Separation of Cadmium Salicylate by Solvent Extraction Using Tris(2-ethylhexyl) Phosphate

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Tris(2-ethylhexyl) phosphate (T2EHP) is used for the extraction of cadmium salicylate. The experimental conditions are established and the probable extractable species is ascertained by log D–log C plots. Microgram amounts of cadmium are determined in the Tris(2-ethylhexyl) phosphate phase with 1-(2-pyridylazo)-2-naphthol as the chromogenic agent. The proposed method is used for the separation of cadmium(II) from zinc(II), mercury(II), lead(II), bismuth(III), antimony(III), and thallium(III) and used for the estimation of cadmium in industrial waste water, kidney stone, cigarettes, and alloy samples.

The presence of cadmium in the biosphere and the ecological system is causing a great concern as it causes a number of diseases including emphysema and bronchitis. Due to chemical similarity of cadmium(II), mercury(II), and zinc(II), the toxic cadmium(II) often compete with the more essential zinc in various biological and enzymatic reactions. For these reasons new and better analytical methods for separation of cadmium from zinc and mercury and its determination in biological and environmental samples are needed. Liquid–liquid extraction is one of the most widely used techniques owing to its simplicity and applicability to both trace and macro amounts of metal ions. Literature survey reveals that various extractants such as tributyl phosphate,[1—3] trioctylphosphine oxide,[4,5] bis(2-ethylhexyl) hydrogen phosphate,[6] (2-carboxyethyl)diphenyl phosphine oxide,[7] trioctylarsine oxide,[8] mesityl oxide,[9] and dioctylarsinic acid[10] are available for extraction of cadmium. High molecular weight amines such as Aliquat 336,[11] Alamine 336,[12] LA-2,[13] tribenzylamine,[14] and trioctylamine[15] have also been used for cadmium extraction. The existing methods however suffer from drawbacks such as long extraction period,[1,4,9,13,14] use of salting out agents,[11] pre-equilibration of the organic phase[12,15] and interference from large number of ions.[5,6] Moreover most of the methods report extraction of cadmium from inorganic acid media and practically no work has been reported on the extraction from salicylate media.

In this paper a simple, rapid, and sensitive method has been developed for separation and determination of cadmium from salicylate solution using tris(2-ethylhexyl)phosphate as an extractant. The method permits separation of cadmium(II) from zinc(II), mercury(II), lead(II), bismuth(III), antimony(III), and thallium(III). The method has been applied for separation and determination of cadmium in industrial waste water, kidney stone, cigarettes, and wood's alloy.

Experimental

Reagents and Chemicals. A stock solution of cadmium was prepared by dissolving 2.85 g of cadmium sulfate in 250 cm^3 of doubly distilled water containing 2 cm^3 of sulfuric acid. The solution was standardized by known method[16] and diluted further to obtain working solutions.

Buffer solution (pH 9.2) was prepared by dissolving 4.8 g of borax (0.05 mol dm^{-3}) in 250 cm^3 of doubly distilled water.

A 0.1% methanolic solution of 1-(2-pyridylazo)-2-naphthol was used for spectrophotometric determination of cadmium.

Tris(2-ethylhexyl) phosphate [T2EHP] (Fluka) dissolved in toluene was used for extraction.

All other chemicals used were of analytical reagent grade.

Apparatus. A shimadzu UV-vis 160A spectrophotometer and a Control Dynamics digital pH meter with combined glass electrode were used for absorbance and pH measurements.

Recommended Extraction Procedure for Determination of Cadmium in Industrial Effluent, Kidney Stone, Cigarettes, and Wood's Alloy. Untreated industrial effluent collected from Maharashtra Pollution Control Board, New Bombay, India, a sample of kidney stone, two popular brands of Indian Cigarettes a) Wills and b) Golden Flair Delux and Wood's alloy were brought into solution as described earlier[17,18] and used for determination of cadmium (Table 1).

