Inorganic Phosphate Enrichment with Iron(III) on Cation Exchanger

Atsushi YOSHINAGA and Yohichi GOHSHI

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo 113

Inorganic phosphate in solution was concentrated on the Fe adsorbed cation exchange resin and its presence was determined by X-ray fluorescence spectrometry. The limit of detection was 6 ppb in the case of an enrichment factor of 4000. Chloride or sulfite ions did not affect this adsorption system, but the functional groups which did not contribute to Fe adsorption decreased the recovery of phosphate. The adsorption mechanism of phosphate was studied by analyzing the correlation between some chemical species, such as H^+ , OH^- , K^+ and PO_4^{3-} , in solution and the resin phase. The adsorption mechanism of phosphate was found to be ion exchange with anions on the Fe sites.

Keywords Phosphate, solid adsorbent, preconcentration, X-ray fluorescence spectrometry

The determination of trace phosphate in solutions is important in the study of the environment. In many cases, phosphate is determined by a method based on molybdenum blue colorimetry.^{1,2} In this method, the analytical procedure is complicated and many experimental parameters need to be optimized. This method is particularly affected by many kinds of anions, and these effects bring more complexity to the analytical procedure.

To avoid these disadvantages, a simple and direct procedure for determination of phosphorus is desired. X-Ray fluorescence spectrometry (XRFS) is widely used because of its simplicity. As XRFS can determine elements directly, this method as appropriate as the desired method. But its sensitivity is not so satisfactory, so an enrichment procedure should be included.³

Among various techniques of preconcentration for XRFS⁴, a method using solid adsorbent is simple and easy to combine with XRFS. Therefore, modification of solid adsorbent suitable for the adsorption of phosphate was undertaken. For this purpose, the weakly acidic cation exchange resin on which metal ion was adsorbed was studied. This paper demonstrates the method's potential application to simple and selective adsorption of phosphate.

Experimental

Reagents and apparatus

All reagents used were of analytical grade, and deionized water was used throughout. A stock solution of phosphate (5000 ppm) was prepared by dissolving 716.5 mg of potassium phosphate monobasic into 100

ml. Reagents for the molybdenum blue colorimetry were prepared according to JIS K 0102 (Testing Method for Industrial Waste Water). The cation exchange resin (Bio-Rex 70, 100–200 mesh, Bio-Rad Laboratory) was treated with hydrochloric acid and potassium hydroxide, and then rinsed with water. This clean resin was dried in a desiccator.

XRFS measurements were performed with a Rigaku-Denki X-ray fluorescence spectrometer, equipped with a chromium tube (Phillips, operated at 50 kV–50 mA), a Ge(111) analyzer crystal and a proportional counter. Intensities of peak and background of $PK\alpha$ line were counted for 20 s, and the difference was used for calibration.

Preparation of metal adsorbed resin

To 2000 ml of metal chloride solution (containing 50 ppm of metal ions), 1 g of the cation exchanger was added and this mixture was stirred overnight. Then this resin was collected on a glass filter and dried in a desiccator.

The amount of metal ion on the resin was determined in the following way. The metal ion on the 50 mg of the resin was eluted with 10 ml of HCl (35%). The eluate was collected in a 50-ml flask, then diluted to volume with water. The concentration of the metal ion in this solution was determined by atomic absorption spectrometry. From this result and the exchange capacity of the resin (3.3 meq/g resin), the substitution ratio of the resin was determined.

Similarly, the amount of potassium on the resin was determined in the study of the adsorption mechanism.

Enrichment procedure of phosphate

Samples (200 ml) were adjusted to pH 5 to 7 and 100

mg of the resin was added, then the sample was stirred for about an hour. The resin was filtrated and then dried in a desiccator. From this resin, the sample for XRFS measurement (Fig. 1) was prepared. The concentration of phosphate in the effluent was determined by molybdenum blue colorimetry, and the recovery of the phosphate was calculated.

