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Separation and Determination of Phosphate, Silicate, and Arsenate

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A method was developed for quantitatively separating and determining phosphate, silicate, and arsenate when they occur together in solution. All three, at a pH of 1.8, form heteropoly molybdate complexes when heated just to boiling. Only the phosphate complex is extracted into ether from a solution that contains one volume of concentrated hydrochloric acid plus nine volumes of solution. After removing the phosphate, only the silicate complex is extracted into butanol from a solution that contains two volumes of concentrated hydrochloric acid plus nine volumes of solution. The arsenate complex is then extracted into methyl isobutyl ketone after readjusting the acidity back to $1+9$ by adding silica-free ammonium hydroxide. The various complexes are reduced by adding stannous chloride to the organic solvent and determined spectrophotometrically. The effect of various salts on the complex formation and the extraction is also reported

1. Introduction

The heteropoly-complex compounds of molybdenum have been known and used by chemists for more than a century.[1] They are used by analytical chemists especially for determining phosphorus, silicate, and arsenate, either as the yellow complexes or as the reduced blue complexes.

The molybdenum salt most frequently used to form these complexes is the so-called ammonium molybdate. For this reagent to be most useful it must not contain, either individually or combined, excessive amounts of phosphate, silicate, and arsenate. The Committee on Analytical Reagents of the American Chemical Society has published a specification for ammonium molybdate.[2] This specification has, in addition to other requirements, a requirement and test for phosphate but not for silicate or arsenate. While trying to improve the test for phosphate and also limit the amount of silicate and arsenate that might be present, it was found that all three of the ions in question could be collectively determined. It was also found that they could be quantitatively separated from one another even though they were contained in the same solution.

The extensive literature concerned with the determination of these ions, which contains so many articles that it is impractical to enumerate them all, is largely the result of the effort to ascertain and control the many variables which influence the formation and reduction of a specific, desired complex. For a partial résumé of the difficulties, see the preprint of an article by Mellon.[3]

Analysts have also used various organic solvents, or mixtures of organic solvents, to extract the desired complex.[4] To the authors' knowledge, a satisfactory method has not been published for separating and determining all three ions, phosphate, silicate, and arsenate, when they occur together in a solution. Such a method has now been developed and the details are given below.

2. Reagents and Standards

2.1. Ammonium Hydroxide (Silica-Free)

The ammonium hydroxide used must be free from silica. Aqueous ammonia in contact with glass, even momentarily, will dissolve a sufficient amount of silica to make it unusable for the purpose here described. Since all ammonium hydroxide available commercially comes in glass containers, one must prepare silica-free ammonium hydroxide in the laboratory. The most convenient method to do this is to saturate distilled water with ammonia gas from a cylinder of compressed anhydrous ammonia. Plastic tubing and bottles must be used throughout.

2.2. Ammonium Molybdate Solution (10 Percent)

Prepare a solution of ammonium molybdate by dissolving 10 g of the ACS reagent in 100 ml of distilled water. This solution should be prepared daily and placed in polyethylene containers.

To determine the suitability of each lot of ammonium molybdate, dissolve 2.5 g of the reagent in 80 ml of distilled water, add a few drops of bromine water, and adjust the pH of the solution to 1.8 with diluted hydrochloric acid $(1+9)$. Heat the solution just to boiling and cool it to room temperature. Add 10 ml of concentrated hydrochloric acid and 1 ml of butanol. Extract the combined phosphate, silicate, and arsenate complexes with methyl isobutyl ketone. After washing the ketone

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[1] L. Svanberg and H. Strune, J. prakt. Chem. **44**, 257 (1848).

[2] Reagent Chemicals, American Chemical Society, Specifications 1955.

[3] M. G. Mellon, Analytical properties of heteropoly anions, presented at a Symposium on Structure and Properties of Heteropoly Anions, Division of Physical and Inorganic Chemistry, American Chemical Society (September 1956).