Suitable quantity of cadmium (1—10 μg or 1—5 mg) was taken in an aliquot of 25 cm^3 containing 2.5×10^{-1} mol dm^{-3} sodium salicylate, adjusted to pH 8.0 with dilute hydrochloric acid and sodium hydroxide solutions. The solution was equilibrated in a separatory funnel for 90 s with 2×5 cm^3 of 50% T2EHP (dissolved in toluene) [For

Table 1. Determination of Cadmium in Biological Environmental and Alloy Samples

Sample	Cd obtained[a] by the proposed method	Cd obtained[a] by AAS	Standard deviation	Coefficient of variation %
1. Industrial waste water	1.02 ppm	1.0 ppm	0.010	0.98
2. Kidney stone	2.07 ppm	2.1 ppm	0.030	1.45
3. Cigarette				
Sample A	2.96 μg	3.0 μg	0.053	1.79
Sample B	2.73 μg	2.8 μg	0.043	1.59
4. Woods alloy (Ind alloy 158) Bi 50% Pb 26.7% Sn 13.3% Cd 10.0%	9.96%	9.98%	0.102	1.03

[a] Mean of triplicate analyses.

microgram amounts of cadmium a single extraction with 5 cm^3 of 50% T2EHP is sufficient]. After phase separation cadmium is stripped with 2×10 cm^3 water and determined complexometrically.[16] Microgram amounts of cadmium is determined in T2EHP phase as follows: Add 5 cm^3 of borax buffer (pH 9.2), 1 cm^3 of 0.1% 1-(2-pyridylazo)-2-naphthol and shake for 1 min. The aqueous layer is discarded and absorbance of the orange coloured organic Cd-PAN layer is determined at 555 nm against reagent blank prepared analogously.

Results and Discussion

Variation in salicylate concentration (1×10^{-2}—6×10^{-1} $mol\,dm^{-3}$), pH (4.5—10.5) and tris(2-ethylhexyl) phosphate concentration (10—60%) (using toluene as diluent) showed that quantitative extraction of cadmium occurs from 2.5×10^{-1} $mol\,dm^{-3}$ sodium salicylate at 6.75—9.0 pH and 50% tris(2-ethylhexyl) phosphate (Figs. 1 and 2).

Variation in shaking period showed that the extraction of cadmium is quantitative in 90 s. Prolonged shaking however showed no adverse effect.

Of the various diluents such as toluene, xylene, benzene, carbon tetrachloride, and chloroform tried, toluene or xylene gave quantitative extraction. Extraction with other diluents such as benzene, carbon tetrachloride, and chloroform was 93.7, 84.3, and 80.6%, respectively. For further studies toluene was preferred as it gave better phase separation.

The stoichiometry of the extracted species was ascertained by $\log D$–$\log C$ plots. The plot of log of distribution ratio versus the log of salicylate concentration (at pH 8.0 and 50% T2EHP concentration) and versus log of T2EHP concentration (at pH 8.0 and 2.5×10^{-1} $mol\,dm^{-3}$ salicylate concentration) (Figs. 3 and 4) gave a slope of 2.2 and 1.94 with respect to the extractant and salicylate. The extractable species is probably Cd-

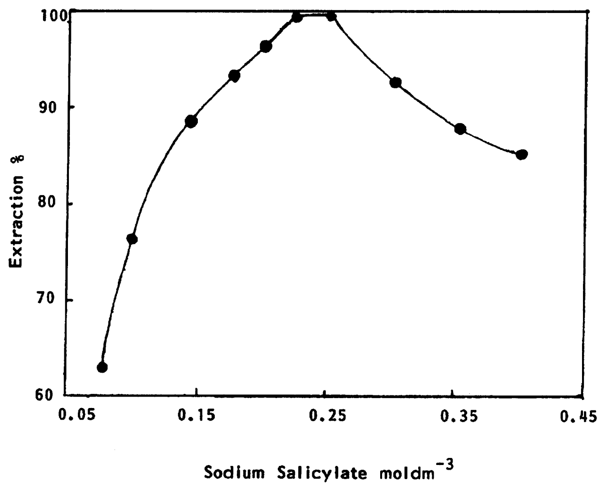

Fig. 1. Extraction of Cd(II) as a function of the salicylate concentration (at pH 8 and 50% T2EHP)

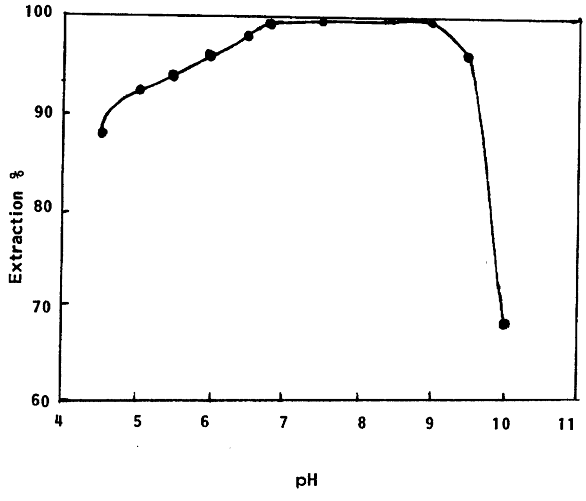

Fig. 2. Extraction of Cd(II) as a function of pH (at 2.5×10^{-1} $mol\,dm^{-3}$ salicylate and 50% T2EHP)

