

Preparation, Properties and Ionic Exchange Behaviour of Titanium (IV) Arsenophosphate

Claudio Airoidi*

*Instituto de Química, Universidade Estadual de Campinas
Caixa Postal 6154, 13081-970 Campinas, SP, Brasil*

Severino F. de Oliveira

*Departamento de Química, Universidade Federal da Paraíba
58000 João Pessoa, Pb, Brasil*

Received: July 20, 1992

O arsenofosfato de titânio (IV) foi sintetizado e caracterizado através de análise elemental, infravermelho e termogravimetria. Foram estudadas em água bidestilada as trocas iônicas de cátions divalentes Co, Ni, Cu, Zn, Cd, Hg e Pb. Para estes cátions as constantes de seletividade termodinâmica e distribuição mostraram a alta seletividade do trocador por Pb^{2+} e Hg^{2+} . Experimentos em coluna de separação comprovam que Pb^{2+} e Hg^{2+} são quantitativamente separados da mistura catiônica. Esta matriz de troca tem boa estabilidade térmica e química, além de alto poder de regeneração.

Titanium (IV) arsenophosphate has been synthesized and characterized through elemental analysis, infrared and thermogravimetric techniques. Ionic exchanges involving divalent cations Co, Ni, Cu, Zn, Cd, Hg and Pb in bidistilled water were studied. For these cations the thermodynamic selectivity constants and distribution coefficients showed that this exchanger has a high selectivity for Pb^{2+} and Hg^{2+} . In column cationic separation experiments, a successful separation of Pb^{2+} and Hg^{2+} from the other cations was obtained. This matrix exchanger has good thermal and chemical stability and powder regeneration.

Key Words: *titanium (IV) arsenophosphate; ion-exchange; cations separation.*

Introduction

The interest in synthetic ion-exchange materials has increased considerably in the last three decades¹⁻⁶ mainly due to their stability at high temperatures and radiation levels. They have been found to be more suitable than commercial or natural ion exchangers, having high selectivity for certain ions or groups of them, which can also be utilized in exchange processes as in the treatment of waste residues originating from nuclear industries⁷⁻⁸. Among these exchangers, hydrous oxides were the most studied; however, they do not have good chemical stability⁹. Exchangers synthesized by reacting a cationic solution with an anionic combination such as arsenophosphate^{10,11}, arsenosilicate^{5,6}, stannosilicate¹², vanadophosphate¹³, tungstophosphate¹⁴, and so on, have showed greater chemical and thermal stabilities associated with an improved ionic exchanger and selectivity behaviour. Thus, insoluble double salts containing tetravalent metals are preferred over their single salts counterparts, due to their high selectivity in ion-exchange processes. In this particular, exchangers having titanium (IV)

have been used in cations separations^{5,11}. For example, titanium (IV) arsenosilicate has high selectivity for lead, whose cation can be separated from some synthetic lead alloys⁵.

The aim of this publication is to report the synthesis, characterization and ion-exchange properties of titanium (IV) arsenophosphate, which is obtained in amorphous form. The thermodynamic selectivity constants and the distribution coefficients of divalent cations as Co, Ni, Cu, Zn, Cd, Hg and Pb were determined, and some applications involving this exchanger for ionic separation on columns are also reported.

Experimental

Reagents

Titanium (IV) chloride (Riedel), disodium hydrogenarsenate (Merck) and disodium hydrogenphosphate (Anidrol) were used. All other chemicals were reagent grade.

Apparatus

pH values were measured by a Digimed pHmeter, complexometric titrations were followed by means of an E