[4] N.A. Fillipova and L.I. Kuznetsova, Zavodskaya Lab., **16,** 536 (1950); C. Wadelin and M. G. Mellon, Analyst **77,** 708 (1952); C. H. Lueck and D. F. Boltz, Anal. Chem. **30,** 183 (1958).

solution and reducing the molybdenum complexes as described later (3.4), any blue color in the ketone should not exceed that produced when 0.01 mg of silica and 0.5 g of the same ammonium molybdate are treated exactly as was the 2.5 g of the ammonium molybdate.

2.3. Stannous Chloride Solution

Prepare a solution of stannous chloride by dissolving 2 g of the ACS reagent $SnCl_2 \cdot 2H_2O$ in concentrated hydrochloric acid and diluting it to 100 ml with concentrated hydrochloric acid.

2.4. Phosphate Solution (0.01 mg of PO_4 in 1 ml)

Prepare a stock solution by dissolving 0.143 g of assayed potassium dihydrogen phosphate, KH_2PO_4, in distilled water and diluting the resulting solution to 100 ml. Dilute 10 ml of this stock solution to 1,000 ml. Since the *p*H of this solution is approximately 4, it is safe to prepare and store it in glass vessels.

2.5. Silicate Solution (0.01 mg of SiO_2 in 1 ml)

Prepare a stock solution of silica by dissolving 9.46 g of assayed $Na_2SiO_3 \cdot 9H_2O$ in 9 ml of silica-free ammonium hydroxide and diluting the resulting solution to 200 ml (199.4 g at 25° C) with distilled water. Dilute a 1-ml aliquot of this solution plus 5 ml of silica-free ammonium hydroxide to 1,000 ml (997.1 g at 25° C) with distilled water. Since volumetric polyethylene ware was not available, the silica solution was diluted on the weight basis.

2.6. Arsenate Solution (0.01 mg of As in 1 ml)

Prepare a stock solution of arsenic by dissolving 0.132 g of NBS standard sample of As_2O_3 in 10 ml of diluted hydrochloric acid (1+1) to which bromine water is added. To prevent loss of arsenic by volatilization, sufficient bromine must be present at all times to impart a strong yellow color to the solution. This may require the addition of more bromine water while the arsenic trioxide is dissolving. Dilute the resulting solution to 1,000 ml. Dilute 100 ml of this stock solution, to which 5 ml of concentrated hydrochloric acid has been added, to 1,000 ml. Since these solutions are acid, they can be prepared, diluted, and stored in glass vessels.

3. General Procedure

3.1. Formation of the Heteropoly Complexes

Dissolve the sample to be analyzed in 80 ml of distilled water and add 5 ml of a 10-percent solution of ammonium molybdate. Adjust the acidity of the solution to approximately *p*H 4 by adding silica-free ammonium hydroxide or hydrochloric acid as required.

If the solution of the unknown is alkaline, it must be prepared in a platinum container to prevent contamination from dissolved silica. After the solution has been adjusted to *p*H 5 or less, as determined with indicator paper, it may be transferred to a glass vessel without danger of dissolving sufficient silica to interfere with the test.

Add enough bromine water to impart a slight yellow color to the solution. The bromine water is added to oxidize the arsenic to the quinquevalent state, because tervalent arsenic does not form a heteropoly complex with molybdate. Readjust the acidity of the solution to *p*H 1.7 to 1.9. Heat the resulting solution just to boiling, cool it to room temperature, and dilute it to 90 ml. Make all *p*H measurements which are less than 7 with a standardized glass electrode system. Do not use glass electrodes in alkaline solutions because sufficient silica may be dissolved to vitiate the results of the test for silica.

3.2. Separation and Determination of Phosphate

Transfer the solution which was prepared as described above to a separatory funnel and add 10 ml of concentrated hydrochloric acid and 35 ml of ethyl ether. Shake the mixture vigorously for a few minutes and allow the two layers to separate. Draw off the aqueous layer and reserve it for the determination of silica and arsenic. Wash the ether layer twice with 10-ml portions of diluted hydrochloric acid (1+9). Draw off and discard the aqueous layers. Add 0.2 ml of the stannous chloride solution to the ether solution and shake the mixture. Dilute the ether solution to 25 ml with more ether and determine its optical density with a spectrophotometer at 630 mμ. Determine the amount of phosphate present from a calibration curve. If greater sensitivity is desired, measurements may be made at approximately 830 mμ.

