Bull. Environ. Contam. Toxicol. (1986) 36:924-928

Bulletin of Environmental Contamination and Toxicology

Separation and Preconcentration of Heavy Metals in Environmental Samples by Nicotinium Molybdophosphate Resin

J. T. Nyangababo and J. W. Hamya

Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda

Industrial growth, increased agricultural machinery municipal inceneration and motor traffic have brought about problems due to the presence in air and soil of pollutants at lower levels than ppb. Among these substances, heavy metals (e.g. cadmium and lead) must be watched with particular attention because of their very low limits of tolerability. Pollutant analysis has always been plagued by several unique problems normally encountered in conventional analysis, most important of these are the matrix effects. This makes a direct determination inapplicable to the analysis of environmental samples. To this end, separation and preconcentration have been accomplished through the use of ion-exchange resin (Riley and Skirrow 1975; Riley and Taylor 1968). Resins containing molybdofunctionality, such as Zirconium molybdophosphate have been synthesized and used as cation exchange resin (Singh and Tandon 1980; Shkarvaskii and Babko 1966). A similar complex resin was prepared (Malik et al 1981) and found it to possess promising exchange properties and specific selectivity for certain cations.

Heteropoly molybdophosphates have been extensively prepared for coordination studies (Shkarvaskii 1963) and as a class of special coordination compounds, they are capable of scavanging on heavy metals selectively from high concentration of alkali and alkaline earth elements. For this reason they are of interest in trace analytical work related to natural environment where some of these elements exist in low concentrations. The purpose of this study was to measure absorption properties of nicotinium molybdophosphate and to test extraction and recovery procedures for different metal pollutants (e.g. Cd, Cr, Cu and Pb). Procedures have been tested for single metal pollutants and for complex synthetic mixtures of them. Furthermore the nicotinium molybdophosphate resin technique is extended to the analysis of environmental samples collected in different areas of Kampala City.

MATERIALS AND METHODS

The following procedure was adopted for the preparation of nicotinium molybdophosphate. Ammonium salt of 12 - molybdophosphoric acid (12-MPA) (36.12g) dissolved in 400 ml of water was acidified to pH 2.0 with suphuric acid. The solution was then added to 30% nicotinium hydrogen suphate solution with stirring. The nicotinium molybdophosphate precipitated was filtered, washed with distilled water and dried with a hot current of air. The column was then loaded with a slurry of nicotinium molybdophosphate and then washed with acid solution of pH 2.5. Synthetic metal solutions (50 ml) of known concentration were prepared by spiking deionized distilled water with respective metals. The individual metal solutions were adjusted to pH 2.5 and passed through the resin under the influence of gravity at a flow rate of 0.5 ml per minute. To selectively elute sodium, potassium, calcium and magnesium, 25 ml of 5 M sulphuric acid was passed through the column in 5 ml aliquots. At the completion of 5 M sulphuric acid, 10 ml of distilled water were passed through to remove residual sulphuric acid. Following this, the metals sequestered by the resin were removed by destructive elution using 4 M ammonia solution. The metal ions recovered by this procedure were analysed by atomic absorption spectrophotometer (AAS). Synthetic metal mixtures were analysed by passing them through the same procedure.

The procedure adopted was extended to the analysis of heavy metals (Cd,Cr,Mn,Pb,Zn,Co,Fe and Cu) as these among others are associated with vehicular traffic, urban wastes, refuse inceneration, industrial process and with combustion of fossil fuels which could both be sigficant sources of pollution within Kampala municipality. These metals were monitored by the analysis of samples of soils collected in various sites of Kampala, using nicotinium molybdophosphate-AAS procedure.

RESULTS AND DISCUSSION

Initial metal recovery studies were performed using cadmium as a test element at concentrations ranging between 100 and 1000 ppb. To effect a separation of cadmium from sample matrix by nicotinium molybdophosphate resin, it is necessary to choose eluting agent that should not produce any adverse effects on the analytes in the AAS analysis. For this purpose ammonia solution was used as eluting agent. Of the metals tested, cobalt, chromium, copper, nickel, iron, zinc, and lead were found to form the strongest complexes with the nicotinium molybdophosphate resin and were removed from solution with greatest efficiency. No sample pretreatment was necessary to achieve quantitative recovery of these elements.

Distribution coefficients (K_d) for various cations are given in Table 1. The copper ion is completely absorbed and the compound also exhibits high affinity for Cd(II), Cr(III), Ni(II), Fe(III), Zn(II), Pb(II) and Mn(II). For the other cations K_d values are very low; the uptake of Na, K, Mg, Cs and Ca ions is negligible, and shows the following selectivity sequence of ions, Cs,Ca, Na, and Mg. The resin is fairly stable in aqueous solution of electrolytes and mineral acids. However, in strong alkali solution the exchanger loses its exchange capacity. On the basis of distribution studies, representative operations of analytical interest have been achieved.