Results and Discussion

Effect of metal ion on the recovery of phosphate

To confirm the ability of the metal adsorbed resin to adsorb phosphate, enrichment of phosphate was performed using Fe, Al, Cr, and Cu form resins. The size of the sample solution was 100 ml and the pH of this

Fig. 1 Sample for XRF measurement.

Fig. 2 Relation between pH of sample solution and recovery of phosphate. Phosphate, 1 ppm; solution, 100 mg; adsorbent, 50 mg.

solution was varied from 3 to 11.50 mg of resin was used, therefore the maximum enrichment factor was 2000.

The result shown in Fig. 2 suggests that Fe form resin was the most suitable for the enrichment of phosphate, because the recovery was the highest and quantitative in the working range of pH. In later experiments, we used this Fe form resin as an adsorbent.

Fig. 3 pH Dependence of Fe elution from adsorbent. Solution, 100 ml; adsorbent, 50 mg. pH of the solution was adjusted by HCl.

Fig. 4 Dependence of recovery of phosphate on Fe substitution ratio of adsorbent. Phosphate, 1 ppm; pH=6; enrichment factor, 2000.

Features of the Fe form resin

To perform quantitative recovery of phosphate, Fe should be retained by the resin during the enrichment procedure. As is shown in Fig. 3, this weakly acidic cation exchanger tends to release Fe below pH 3. Thus the pH of the working solution should be kept above 3 to achieve quantitative recovery with this resin.

The relationship between Fe substitution ratio of the resin and the recovery of phosphate was investigated to confirm the efficiency of Fe. The result is shown in Fig. 4. In these experimental conditions, the Fe on the resin and phosphate in solution becomes equal in molarity at the Fe substitution ratio of 10%. As Fig. 4 shows, however, the yield of phosphate decreases even though an excess of iron exists on the resin.

In the case of the Fe substitution ratio is below 100%, an excess of the functional groups for the adsorption of Fe will occur. So these functional groups would be a cause of this result. Though the mechanism of the interference of them with the adsorption of phosphate is not clear, it appears that to accomplish quantitative recovery of phosphate, Fe substitution ratio of the resin should be 100%.

To apply this concentration method to a saline water sample, interferences of chloride and sulfate were studied. Up to 2% of chloride and 0.5% of sulfate didn't affect the preconcentration of phosphate. So this Fe form resin is found to be highly selective for phosphate.

Limit of detection

XRFS measurement was performed, as has been mentioned in the experimental section. A calibration curve with good linearity was obtained in the range of 0.2 to 1.0 ppm of phosphate in solution with an enrichment factor of 4000. The limit of detection (3σ , standard) was 6 ppb in solution and the relative standard deviation was 5%.

Adsorption mechanism of phosphate

In this adsorption system, a remarkable pH decrease was observed. Typically, the initial pH of the solution prior to the addition of the adsorbent was 7.0, and after the adsorption of phosphate, the final pH became about 4.0. This pH decrease corresponds to 3.1×10^{-5} mol/dm³ of the concentration increase of H⁺. If only the release of H⁺ ion from H₂PO₄⁻, which is a dominant chemical species in the initial state, is considered in this adsorption process, the increase in H⁺ ion of 1 ppm of phosphate solution is 2.0×10^{-5} mol/dm³ at most. This indicates that the adsorption of OH⁻ leads to a pH decrease of the solution.

All of the chemical species in this adsorption system are ionic; then two mechanisms can be considered for the OH⁻ adsorption. The first one is ion association with cation in solution (K⁺ in this experiment). If OH⁻ adsorption takes place with this mechanism, the same molarity of cations is transferred into the resin phase.

s, ions in solution; r, ions in resin.

The concentration of K⁺ in solution can be considered as a constant if this concentration is much higher than that of other ions. This condition can be achieved by adding KCl to the working solution. Then, from the equilibrium constant of the upper reaction, it is found that the pH of the solution is proportional to the log of the concentration of K⁺ in resin phase.