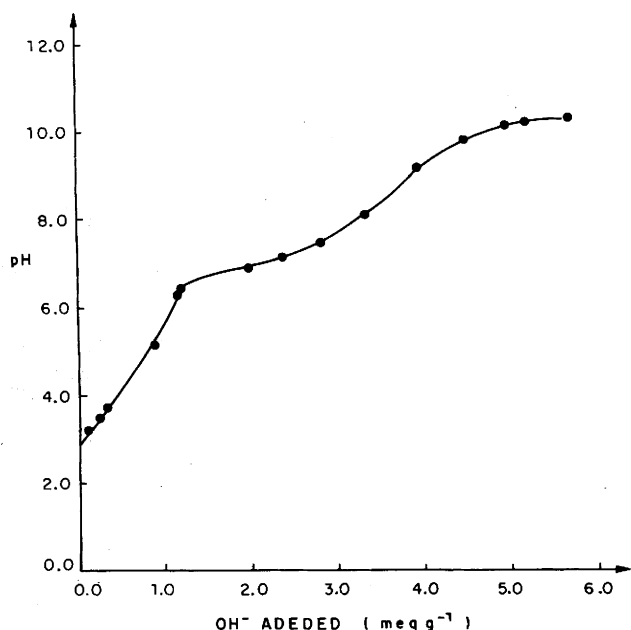


Figure 1. Potentiometric titration of titanium (IV) arsenophosphate with 0.10 mol dm^{-3} of (NaCl + NaOH) solution.

Metrohm Herisau spectrophotometer, loss of mass determinations were performed on a DuPont model 1090B thermogravimetric instrument coupled with a thermobalance, infrared spectra were obtained on a Perkin-Elmer 180 spectrometer, atomic absorption measurements were made on a Zeiss FMD3 spectrometer and a peristaltic pump was used to control the flux of the metallic solution eluant through the column.

Synthesis of titanium (IV) arsenophosphate (TAP): this exchanger was prepared by slowly adding a mixture of $0.050 \text{ mol dm}^{-3}$ disodium hydrogenphosphate solution and disodium hydrogenarsenate solution to a $0.050 \text{ mol dm}^{-3}$ titanium (IV) chloride in 1:1 volume proportion. A gelatinous precipitate appeared immediately and the pH of the mixture was adjusted to 4.0 by using ammonium hydroxide. The solid was allowed to stand for 24 h at room temperature after which it was filtered, washed with bidistilled water and dried at 313 K. This product was broken into water and sieved to obtain the desired mesh size (48 to 60 mesh) and then was converted into acid by immersion in 1.0 mol dm^{-3} nitric acid for 72 h¹¹.

Elemental analysis: 250 mg of TAP was dissolved in 20 cm^3 of hot aqua regia. Titanium was precipitated with ammonium hydroxide, filtered, transferred to a platinum crucible, calcinated at 1170 K to constant mass and weighed as TiO_2 ¹¹. Arsenic in the filtrate was homogeneously precipitated with thioacetamide as As_2S_5 . Finally, the amount of phosphorus was determined in the preceding filtered solution by using the ammonium molybdate method^{15,16}. The molar relation found for this compound was 5:1:1 for titanium, arsenic and phosphorus, respectively.

Exchange kinetics: twelve samples of the exchanger in acid form (~200 mg) were immersed in appropriate vessels containing 50.0 cm^3 of 1.0 mol dm^{-3} of sodium chloride solution. The samples were thermostated at $(298.0 \pm 0.1) \text{ K}$ with continuous mechanical agitation. In one hour intervals, aliquots of the supernatant of one sample was analysed for protons liberated from the matrix by titration with 0.10 mol

Table 1. Thermodynamic selectivity constant (K_T) values for divalente cations.

M	$K_T \times 10^4$
Co	1.0
Ni	1.0
Cu	8.0
Zn	0.5
Cd	0.8
Pb	500
Hg	250

dm^{-3} sodium hydroxide solution. The exchange capacity 0.79 meq g^{-1} after two hours of equilibration increased to 0.98 meq g^{-1} after four hours and remained constant at this value.

Ion-exchange capacity: the ion-exchange capacity was obtained from the titration curve of the exchanger in H^+ form with 0.10 mol dm^{-3} of (NaCl + NaOH) solution. For this operation variable volumes of this solution were equilibrated with 200 mg of the exchanger in 50.0 cm^3 polyethylene flasks. The flasks were continuously agitated as before, in a thermostated bath at $(298.0 \pm 0.1) \text{ K}$. After six hours the pH of these solutions was carefully measured and plotted against the miliequivalens of hydroxide ions added, as it is shown in Figure 1.

Ion-exchange with metallic ions: divalent metallic ionic solutions varying from 1.0×10^{-3} to $4.0 \times 10^{-2} \text{ mol dm}^{-3}$ of Co, Ni, Zn, Cd, Hg and Pb were submitted to ion exchange with TAP in H^+ form, having particle sizes of 48 to 60 mesh, using the same procedure described above. The solutions were agitated for 6 h, which was observed to be sufficient for the system to reach equilibrium in all cases. The thermodynamic selectivity constants for each cation are listed in Table 1.

