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The Spectrophotometric Determination of Phosphate and Arsenate by Selective Extraction with Mixed Solvents

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Synopsis. A spectrophotometric method for the simultaneous determination of phosphate and arsenate by selective solvent extraction was examined. First, molybdophosphate was extracted with 1-butanol–chloroform in the presence of molybdoarsenate, and then the molybdoarsenate in the aqueous phase was extracted with MIBK, followed by reduction directly in the organic phase to Molybdenum Blue.

Most methods for the determination of phosphate and arsenate are spectrophotometric methods, based on the formation of the yellow molybdophosphate and molybdoarsenate, followed by the reduction of these complexes to Molybdenum Blue. Arsenate interferes seriously with the determination of phosphate, since their chemical properties are similar.[1–3]

Previous studies of the separation of phosphate, silicate, arsenate, and germanate have shown that phosphate can be separated from mixtures of the four elements as the molybdophosphate by mixed-solvent extraction with (1+3) 1-butanol–chloroform[4] or (2+3) isobutyl alcohol–chloroform.[5]

Paul[6–9] has reported methods for the simultaneous determination of phosphorus, arsenic, silicon, and germanium as heteropoly-blue complexes. However, while simple, these methods lack precision, sensitivity, and rapidity. The present authors have now examined the separation of phosphate and arsenate by selective extraction with various mixed solvents. This paper will report a rapid, sensitive, and accurate method combining solvent extractions and spectrophotometry for the determination of phosphate and arsenate.

Experimental

Apparatus and Reagents. A Hitachi, model 139, spectrophotometer with 10-mm silica cells was used. An Iwaki, model S-L type KM, shaker was used to shake the separatory funnel. All the chemicals were of analytical-reagent grades and were stored in polyethylene bottles to prevent contamination by silica. The water was deionized after distillation.

Standard Phosphate Solution, 200 μg ml^{-1}: Dissolve 0.2198 g of potassium dihydrogenphosphate in water and dilute to 250 ml. This solution is then diluted as required to 2 μg P(V) ml^{-1} with water.

Standard Arsenate Solution, 200 μg As(V) ml^{-1}: Dissolve 0.2082 g of disodium hydrogenarsenate in water and dilute to 250 ml. This solution is then diluted as required to 10 μg As(V) ml^{-1} with water.

Ammonium Molybdate Solution, 0.1 M†: Dissolve 1.77 g of hexaammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water and dilute to 1 l.

Procedure. a) Determination of Phosphate: Transfer a 20-ml portion of the sample solution (previously neutralized) containing less than 20 μg P(V) and 50 μg As(V) into a 100-ml separatory funnel. Add 4 ml of 0.1 M molybdate solution, 5 ml of 0.5 M potassium chloride, and 3 ml of 2.5 M hydrochloric acid. Dilute with water to 25 ml, mix well, and allow to stand for 10 min. Then, add 10 ml of (7 : 13, v/v) 1-butanol–chloroform and shake the funnel vigorously for 5 min with a mechanical shaker. After the phase separation, drain the organic phase into a 20-ml stoppered test tube containing *ca.* 2 g of anhydrous sodium sulfate. Transfer the organic solvent into a 10-ml silica cell, measure the absorbance at 310 nm against a reagent blank. Then, add 10 ml of (3 : 7, v/v) 1-butanol–chloroform to the originasl eparatory funnel, and repeat the extraction and measurement of the absorbance until the molybdophosphate is removed. Refer the total absorbance reading to a calibration curve obtained using a standard phosphate solution.

b) Determination of Arsenate:[10] Add 10 ml of isobutyl methyl ketone (MIBK) to an aqueous solution containing the molybdoarsenate by means of the procedure *a*) described above. Shake the funnel vigorously for 1 min and allow to stand for about 5 min to separate the phases. Discard the aqueous phase and wash the MIBK extract with 10 ml of (1+20)hydrochloric acid. Repeat the washing with 10 ml of (1+20)hydrochloric acid once more to remove the excess of molybdate. Transfer the MIBK extract into a 25-ml volumetric flask, add 4 ml of ethanol and 1 ml of 0.4 M tin(II) chloride, and dilute to the mark with ethanol. Mix well and allow to stand for 20 min. Measure the absorbance at 740 nm against a reagent blank.