The second mechanism is ion exchange with anions on the Fe sites. In this case, there is no relation between the pH of the solution and the concentration of K⁺ in resin.

Fig. 5 Relation between pH and potassium concentration in resin phase. [K⁺]_r, potassium concentration in resin; resin, 50 mg; solution, 100 ml (0.01 mol dm⁻³ KCl).

Fig. 6 Relation between potassium concentration in resin phase and distribution coefficient of phosphate. [K⁺]_r, potassium concentration in resin; K_d, distribution coefficient of phosphate; adsorbent, 50 mg; solution, 100 ml (1–20 ppm phosphate).

Fig. 7 ESR spectrum.

Table 1 ESR Measurement

Sample	Form ^a	g_1	h_1	g_2	h_2
Bio-Rex 70 (100) ^b	Fe	2.06	109	3.06	8.5
	PO ₄	2.04	140	3.03	8.5
Bio-Rex 70 (85) ^b	Fe	2.05	88	3.03	14.3
	PO ₄	2.04	118	3.03	15.6

a. Fe=resins before the adsorption of phosphate; PO₄=resins after the adsorption of phosphate.

b. Fe substitution ratio (%).

Therefore, by analyzing the relation between the concentration of K⁺ in resin and pH of the solution, the adsorption mechanism can be determined. From the result shown in Fig. 5, it is concluded that OH⁻ adsorption takes place as ion association with K⁺.

In a similar way, the adsorption mechanism of phosphate can be determined. The relation between the concentration of K⁺ in resin ([K⁺]_r) and the distribution coefficient of phosphate (K_d) was studied (Fig. 6). Similarly, two adsorption mechanisms can be considered. If the adsorption of phosphate takes place by ion association with K⁺, K_d will be proportional to K⁺. And if it takes place by ion exchange with OH⁻, K_d will be reciprocally proportional to K⁺. This is because K⁺ is introduced into the resin phase due to ion association with OH⁻, as was mentioned before.

The result (Fig. 6) indicates the latter case. Then the adsorption mechanism of phosphate is found to be ion exchange.

ESR measurement of the resins

To confirm the result mentioned above, the ESR spectrum of the resin was measured. The results are summarized in Fig. 7 and Table 1. Two peaks are observed in the spectrum. This indicates that two different types of Fe exist in the resin phase. The difference between them may be related to the excess of functional groups for the Fe adsorption.

The intensity of the g_1 peak (h_1) is higher for the resin of the Fe substitution ratio 100% than that of the substitution ratio 85%. Then it seems that the Fe which corresponds to this peak can contribute to the adsorption of phosphate. The intensity of the g_2 peak is larger for the resin of lower Fe substitution ratio. Then it seems that the Fe corresponding to this peak does not contribute to the adsorption of phosphate. These results are consistent with the relation between the substitution ratio and the recovery of phosphate shown in Fig. 4.

In conclusion, the Fe adsorbed weakly acidic cation exchange resin appears to be an excellent adsorbent for the enrichment of phosphate in solution. This resin adsorbs phosphate selectively; the enrichment procedure is simple and easy to combine with XRFS. The limit of detection of this method is 6 ppb in the case of an enrichment factor of 4000. The ion exchange groups which do not contribute to Fe adsorption affect the adsorption of phosphate. Though the mechanism of their interference isn't clear yet, it can be concluded that to achieve quantitative recovery of phosphate, the Fe substitution ratio of the resin should be 100%. It appeared that this resin adsorbs not only phosphate but also OH⁻. And adsorption mechanisms of phosphate and OH⁻ to this resin were analyzed by determining the relation between the distribution coefficient of phosphate or pH of the solution and the concentration of potassium in resin. From our experiment, it was concluded that the adsorption mechanism of phosphate to the resin was ion exchange with OH⁻ on Fe sites and that of OH⁻ was ion association with K⁺ in solution.

