting aliquots of phosphate standard between 2 and 17 μg into the procedure in place of sample and the data processed by a least squares regression analysis. The resulting equation is then used for calculating the concentration of phosphate in the unknown samples.

$$\text{g/liter PO}_4^{3-} = (A - I)(1/S)(DF)$$

where

A = Absorbance (absorbance units)

I = Intercept (absorbance units)

$1/S = \text{Slope} = \frac{\text{mg PO}_4^{3-}}{\text{absorbance}}$

DF = Dilution Factor = 1/ml