

Extraction-Spectrophotometric Determination OF Cadmium(II) by High Molecular Weight Amine. Application to Industrial Effluents

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Summary: An investigation of the complex formation between Cadmium(II) and Potassium iodide in Sulphuric acid solution has been carried out and its extractability by high molecular weight tertiary amine (HMWA) in organic solvent was examined. The yellow colored complex of Cd(II)-I₂ is quantitatively extractable into organic phase containing tribenzyle amine. On the basis of this extractability a method has been developed for the spectrophotometer determination of Cadmium in the presence of many other interfering radicals. The extractability of the Potassium iodide complex by HMWA suggests that the colored species is anionic.

Introduction

Liquid-liquid extraction is one of the most widely used techniques of separation and preconcentration. There are a correspondingly large number of applications of radiotracers to study the extraction behavior of elements and to obtain distribution coefficients and kinetic data as a function of experimental parameters involved in the extraction. The procedure is simple and rapid and can be used for various problems of trace analysis to separate selectively the matrix, the trace elements of interest, or a group of trace elements. Metals are usually extracted from aqueous solutions in the form of chelate complexes into an organic solvent [1-2]

Solvent extraction of metals utilizing chelating agents offers striking contrast to the conditions employed in many ion association systems.

In general, the distribution co-efficient of the extraction reagent itself is rather large. Metal chelate extraction is highly dependent on the P_H of the aqueous phase and the concentration of the reagent in the organic phase.

Solvent extraction is employed to separate the solute of interest from substances that interfere in the ultimate quantitative determination of the material.

High molecular weight amines are particularly the high-branched alkyl amines extensively used for the separation of several pairs of metals as anions and for the extraction metals such as uranium and Plutonium [3-5]. Iodide method is cheapest method of extraction and separation of

metals as an iodide complex from Sulphuric acid into an organic phase containing amine. The HMWA used as liquid anion exchanger and as extractant for anionic complexes [6-8].

Looking at the pattern of previous research, the present work was undertaken with specific view to investigate sensitive and rapid analytical procedure for the estimation of trace amount of Cadmium, which had not previously employed, when the survey of literature revealed.

The procedure is based on the extraction of Cadmium as its iodide complex into tribenzylamine.

As the colored species from series of complexes, efforts were made to establish the parameters that are favorable towards formation of an extractable stable species.

Investigation leads to the quantitative extraction of the colored species under optimal conditions for the determination of cadmium by spectrophotometer.

The present investigation was undertaken in continuation of the earlier studies on the extraction and spectrophotometer determination of traces of transition metals [5-12].

Results and Discussion

The anionic complex of Cadmium formed with iodide in the presence of Sulphuric acid was studied. Various parameters which effect the extraction of Cd(II)I₂ such as the change in organic

diluents, type of amines, acid concentration, time etc., have been studied. The complex of Cadmium(II)I₂ is readily extracted into tribenzyleamine in Chloroform. Advantage of this method for extraction of Cd(II) by liquid-liquid extraction system is that it is rapid and sharp and utilize readily available equipment. Aliphatic amines of comparable efficiency may be commercially available.

TBA extracted 99.94% Cadmium and negligible amount left in aqueous phase as colored complex.

The TBA in Chloroform acts as liquid anion exchanger and it is assumed that the colored complex is anionic in nature and that the liquid anion exchange occurs between the charge complex and the high molecular weight amine.

Analytical Procedure

Formation of Cd(II)I₂ Complex and its Extraction by TBA

The brighter yellow colored complex of Cd(II)-I₂ was formed by adding one cm³ (2M) iodide solution into one cm³ (20µg) Cadmium solution followed by one cm³(2M) Sulphuric acid. Five cm³ (1M)TBA solution was added to the coloured solution in separating funnel and shaken for one minute. The phases were allowed to separate and the coloured complex was quantitatively extracted into the organic phase, as no trace was ever found in the aqueous phase. The color of the complex after extraction was same as in the aqueous phase.

The organic phase was collected in a dried flask after passing it through a small filter paper (5cm) to remove suspended water droplets.

The absorption spectrum after extraction is shown graphically in Fig. 1.

Effect of Acid Concentration

The effect of different molar concentration of Sulphuric acid on the extraction of Cadmium as its iodide complex was studied in the range of 0.1-2M H₂SO₄ with the same procedure to find the suitable concentration of efficient extraction and constancy in absorbance. It was found that 0.5M H₂SO₄ was the most suitable for efficient extraction. The effect shown in Fig. 2.

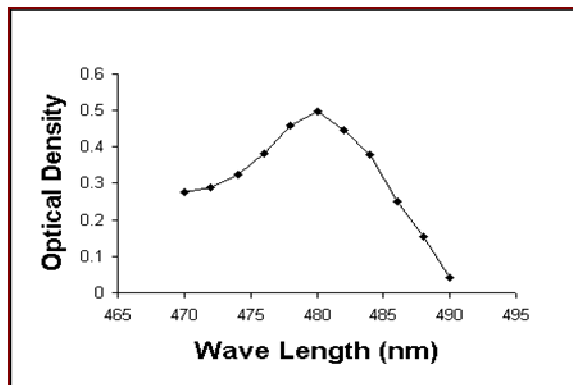


Fig. 1: Absorption Curve of Cd(II) after extraction in Tribenzylamin.