References

1. W. D. Basson, J. F. Van Staden and P. M. Cattin, *Fresenius' Z. Anal. Chem.*, **307**, 373 (1981).
2. S. Motomizu, T. Wakimoto and K. Tōei, *Anal. Chim. Acta*, **138**, 329 (1982).
3. D. E. Leyden, W. K. Nonidez and P. W. Carr, *Anal. Chem.*, **47**, 1449 (1975).
4. R. E. Van Grieken, *Anal. Chim. Acta*, **143**, 3 (1982).

(Received February 20, 1986)

(Accepted July 24, 1986)

Determination of Cadmium by Inductively Coupled Plasma Atomic Emission Spectrometry after Ion-Pair Extraction with Zephiramine

Takahiro KUMAMARU*, Yasuaki OKAMOTO*, Takefumi SAKO* and Hiroshi MATSUO**

*Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Naka, Hiroshima 730

**Faculty of Engineering, Kinki University, Hiro-machi, Kure 737-01

Inductively coupled plasma atomic emission spectrometry combined with solvent extraction was investigated for the sensitive determination of cadmium. Cadmium(II) was converted to iodocadmiate and extracted quantitatively into carbon tetrachloride as the ion-pair with Zephiramine over the wide range of 1 mol dm^{-3} in hydrochloric acid to pH 12. The extract was introduced into the ICP operated under the optimum conditions. In this manner, the sensitivity and detection limit were significantly improved, being ca. 125- and 75-times higher, respectively, than those obtained by direct aspiration of the aqueous solution, when the aqueous phase/organic phase volume ratio was $25 \text{ cm}^3/5 \text{ cm}^3$. These improvements were due to both enrichment by extraction and solvent enhancement effect. The proposed method was applied to the analysis of human organ samples.

Keywords ICP-AES, cadmium determination, ion-pair solvent extraction, Zephiramine, carbon tetrachloride, human organs

Inductively coupled plasma atomic emission spectrometry (ICP-AES) has been widely used for the determination of various elements to the extent of trace levels. However, it is often required to concentrate the analytes prior to measurement owing to the lack of sensitivity. For this purpose, solvent extraction is one of the most practical techniques because of its simplicity and rapidity, and several papers¹⁻⁴ based on the principle have been reported. We have also demonstrated the ICP-AES of gold and platinum by using the ion-pair extraction of their iodide complexes with tetradecyldimethylbenzylammonium (Zephiramine).⁵ In the course of our study on ICP-AES combined with solvent extraction, it was found that some organic solvents such as carbon tetrachloride and chloroform showed a significant enhancement effect on emission intensities of metals when the extracts of the ion-pairs or metal chelates were introduced into the ICP.⁶

The present paper deals with ICP-AES of cadmium in the similar manner to our previous work.⁵ Cadmium(II) is converted to iodocadmiate and extracted into carbon tetrachloride as the ion-pair with Zephiramine, and the extract is introduced into the ICP to measure the cadmium emission intensity. This method is very sensitive and almost free from interferences. Moreover, quantitative extraction can be carried out over the wide pH range. In most cases,

therefore, the pH adjustment of the aqueous phase would be omitted in practical analysis. Analytical results of biological samples will be also presented.

Experimental

Apparatus

A Kyoto Koken Model UOP-1S high-resolution inductively coupled plasma atomic emission spectrometer was used with a glass concentric nebulizer. The spectrometer with a modified Czerny-Turner configuration incorporated an echelle grating and an oscillating quartz refractor plate, by which the second derivative emission intensity was measured on a strip chart recorder.

Reagents

All the reagents used were of analytical-reagent grade. Pure water (Miniclear Model DC-610 system, Organo) was used.