The thermodynamic selectivity constants (K_T) were calculated based on the equilibrium in Eq. 1:

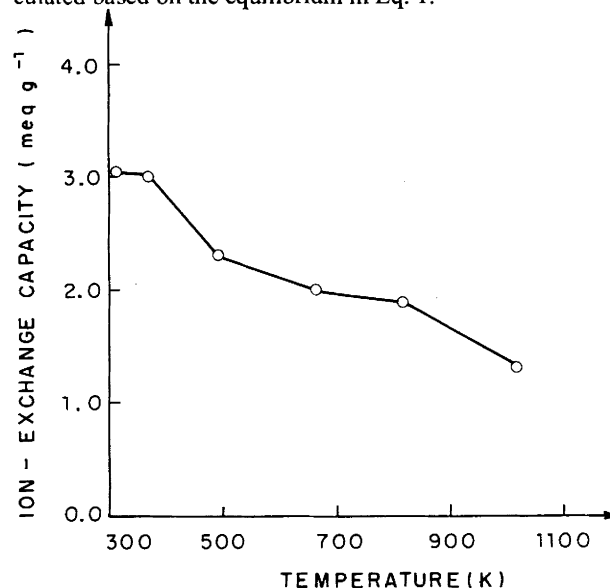
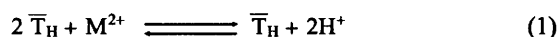


Figure 2. Variation of titanium (IV) arsenophosphate ion-exchange capacity with heating.

Table 2. Distribution coefficients (K_d) for some divalent cations on titanium (IV) arsenophosphate.

M	Taken as	K_d (cm ³ g ⁻¹)
Co	chloride	124
Ni	chloride	61
Cu	chloride	138
Zn	nitrate	217
Cd	nitrate	450
Hg	nitrate	TA ^a
Pb	nitrate	TA

^a Total absorption.

In this process the exchanger in acid form (\bar{T}_H) exchanges protons with cations in solution to give a new matrix (\bar{T}_M), which is expected to be surface saturated in equilibrium. Therefore, the equilibrium constant can be calculated through the established procedure¹⁷.

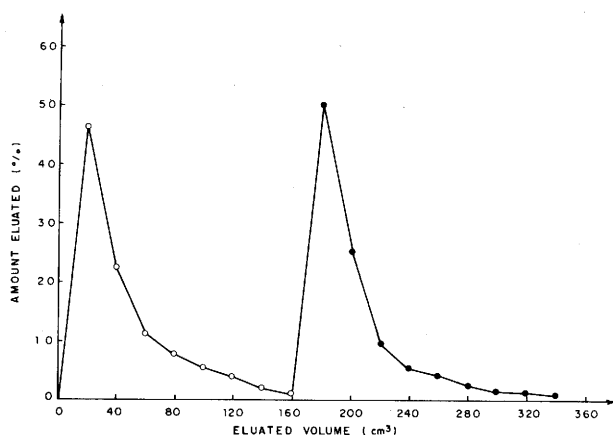
$$K_T = \frac{K_c f_{M^{2+}}}{f_{H^+}^2} \quad (2)$$

$$K = \frac{\bar{X}_{M^{2+}}}{\bar{X}_{H^+}^2} \cdot \frac{m_{H^+}}{m_{M^{2+}}} \cdot \frac{\gamma_{H^+}^2}{\gamma_{M^{2+}}} \quad (3)$$

K_c is the selectivity coefficient, $f_{M^{2+}}$ and f_{H^+} are activity coefficients of the cation and proton in the exchanger $\bar{X}_{M^{2+}}$ and \bar{X}_{H^+} are equivalent molar fractions of cation in the solid phase, $m_{M^{2+}}$ and m_{H^+} are metal and proton molalities in solution, γ_{H^+} and $\gamma_{M^{2+}}$ are activities of these ions in solution. Neglecting any transference of solvent:

$$\log K_T = \int_0^1 \log K_c d\bar{X}_{M^{2+}} \quad (4)$$

Since the evaluation of the integral over the zero to 1 range is difficult, K_T was determined from the $\log K_c$ versus $\bar{X}_{M^{2+}}$ plot, where K_T is obtained in the medium point¹⁸, i. e., $\bar{X}_{M^{2+}} = 0.5$.