3.3. Separation and Determination of Silica

Add 10 ml of concentrated hydrochloric acid to the aqueous solution reserved from the separation of phosphate and transfer it to a separatory funnel. Pour into the solution 50 ml of butanol, shake the mixture vigorously, and allow the layers to separate. Draw off the aqueous layer and add to it 10 ml of silica-free ammonium hydroxide and reserve this solution for the extraction and determination of arsenic.

Wash the butanol layer three times with 20-ml portions of diluted hydrochloric acid (1+99). Draw off and discard the aqueous layers. Add 0.5 ml of the stannous chloride solution to the butanol solution and shake the mixture. Dilute the butanol solution to 50 ml with more butanol and determine its optical density with a spectrophotometer at 630 mμ. Determine the amount of silica present from a calibration curve.

The optical density should be determined immediately after the reduction by stannous chloride. If this is not done, the blue color begins to fade, but treatment with stannous chloride as described above will restore the blue color to its original intensity.

This fading may be attributed to some impurity in the butanol, because the reduced molybdenum blue color was found to be stable for 24 hr or more in some lots of butanol.

3.4. Separation and Determination of Arsenic

Transfer to a separatory funnel the aqueous solution reserved from the separation of silica, to which 10 ml of silica-free ammonium hydroxide had been added. Pour into the solution 25 ml of methyl isobutyl ketone, shake the mixture thoroughly, and allow the layers to separate. Draw off and discard the aqueous layer. Wash the ketone solution three times with 10-ml portions of diluted hydrochloric acid (1+9). Draw off and discard the aqueous layers. Add a freshly prepared solution of 0.2 ml of the stannous chloride solution in 10 ml of water to the ketone solution, shake the mixture, and allow the layers to separate. Draw off and discard the aqueous layer. If the ketone layer is cloudy, it may be cleared by washing it with diluted hydrochloric acid (1+99). Dilute the ketone solution to 30 ml with more ketone and determine its optical density with a spectrophotometer at 630 mμ. Determine the amount of arsenic present from a calibration curve.

3.5. Reliability of the Method

The calibration curves shown in figures 1, 2, and 3 were determined for each of the complexes studied. The optical densities were determined at a wavelength of 630 mμ with a spectrophotometer provided with absorption cells that were 50 mm long. The partition coefficients for the various complexes were not determined. However, when quantities of the three ions were present in considerable excess of 30 mg each, each one was completely extracted in a single operation as specified. To obtain complete extraction of the arsenic in one operation with methyl isobutyl ketone, the aqueous phase must be saturated with butanol.

The reliability of the method was ascertained by preparing synthetic solutions containing known amounts of the three elements and subsequently separating them and determining the amount of each. The results of the experiments are given in table 1.