A $1000 \mu\text{g cm}^{-3}$ cadmium(II) standard stock solution was prepared by dissolving cadmium metal (99.999%, Mitsuwa Pure Chemicals) in nitric acid, warming nearly to dryness and diluting with water. Solutions of suitable concentrations were prepared by dilution with 0.1 mol dm^{-3} nitric acid before use. A $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ Zephiramine solution was prepared by dissolving

Table 1 Instrument operating conditions

ICP atomic emission spectrometer	Kyoto Koken UOP-1S
R.F. power	2.0 kW
Reflected power	~0 kW
Ar flow rate	
Outer gas	12 dm ³ min ⁻¹
Intermediate gas	1.0 dm ³ min ⁻¹
Nebulizer gas	0.325 dm ³ min ⁻¹
Observation height	12 mm above load coil
Slit width	100 μ m - 2000 μ m
Gain	4 - 8
Applied voltage	800 V
Response	10 s time constant
Analytical line	Cd II 214.438 nm

1.84 g of Zephiramine chloride (Wako Pure Chemicals) to 100 cm³ with water. A 2.0 mol dm⁻³ potassium iodide solution was prepared by dissolving 33.2 g of potassium iodide (Wako Pure Chemicals) to 100 cm³ with water.

Standard procedure

Transfer an aliquot of the cadmium(II) solution containing not more than 250 μ g cadmium into a 50-cm³ separatory funnel. Add 2 cm³ of the potassium iodide solution and 0.5 cm³ of the Zephiramine solution, and dilute the mixture to 25 cm³ with water. Then, add 5 cm³ of carbon tetrachloride. Shake the funnel for *ca.* 5 min by means of a mechanical shaker. After standing for *ca.* 15 min, separate the organic phase. Then, measure the atomic emission peak signal of cadmium (214.438 nm) by introducing the organic phase into the ICP *via* the nebulizer. The instrument operating conditions are listed in Table 1.

Results and Discussion

Optimization of ICP operating conditions

The radio-frequency power, the observation height and especially the nebulizer gas flow rate usually affect the emission intensity in ICP-AES. The effects of variation of these parameters on the emission intensity of the organic extract are shown in Fig. 1. In this work, the radio frequency power, the observation height above the load coil and the nebulizer gas flow rate selected were 2.0 kW, 12 mm and 0.325 dm³ min⁻¹, respectively. These operating conditions gave the highest sensitivity and signal-to-noise ratio.

Optimization of conditions of solvent extraction

The effect of pH on the extraction was investigated by extracting cadmium(II) from a series of aqueous solutions buffered at various pH values, while the other variables in the standard procedure were kept constant. The atomic emission intensity of the extract was maximum and constant when the acidity of the

Fig. 1 Three dimensional profiles for cadmium emission signals at different nebulizer gas flow rates. Nebulizer gas flow rate/dm³ min⁻¹: (a) 0.300, (b) 0.325, (c) 0.350; Analytical line: Cd II 214.438 nm; *I*, relative emission intensity; *H*, observation height/mm; *P*, R.F. power/kW; $V_w/V_o=25$ cm³/5 cm³; Cd(II), 50 μ g.

aqueous phase was within the tested range of 1 mol dm⁻³ in hydrochloric acid to pH 12. Therefore, the extraction could be usually carried out without adjusting pH in the aqueous phase. This is one of the merits of the present method in practical application.

The effects of the concentrations of potassium iodide and Zephiramine in the aqueous phase on the extraction were also examined according to the standard procedure. When the concentration of cadmium(II) in the aqueous phase was kept at less than 10 μ g cm⁻³, it was sufficient for the maximum and constant extraction efficiency that the concentrations of potassium iodide and Zephiramine were 0.16 mol dm⁻³ and 1.0×10^{-3} mol dm⁻³, respectively.

Extraction percentage

The extraction efficiency was estimated by graphite furnace(GF)-AAS of cadmium(II) in the aqueous phase after extraction. The extraction percentage was 99.9%, when the aqueous phase/organic phase volume ratio (V_w/V_o) was 25 cm³/5 cm³ and the initial concentration of cadmium(II) in the aqueous phase was kept at 2.0 μ g cm⁻³.