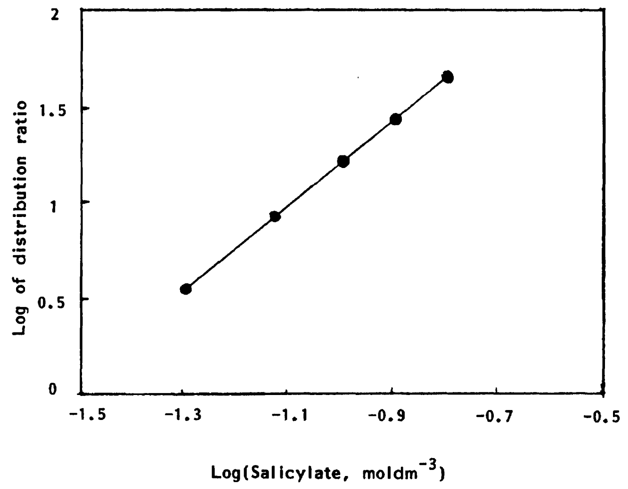

Fig. 3. log–log plot of the distribution ratio of cadmium(II) as a function of salicylate concentration.

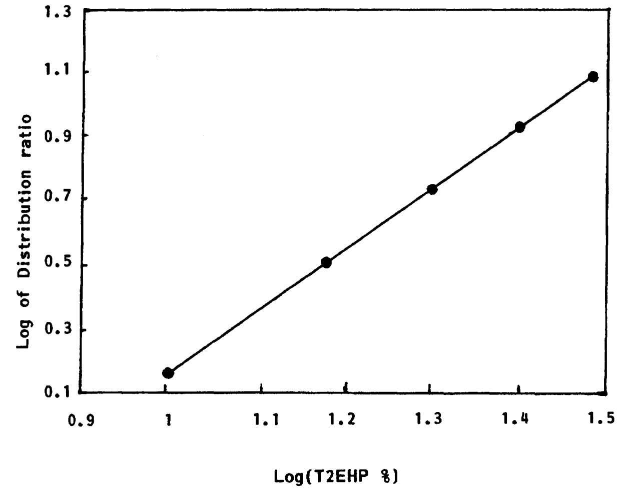

Fig. 4. log–log plot of the distribution ratio of Cadmium(II) as a function of T2EHP concentration.

$(HSal)_2 \cdot 2T2EHP$. The probable extraction mechanism is as follows:

$$Cd(HSal)_2 \cdot 2H_2O + 2T2EHP \rightleftharpoons Cd(HSal)_2 \cdot 2T2EHP + 2H_2O.$$

The above mechanism shows that solvation of cadmium salicylate with T2EHP promotes extraction. T2EHP with phosphoryl group is more basic and renders cadmium salicylate hydrophobic.

The determination of cadmium in T2EHP phase with 1-(2-pyridlazo)-2-naphthol (PAN) as chromogenic agent at 555 nm conforms to Beer's law in the concentration range 0.2—2.0 $\mu g\,cm^{-3}$; the molar absorptivity is 6.5×10^4 $dm^3\,mol^{-1}\,cm^{-1}$. The standard deviation and coefficient of variation (average of six determinations) for solution containing 0.6 $\mu g\,cm^{-3}$ of cadmium is 5.1×10^{-3} and 0.85% respectively.

An interference study showed that 80 μg each of Fe(III), Te(IV), Se(IV), Cr(VI), Cl^-, Br^-, I^-, Pd(II), Tl(III), and thiourea; 60 μg each of Bi(III), Sb(III), Al(III), Sn(II), and sulphate; 40 μg each of Ag(I), Ba(II), Ca(II), Ti(IV), V(V), ascorbate and thiocyanate; 30 μg each of Pb(II) and citrate; 15 μg each of Zr(IV) and Hf(IV) did not interfere with the extraction and determination of 3 μg of Cd(II) by PAN as per the recommended procedure. 10 μg of EDTA and 3 μg each of Mn(II) and Ni(II) interfered with the estimation of cadmium.

Conclusions

Extraction of cadmium with T2EHP is fast and occurs in a single step at microgram level. The method is free from pre-equilibration, multiple extraction, and interference of ions. It permits extraction and subsequent determination of cadmium in organic phase. Environmental, biological and alloy samples can be analyzed for determination of cadmium. The precision and reproducibility of the method is excellent.

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