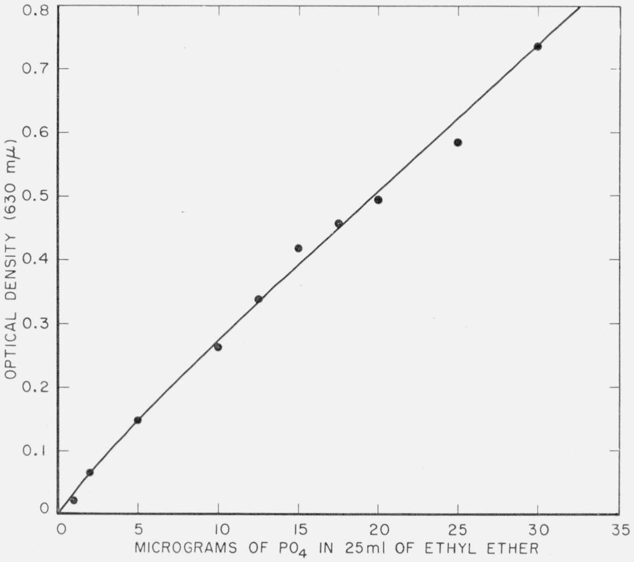

FIGURE 1. *Calibration curve for reduced molybdophosphate in ethyl ether.*

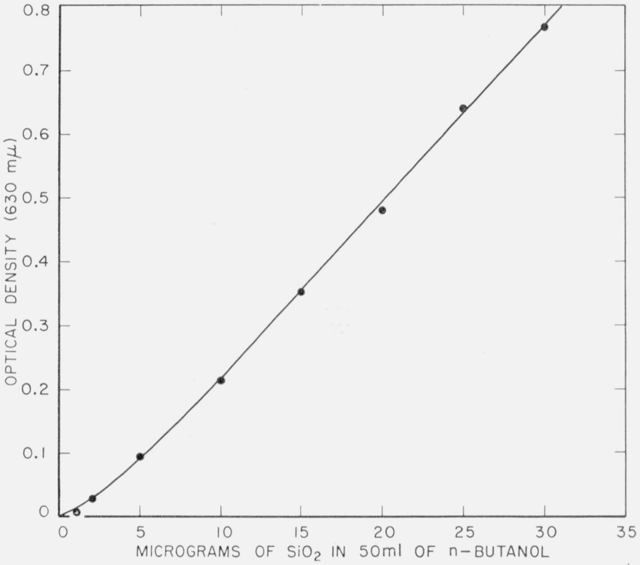

FIGURE 2. *Calibration curve for reduced molybdosilicate in butanol.*

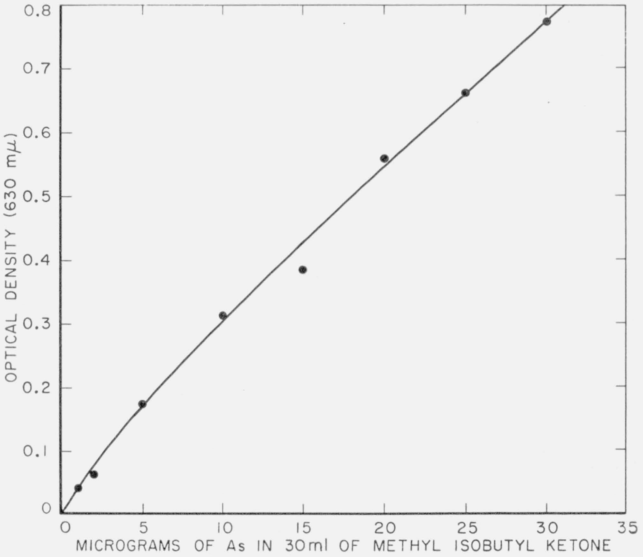

FIGURE 3. *Calibration curve for reduced molybdoarsenate in methyl isobutyl ketone.*

TABLE 1. *Separation and determination of known quantities of phosphate, silicate, and arsenate*

Solution No.	Phosphate (PO_4)		Silicate (SiO_2)		Arsenate (As)	
	Added	Recovered	Added	Recovered	Added	Recovered
	μg	μg	μg	μg	μg	μg
1	1	1	1	1	1	1
2	10	10	10	10	10	10
3	30	30	30	30	30	30
4	30	30	2	2	2	2
5	2	2	30	30	2	2
6	2	2	2	2	30	29

4. Interference of Salts in the Extractions

To determine the effect of salt concentration on the accuracy of the determinations, experiments were made by adding 10 mg of each of the three elements to solutions of various salts. The amounts of salts taken were 1, 2, and 5 g, which would correspond to 1, 2, and 5 percent at the start of the extraction of phosphate by ethyl ether.

4.1. Extraction From Solutions Containing 1 g of salt

Complete recovery was obtained when 10 μg of each of the three ions in question was added to 1 g of each of the following salts: Ammonium carbonate, chloride, nitrate, and sulfate; sodium carbonate, chloride, hydroxide, nitrate, perchlorate, and sulfate; potassium carbonate, chloride, hydroxide, nitrate, and sulfate; and ferric chloride. When sodium or potassium acetate was used, the acetate ion interfered with the recovery of phosphate. If the acetate was converted to nitrate by evaporating to dryness several times in the presence of nitric acid, the added phosphate was recovered. Recoveries of silicate and arsenate and the effect that salts of other organic acids might have on the reaction were not investigated.