Results and Discussion

Effect of the Hydrochloric-acid Concentration. The optimum acidity of the aqueous phase for he formation of the molybdophosphate was found to be 0.15—0.50 M

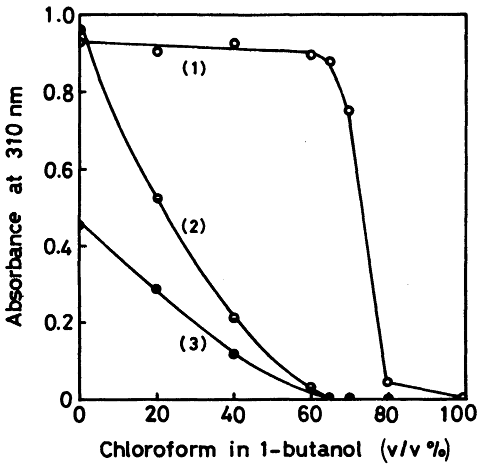

Fig. 1. Effect of the concentration of chlororm in 1-butanol on the extraction.
(1) P(V): 10 μg, (2) As (V): 40 μg, (3) As(V): 20 μg. [HCl]: 0.3 M, [Mo]: 1.6×10^{-2} M, reference: reagent blank.

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† 1 M=1 mol dm^{-3}.

hydrochloric acid. Molybdoarsenate was extracted into MIBK in the same range as molybdophosphate. The concentration of 0.3 M hydrochloric acid in the initial solution was, therefore, chosen as the optimum.

Effect of the Concentration of Chloroform in 1-Butanol on the Extraction of Molybdophosphate and Molybdoarsenate. As is shown in Fig. 1, the optimum range was 60—65 v/v % chloroform in 1-butanol to separate the molybdophosphate from the molybdoarsenate. Therefore, 65 v/v% chloroform in 1-butanol, that is, (7 : 13, v/v) 1-butanol–chloroform, was used in the subsequent work. In order to remove the molybdophosphate completely, it was necessary to extract it twice or three times with 1-butanol–chloroform. When the molybdophosphate was extracted with 10 ml of 65 v/v% chloroform in 1-butanol, it was found that the concentration of chloroform in the organic phase turned to 70 v/v%. Then, for the second or third extraction, 70 v/v% chloroform in 1-butanol, that is, (3 : 7, v/v) 1-butanol–chloroform, was used.

The Choice of Extractant. Several mixed organic solvents (1-butanol–cyclohexane, MIBK–chloroform, MIBK–cyclohexane,1) *etc.*) were examined as extractants. The considerations for the choice of the organic solvents to extract the molybdophosphate are as follows: (1) The solvent should have a greater specific gravity of the organic solvents than that of water, such a greater specific gravity being advantageous for the continuous extraction of molybdoarsenate; (2) the absorbance of reagent blank is low, and (3) it should be possible to separate the phases rapidly after shaking. The mixture of 1-butanol and chloroform was most suitable.

Calibration Curves. The calibration curves for the phosphate and arsenate obtained by the proposed procedure were linear in the ranges of 0—10 μg P(V) and 0—100 μg As(V), and the molar absorptivities, as calculated from the slope of the curve, were 3.0×10^4 l·mol^{-1}·cm^{-1} (at 310 nm) and 1.6×10^4 l·mol^{-1}·cm^{-1} (at 740 nm) respectively.

Recovery of Phosphate and Arsenate. The recovery of phosphate and arsenate in mixtures of the other was examined by the procedure previously described. The results are shown in Table 1. The values were means of the six determinations, and the coefficient of variation was 3—5%. A good recovery and reproducibility were obtained. At higher As(V) concentrations, however, As(V) caused positive error in the determination of P(V).

TABLE 1. RECOVERY OF PHOSPHORUS(V) AND ARSENIC(V)

Amount of elements added μg		Found μg		Recovery %	
P(V)	As(V)	P(V)	As(V)	P(V)	As(V)
4.0	100.0	4.4	98.0	110	98
4.0	50.0	4.2	50.0	105	100
6.0	40.0	6.0	40.8	100	102
20.0	50.0	19.6	51.0	98	102
6.0	15.0	6.0	15.3	100	102
15.0	12.0	14.7	12.0	98	100
20.0	10.0	19.6	10.2	98	102
20.0	6.0	20.0	5.9	100	98

Effect of Diverse Ions. The effect of silicate and germanate ions, which form heteropoly acids, was investigated on the absorbance produced from 6.0 μg P(V) by the proposed procedure. Less than a 2500-fold Si(IV) and a 120-fold Ge(IV) weight excess did not interfere.

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