**Figure 3.** Divalent cationic separation of Cu (II) (o) eluted with $0.01 \text{ mol dm}^{-3} \text{ HNO}_3$ and Pb (II) eluted with $1.0 \text{ mol dm}^{-3} \text{ HNO}_3$ on titanium (IV) arsenophosphate column.

Distribution coefficients: distribution coefficients (K_d) for the metal ions Co, Ni, Cu, Zn, Cd, Hg and Pb were determined by batch process. In this case, 50.0 cm^3 of aqueous solution of $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ of metallic ion was equilibrated with $\sim 300 \text{ mg}$ of the exchanger during 6 h in a thermostated bath as described above. Aliquots of the supernatant were analysed by atomic absorption spectrometry and K_d values were calculated using the following equation:

$$K_d = \frac{I - F}{F} \frac{V}{A}$$

where I and F are the initial and final concentration, respectively, V is volume of the metal ion solution and A is the mass of the exchanger taken⁶. The K_d values of the metal ions are summarised in Table 2.

Thermal stability: the thermal stability was studied by heating 500 mg samples of TAP at various temperatures during one hour. After cooling to room temperature the ion-exchange capacity was determined in aqueous solution with lead nitrate, using the preceding procedures. The results are shown in Figure 2.

Column operation: for separation studies about 2.0 g of the exchanger in H^+ form was used in a glass column of 10 cm length and 0.5 cm internal diameter. This column was coupled to a peristaltic pump to maintain a constant flow-rate of $1.0 \text{ cm}^3 \text{ min}^{-1}$. A solution containing a mixture of cations not superior to 5 % of the ion-exchange capacity of the exchanger was passed through the column. The cation mixture was composed of 10.0 cm^3 of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ for each cation used. After percolating the collected solution was added to the column, washed with bidistilled water and analysed. However no cation was detected. The eluate for Co, Ni, Cu, Zn and Cd was $0.01 \text{ mol dm}^{-3} \text{ HNO}_3$ solution while Pb and Hg were eluted with $1.0 \text{ mol dm}^{-3} \text{ HNO}_3$ solution. The amount of recovered cation was analysed by atomic absorption spectrometry. Table 3 lists cation mixture separations. Table 4 summarizes some binary separations involving Pb and other M (II) cations. Figure 3 illustrates the lead-copper separation.

Table 3. Divalent cations separations from mixtures on titanium (IV) arsenophosphate column.

M	Amount loaded (μg)	Amount recovered (μg)	Error (%)	Eluant	Volume of eluant (cm^3)
Co	568.7	563.9	-0.85	A	240
Ni	554.5	548.3	-1.13	A	240
Cu	653.7	648.9	-0.73	A	300
Zn	653.7	661.7	+1.23	A	260
Cd	1124.0	1137.5	+1.20	A	320
Pb	2070.2	2076.0	+0.28	B	200
Hg	787.0	826.4	+5.00	B	170

A = $0.01 \text{ mol dm}^{-3} \text{ HNO}_3$, B = $1.0 \text{ mol dm}^{-3} \text{ HNO}_3$.

Exchanger regeneration: a column containing TAP in acid form was saturated by Cu (II) aqueous solution and the excess of cations was analysed. Then, the column was eluated with 2.0 mol dm⁻³ HNO₃ solution and the cation was also analysed. After the excess of the acid in the exchanger was eliminated by washing with bidistilled water, the exchanger was submitted to the same procedure with a new cooper (II) solution and the process was successively repeated.

Results and Discussion

The titanium (IV) arsenophosphate was obtained as a hard mass which was amorphous in nature, but could easily be sieved to desirable size. It is stable in acids and sodium chloride solution, however, basic medium emphasized the hydrolysis. This exchanger synthesized at pH 4 had a phosphorus and arsenic molar proportion in relation to titanium, quite different from that in sample prepared in the pH 0 to 1 range(11), which ratio found was 1:1:3. The higher titanium content in the first exchanger can be attributed to cation hydrolysis at higher pH.