4.2. Extraction From Solutions Containing 2 g of Salt

When the quantities of the above salts, except ferric chloride which was not tried, were increased to 2 g, complete recoveries of the added phosphate, silicate, and arsenate were obtained unless the anion was chloride. In addition, 2 g of calcium chloride and barium nitrate were tried and the calcium and barium did not interfere. Complete recovery of the three ions was obtained from 2 g of the chloride salts if the initial acidity of the solution was adjusted to a *p*H of 1.7 to 1.9 with diluted sulfuric acid instead of with diluted hydrochloric acid. The other conditions remained as described.

4.3. Extraction From Solutions Containing 5 g of Salt

a. Extraction From Nitrate Solutions

Experiments were made to determine the recoverability of phosphate, silica, and arsenic from solutions containing 5 g each of ammonium nitrate, sodium nitrate, potassium nitrate, barium nitrate, calcium nitrate, and aluminum nitrate. The results are given in table 2.

b. Extraction From Sulfate Solutions

Experiments were made to determine the recoverability of phosphate, silica, and arsenic from solutions containing 5 g each of ammonium sulfate, sodium sulfate, potassium sulfate, and aluminum sulfate. The results are given in table 3.

TABLE 2. *Separation and determination of phosphate, silicate, and arsenate from solutions containing 5 g of nitrate salts*

Salt	Phosphate		Silicate		Arsenate	
	Added	Recovered	Added	Recovered	Added	Recovered
	μg	μg	μg	μg	μg	μg
NH_4NO_3	10	10	10	11	10	9
$NaNO_3$	10	11	10	10	10	10
KNO_3	10	9	10	11	10	12
$Ba(NO_3)_2$	10	12	10	9	10	9
$Ca(NO_3)_2$	10	9	10	11	10	9
$Al(NO_3)_3 \cdot 9H_2O$	10	12	10	10	10	10

TABLE 3. *Separation and determination of phosphate, silicate, and arsenate from solutions containing 5 g of various sulfates*

Salt	Phosphate		Silicate		Arsenate	
	Added	Recovered	Added	Recovered	Added	Recovered
	μg	μg	μg	μg	μg	μg
$(NH_4)_2SO_4$	10	5	10	10	10	10
Na_2SO_4	10	4	10	12	10	10
K_2SO_4	10	3	10	12	10	11
$Al_2(SO_4)_3 \cdot 18H_2O$	10	4	10	10	10	9

It is seen that whereas the recovery of silica and of arsenic was satisfactory, only one-third to one-half of the added phosphate was recovered. It was found, however, that by operating in a less acid solution than that originally specified, extraction and recovery of phosphate could be accomplished from the solutions containing 5 g of sulfates. Depending on the particular sulfate, from 80 to 86 percent of the original volume of hydrochloric acid sufficed.

To remove the silica complex, the acidity of the solution was increased to a concentration of (2+9), which was the concentration originally specified for the extraction of silica. To extract arsenic, the acidity was then reduced by the addition of silica-free ammonium hydroxide to that found experimentally suitable for the extraction of phosphate. The results, given in table 4, show that phosphate, silica, and arsenic can be separated from one another and completely recovered in the presence of 5 g of various sulfate salts.

TABLE 4. *Recovery of 10 μg each of phosphate, silicate, and arsenate added to solutions containing 5 g of various sulfates by the modified method*

Salt	Phosphate		Silicate		Arsenate	
	Concentrated HCl	PO_4 recovered	Concentrated HCl	SiO_2 recovered	Concentrated NH_4OH	As recovered
	ml	*μg*	*ml*	*μg*	*ml*	*μg*
$(NH_4)_2SO_4$	8.0	11	12.0	11	12.0	9
Na_2SO_4	8.6	10	11.4	11	11.4	8
K_2SO_4	8.0	10	12.0	11	12.0	11
$Al_2(SO_4)_3 \cdot 18H_2O$	8.5	11	11.5	11	11.5	9

c. Extraction From Chloride Solutions

Experiments were made to determine the recoverability of phosphate, silica, and arsenic from solutions containing 5 g each of ammonium chloride, sodium chloride, potassium chloride, barium chloride, calcium chloride, and aluminum chloride. The operating conditions were those specified in section 3. The results are given in table 5.