Sensitivity, precision and interferences

The standard procedure was established on the basis of the results discussed earlier. The calibration curve was linear up to the concentration of 10 μ g cm⁻³ of cadmium(II) initially present in the aqueous phase and the 3 σ detection limit⁷ was 1.0 ng cm⁻³, when the V_w/V_o was 25 cm³/5 cm³. The sensitivity⁷ and detection limit were much improved, being *ca.* 125- and 75-times higher, respectively, than those obtained by direct aspiration of the aqueous solution. These improvements are attributed not only to the preconcentration of cadmium(II) by extraction, but also to the enhancement effect of carbon tetrachloride.⁶ The reproduci-

Table 2 Determination of cadmium in human organ samples

Sample ^a	Cadmium found ^b /μg g ⁻¹	
	ICP-AES	GF-AAS ^c
Liver	0.69±0.03	0.64±0.04
Kidney	14.5 ±0.7	14.2 ±0.8
Pancreas	0.97±0.05	0.89±0.06

a. A hepatocirrhosis patient (male aged 35).

b. Wet weight base, mean±ave. dev., 3 results.

c. Xanthate-MIBK extraction method.

bility of the proposed method was estimated from the results obtained by using 10 sample solutions, each 0.1 μg cm⁻³ cadmium(II) in the aqueous phase. The relative standard deviation was calculated to be 2.0%. The stability of the extract was also tested and no appreciable change in the atomic emission intensity was observed over the period of three weeks.

As to the interferences, only platinum(IV) gave a significant positive error, because platinum(IV) was similarly extracted as Zephiramine-iodoplatinate ion-pair into carbon tetrachloride and the emission of the platinum at Pt II 214.423 nm line interfered with the cadmium determination at Cd II 214.438 nm. However, the spectral interference of platinum could be avoided by using Cd I 228.802 nm line, though the detection limit was inferior by a factor of ca. 1.8 to those obtained at 214.438 nm.

Application to the determination of cadmium in human organs

The present method was applied to the analysis of human organs, and the results were compared with the data obtained by GF-AAS. A 3.0-g wet sample was weighed in a quartz beaker and 3 cm³ of nitric acid was

added to it. The mixture was allowed to stand overnight. Then 1 cm³ of perchloric acid was added and it was heated on a hot plate until the white fumes of perchloric acid was vaporized. After cooling to room temperature, it was transferred to a 50-cm³ volumetric flask and diluted with water. For each analysis, 15-cm³ aliquot of the sample solution was used and the determination of cadmium was carried out according to the standard procedure. The analytical results are shown in Table 2, and they are in good agreement with those analyzed by GF-AAS.

The authors wish to express their thanks to Professor Mitsuo Kiboku of Kinki University for his valuable suggestion and to Kure National Hospital for providing the human organ samples.

Preliminary results of this work were presented at the 49th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 4, 1984.

References

1. A. Sugimae, *Anal. Chim. Acta*, **121**, 331 (1980).
2. A. Miyazaki, A. Kimura and Y. Umezaki, *Anal. Chim. Acta*, **127**, 93 (1981).
3. C. W. McLeod, A. Otsuki, K. Okamoto, H. Haraguchi and K. Fuwa, *Analyst* [London], **106**, 419 (1981).
4. R. W. Whiteley, Jr. and R. M. Merrill, *Fresenius' Z. Anal. Chem.*, **311**, 7 (1982).
5. T. Kumamaru, Y. Nitta, H. Matsuo and S. Hara, *Bunseki Kagaku*, **34**, 671 (1985).
6. T. Kumamaru, H. Matsuo and Y. Yamamoto, *Proceedings of The 1984 International Chemical Congress of Pacific Basin Societies*, No. 01105 (1984).
7. IUPAC, *Pure Appl. Chem.*, **45**, 99 (1976).

(Received June 30, 1986)

(Accepted September 10, 1986)