The ion exchange capacity of 2.80 meq g⁻¹, determined through titration curve as shown in Figure 1, is in agreement with 3.26 meq g⁻¹ value calculated from the TAP chemical composition. The potentiometric titration curve showed two inflections at pH 6.3 and 7.5, respectively, indicating a bifunctional behaviour in relation to proton exchange.

The variation of the ion-exchange capacity determined through column procedure indicated that the initial exchange capacity of 1.09 meq g⁻¹ for Cu (II), decreases near 10% after the first regeneration, but thus same value was maintained constant up to the fourth regeneration.

Another important property of this exchanger was followed through thermal stability. In that case, after heating, the exchanger was successively heated to a new Pb (II) solution. The exchanger dried at 313 K showed an ion-exchange capacity of 3.06 meq g⁻¹. On heating at 373 K this capacity decreased only 2%. However, a pronounced decrease of 25% occurred near 500 K due to the condensation of monohydrogen-arsenate¹⁹ and monohydrogenphosphate²⁰ groups, which started above 400 and 470 K, respectively. This condensation continued to affect this property at higher temperatures, but, this capacity was 43% of the initial value at 1020 K, as shown in Figure 2. These data confirmed a high thermal stability of this kind of exchanger. The small decrease of 2% in ion-exchange capacity at 373 K, is a great advantage in comparison with an organic exchanger, which temperature could be enough to damage it²¹.

The infrared spectrum of the exchanger showed the presence of a broad band near 3300 cm⁻¹ due to water of crystallization and another sharp peak at 1630 cm⁻¹, which is also consistent with the existence of OH groups on surface. Other peaks near 1050 and 850 cm⁻¹ indicated the presence of phosphate¹¹ and arsenate⁶ anions bonded to the structure of the exchanger, as observed for similar tin and chromium compounds²².

The exchanger chemical composition was established by elemental analysis and from the thermogravimetric curve, which can indicate the amount of water held in the solid, by expression²³:

$$18n = \frac{X(M + 18n)}{100}$$

Table 4. Some binary mixtures achieved involving M (II) (eluated with 0.01 mol dm⁻³ HNO₃) and Pb (II) (eluated with a 1.0 mol dm⁻³ HNO₃) on titanium (IV) arsenophosphate column.

Sample	Mixture	Amount loaded (μg)	Amount recovered (μg)	M (II) (% error)	Volume of eluant used (cm ³)
1	Co	589.3	599.3	Co (+1.7)	200
	Pb	2070.2	2101.9	Pb (+1.5)	180
2	Ni	459.5	459.1	Ni (-0.08)	160
	Pb	2070.2	2082.3	Pb (+0.58)	180
3	Cu	635.4	640.8	Cu (+0.85)	160
	Pb	2070.2	2098.8	Pb (+1.38)	180
4	Zn	653.7	659.6	Zn (+0.9)	160
	Pb	2070.2	2148.6	Pb (+3.8)	160
5	Cd	1124.0	1125.9	Cd (+0.17)	140
	Pb	2070.2	2082.2	Pb (+0.58)	180

where X is the percent mass loss, n is the number of external moles of water and M is the molar mass of the compound minus external water molecules.

The elemental analysis results are consistent to a general formulae Ti(HPO₄)_{0.2}(HAsO₄)_{0.2}.n H₂O, which M value is 95.1 g mol⁻¹. From the thermogravimetric curve residue up to 790 K, a total mass loss of 22.5% can be deduced. A complete condensation of both monohydrogenarsenate and monohydrogenphosphate groups occurred at this temperature. In addition, As₂O₅ decomposes to As₂O₃, which is proposed to occur up to 520 K⁶. In assuming that the external water molecules are completed released up to 470 K, then a percentage of mass loss is 18% which permitted from the expression to deduce the final formulae Ti(HPO₄)_{0.2}(HAsO₄)_{0.2}.1.16 H₂O.