TABLE 5. *Separation and determination of phosphate, silicate, and arsenate added to solutions containing 5 g of various chlorides*

Salt	Phosphate		Silicate		Arsenate	
	Added	Recovered	Added	Recovered	Added	Recovered
	μg	*μg*	*μg*	*μg*	*μg*	*μg*
NH_4Cl	10	2	10	12	10	9
$NaCl$	10	3	10	11	10	11
KCl	10	4	10	9	10	12
$BaCl_2 \cdot 2H_2O$	10	7	10	11	10	11
$CaCl_2 \cdot 2H_2O$	10	7	10	10	10	11
$AlCl_3 \cdot 6H_2O$	10	1	10	10	10	10

The results show that the phosphate was not completely recovered. However, the amount of phosphate remaining in solution did not seriously interfere in the determination of either silica or arsenic.

Attempts were then made to modify the original procedure in the manner similar to that followed for solutions containing 5 g of sulfate salts. That is, the acidity at which the phosphate could be quantitatively extracted was established experimentally. This acidity was found to be lower than that for the sulfate salts. To extract the silica the acidity was increased to (2+9), the original concentration specified for the extraction of molybdosilicate. Finally, to extract the arsenic the acidity was again lowered to that required to extract the molybdophosphate, as determined experimentally for a particular chloride salt. Complete recovery of phosphate and of silica was obtained, but not of arsenic. These results are given in table 6.

Even when an amount of nitric acid, 7.5 ml, was substituted for the 10 ml of hydrochloric acid, the recovery of arsenic remained incomplete.

TABLE 6. *Separation and determination of 10 μg each of phosphate, silicate, and arsenate added to solutions containing 5 g of various chlorides by the modified method*

Salt	Phosphate		Silicate		Arsenate	
	Concentrated HCl added	PO_4 recovered	Concentrated HCl added	SiO_2 recovered	Concentrated NH_4OH added	As recovered
	ml	*μg*	*ml*	*μg*	*ml*	*μg*
NH_4Cl	4.0	11	16.0	11	10.0	6
$NaCl$	7.0	12	13.0	11	10.0	5
KCl	5.5	11	14.5	10	10.0	6
$BaCl_2 \cdot 2H_2O$	8.0	12	12.0	11	10.0	9
$CaCl_2 \cdot 2H_2O$	8.5	11	11.5	9	10.0	7
$AlCl_3 \cdot 6H_2O$	7.0	12	13.0	10	10.0	5

The determination of all three elements in question when 5 g of a chloride salt is present requires two procedures. One procedure, that by which the results reported in table 5 were obtained, is to determine the silica and arsenic. The other procedure, that by which the results reported in table 6 were obtained, is to determine the phosphate and silica. It should be noted that silica may be determined by either method.

It should be emphasized that the separation and determination of the silica appeared to be complete regardless of the salt concentration, provided the molybdosilicate complex was extracted with butanol from a solution that contained 2 volumes of concentrated hydrochloric acid plus 9 volumes of solution.

5. Discussion of Results

The procedure described in section 3 is suitable for the quantitative separation of small amounts of phosphate, silica, and arsenic from one another and for their subsequent determination when they occur in solutions containing as much as 1 g in 100 ml of solution of either a chloride, nitrate, sulfate, or perchlorate.

If the quantity of salt is increased to 2 g, complete separation and recovery is effected except in the case of a chloride salt.

In the presence of 5 g of either a sulfate or chloride salt, the extraction of phosphate is incomplete. By lowering the acidity at which the phosphate is extracted, then establishing the acidity originally specified for the extraction of silica, and finally, to extract the arsenic, reestablishing the acidity found suitable for the extraction of the phosphate, the three substances in question can be quantitatively separated from one another even in the presence of 5 g of a sulfate salt. By following a similar procedure in the case of 5 g of a chloride salt, phosphate and silica can be successfully extracted and determined, but not the arsenic. It becomes necessary, in the case of 5 g of a chloride salt, to determine phosphate and silica in one solution and silica and arsenic in another.

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