Table 1. Distribution coeficients for different metal ions on nicotinium molybdophosphate resin (R_3 MPC)

Metal ion	Kd-value
Na (I)	3.4
K (I)	4.2
Mg (II)	2.3
Cs (I)	8.0
Ca (II)	7.9
Cd (II)	1520
Cr (III)	1610
Cu (II)	2478
Ni (II)	2209
Fe (III)	1904
Zn (II)	1312
Pb (II)	1820
Mn (II)	2210
Kd determined at pH	2.5

The details of recoveries are given in Table 2. For Cd(II), Cr(III), Cu(II), Fe(III), Pb(II), Co(II), and Mn(II) only 97-103% recovery is possible. A large number of separations of these heavy metal ions from other cations have been performed on columns of this ion exchanger. Heavy-metal scavanging, by the nicotinium molybdophosphate, offers the immediate prospect of a new analytical tool for monitoring levels of these metals in air, water and soil. As one can see, recovery is practically independent of the initial concentration of the heavy metal ion; and it is possible to analyse these metals in a complex mixture. Finally the resin was tested for separating and determing of heavy metals in environmental samples collected from various parts of Kampala City. The usefulness of the nicotinium molybdophosphate is realised in the determination of trace metals in complex matrices. Of particular interest were soil samples where high concentrations of alkali and alkaline earth elements often cause interference. Also, biological materials present problems due to the high level of organic material in the matrix. Samples of soil were analyzed for cadmium, cobalt, chromium, copper, nickel, iron, zinc, lead and manganese using the same recovery procedure developed for the standard recovery experiments. The results of considerable variation is noted with respect to elemental content. The measured levels in these materials serve as an index of the many ecological phenomenon can be formulated.

Table 2. Recovery of elements added to synthetic mixtures.

Element	Amount taken (ug/ml)	Amount found (ug/ml)	Recovery (%)
Cd	10.0	10.2	102
	5.0	4.98	99.6
Cr	10.0	99.0	99.0
	5.0	5.10	102
Mn	10.0	10.0	100
	5.0	4.99	99.8
Ni	10.0	9.78	97.8
	5.0	5.0	100
Pb	10.0	10.3	103
	5.0	5.10	102
Zn	10.0	10.0	100
	5.0	5.0	100
Co	10.0	9.78	97.8
	5.0	4.90	98.0
Fe	10.0	10.0	100
	5.0	5.0	100
Cu	10.0	10.0	100
	5.0	5.00	100

Table 3. Heavy metal content (ug g^{-1}) of soil collected from different sites in Kampala.

	Element								
Site	Cd	Co	Cr	Ni	Pb	Zn	Mn	Fe	Cu
Bat Valley	0.453	2.64	61.4	38.6	117	88.8	1250	38500	136
Wandegeya	1.330	3.82	74.5	42.9	274	93.3	1370	46600	139
Nsambya	0.264	3.05	52.8	21.5	214	74.7	872	47400	104
Katwe	2.430	3.10	73.6	52.2	380	92.6	1480	57400	237
Kasubi	0.760	1.20	61.2	44.8	14.3	91.3	1020	36200	94
Nakivubo	1.470	1.56	58.9	135	378	92.8	1160	6330	194
Nakulabye	0.870	0.88	70.2	49.4	55	87.6	1080	49800	153
Industrial Area	2.970	1.98	88.7	169	343	97.8	1330	56200	158
Golf Course	0.246	0.87	44.3	126	80	80.1	1230	34400	92.6
Coffee Area	2.140	1.23	64.1	39.8	179	87.6	1010	44100	80.8
Katalemwa	1.470	0.86	41.6	33.4	8.41	85.7	957	31600	54.7

Acknowledgements. This work was initiated under Uganda National Research Council funds. Special thanks go to Rugyendera for his efforts in collecting and treating soil samples.

REFERENCES

Malik W.U., Srivastav S.K. and Bansal A., (1982) Application of zirconium molybdophosphate gel for the selective separation of thallium (1) ions. Analyst 108:340

Shkarvaskii Y.F., (1963) cerimolybdic complex: Two types of molybdenum heteropoly complexes Russ. J. Inorg. Chem. 1399

Shkarvaskii Y.F., and Babko A.K. (1966) Determination of niobiun and titanium as ternary complexes with molybdophosphoric acid Zh. Neorg. Khim 11:792

Singh N.J., and Tandon S.N., (1980) Preparation and utilization of zirconium molybdophosphate and titanium molybdophosphate as ion-exchanger Indian J. Chem. 19A:502

Riley J.P., and Taylor (1968) Chelating resins for the concentration of trace elements from sea water and their analytical use in conjuction with atomic absorption spectrophotometry Anal. Chimica Acta 40:479

Riley J.P., and Skirrow G., (1975) Chemical Oceanography, Vol. 111 Academic Press, New York.

Received June 18, 1985; accepted September, 1985