The ion-exchange experiments involving the studies with divalent cations demonstrated that the exchanger has a high affinity for Hg and Pb cations. This fact has been confirmed by their high thermodynamic selectivity constants (Table 1) and by the total adsorption of these cations by the exchanger in the distribution coefficient determinations (Table 2). The order of thermodynamic selectivity constants Zn < Cd < Ni ≈ Co < Cu < Hg < Pb, is in agreement with the maximum of their isotherms. However, the selectivities reflected by the distribution coefficients, Ni < Co < Cu < Zn < Cd < Hg ≈ Pb, are correlated with the respective exchange isotherm in the lower of concentration limit.

Affinity of the exchanger for Hg and Pb cations is also evidenced by column experiments. When a column is loaded with a cations mixture, Co, Ni, Cu, Zn and Cd are easily and quantitatively separated from both Hg and Pb as observed in Table 3. While the lighter cations are eluated from the exchanger on a column by 0.01 mol dm⁻³ HNO₃ solution, Hg and Pb are only eluated by 1.0 mol dm⁻³ HNO₃ solution. These two distinct sets of cations showed a variation of less than 3% for successive determinations. The recovery ranged from 98 to 100%. On the other hand, components of binary mixtures can be quantitatively separated by using different eluants (Table 4) and this behaviour is well illustrated for lead-coper separation as illustrated in Figure 3.

Conclusion

The results obtained for titanium (IV) arsenophosphate prepared at pH 4.0 show that a quantitative and efficient separation of Hg and Pb cations from a series of binary mixtures or both cations from the studied mixture of divalent cations is feasible.

Acknowledgments

The authors are indebted to CNPq and S.F.O. grateful acknowledges CAPES-PICD for a fellowship.

References

1. C. B. Ampheltt, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964.
2. V. Vesely and V. Pekarek, *Talanta* **19**, 219 (1972).
3. V. Pekarek and V. Vesely, *Talanta* **19**, 1254 (1972).
4. T. Ito and T. Kenjo, *Bull. Chem. Soc. Jpn.* **41**, 614 (1968).
5. K.G. Varshney, K. Agrawak, V. Saxena and A. R. Khan, *Colloids Surfaces* **29**, 175 (1988).
6. K.G. Varshney, A.A. Khan and M.S. Siddigui, *Colloids Surfaces* **36**, 405 (1989).
7. J. S. Gill and S. N. Tandon, *Radiochem. Radioanal. Lett.* **14**, 379 (1973).
8. L. Zsinka, L. Szirtes, J. Mink and A. Kalman, *J. Inorg. Nucl. Chem.* **36**, 1147 (1974).
9. N. J. Singh and S. N. Tandon, *J. Radioanal. Chem.* **49**, 195 (1979).
10. K. G. Varshney, S. Naheed, A. A. Khan, S. N. Tandon and C. B. Gupta, *Chromatographia* **12**, 473 (1979).
11. K. G. Varshney and A. Premadas, *Sep. Sci. Technol.* **16**, 793 (1981).
12. A. Dyer and J. J. Jafar, *J. Chem. Soc. Dalton Trans.* **2639** (1991).
13. M. Qureshi and R. C. Kaushik, *Anal. Chem.* **49**, 165 (1977).
14. A. P. Gupta, M. Qureshi, V. Sharma, R. C. Kaushik and H. O. Gupta, *J. Indian Chem. Soc.* **63**, 206 (1986).
15. I. M. Kolthoff, E. B. Sandell, E. I. Neehan and S. Bruckenstein, *Quantitative Chemical Analysis*, 4th ed., MacMillan Ltd., London, 1971.
16. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Vol. 7 and 10, Interscience, New York, 1961.
17. G. L. Gaines and H. C. Thomas, *J. Chem. Phys.* **21**, 714 (1953).
18. J. A. Marinsky, *Ion-Exchange: A Series Advances*, Vol. 2. Marcel-Dekker, Inc., New York, 1966.
19. M. Qureshi and S. A. Nabi, *J. Inorg. Nucl. Chem.* **32**, 2059 (1970).
20. G. Alberti, A. Conte and E. Torraca, *J. Inorg. Nucl. Chem.* **28**, 225 (1966).
21. A. Clearfield, *Chem. Rev.* **88**, 125 (1988).
22. K. G. Varshney and A. A. Khan, *J. Inorg. Nucl. Chem.* **41**, 241 (1979).
23. G. Alberti, E. Torraca and A. Conte, *J. Inorg. Nucl. Chem.* **28**, 607 (1966).