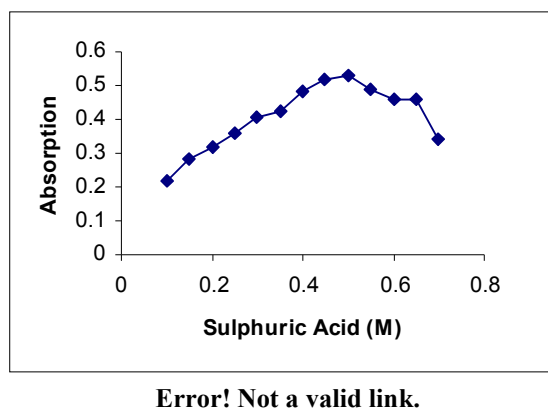


Fig. 2: Effect of Acid Concentration on the Extraction of Cadmium.

Effect of Iodide Concentration

The effect of Potassium iodide ranging 0.05-2M was studied and 0.35M iodide solution was found to be most suitable concentration for maximum colour intensity and quantitative extraction. The results are shown in Fig. 3.

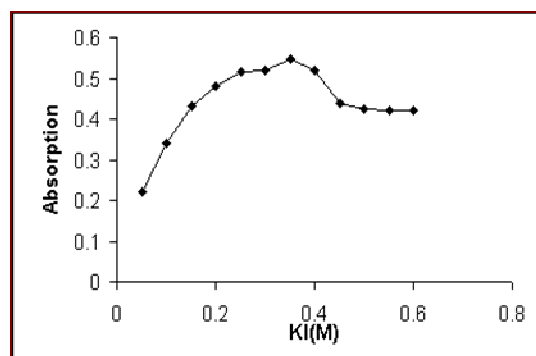


Fig. 3: Effect of Potassium Iodide on maximum extraction of Cadmium.

Effect of Time

Having studied the effect of H_2SO_4 and KSCN concentration, efforts were also made to undertake studies to choose the optimum time for shaking the two phases. The time effect in the range of 10-120 sec, was studied and 50-60sec was found suitable for maximum extraction. Results are given in Fig. 4.

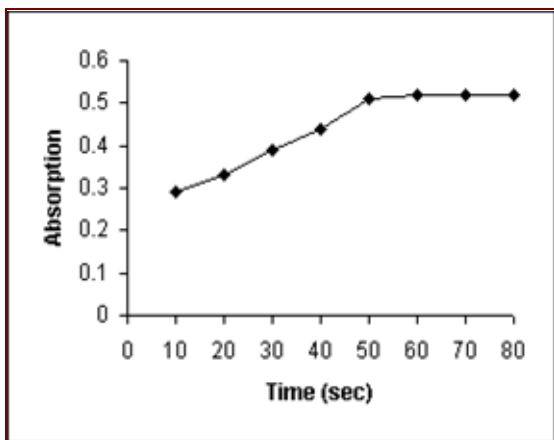


Fig. 4: Effect of Time on maximum recovery of Cadmium.

Effect of Amine Concentration

Tribenzylamine was used as the extractant and extraction efficiency was studied in the range 0.02-0.3M chloroform solution of tribenzylamine. It was found that 0.2M high molecular weight amine(chloroform solution of Tribenzylamine) gave better result in subsequent extraction of the system. Results are shown in Fig. 5.

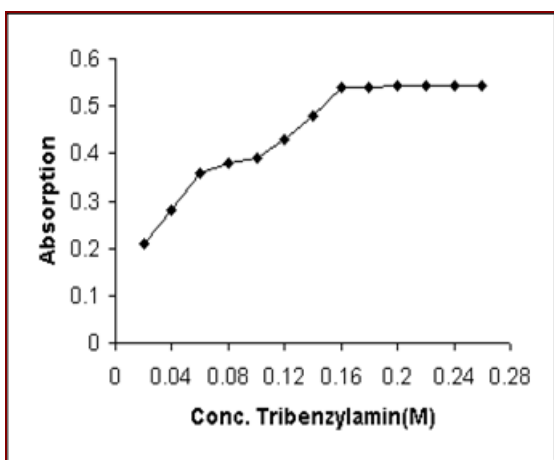


Fig. 5: Effect of Tribenzylamine on maximum extraction of Cadmium.

Effect of Dilution / Phase volume Ratio.

Keeping the acid concentration 0.5M, organic amine 0.2M and iodide concentration 0.35M constant, the effect of phase volume ratio V_{org} / V_{aq} was studied by varying the volume of the aqueous phase. It was observed that the ratio 1:1 is the most suitable ratio for quantitative and excellent extraction.

Effect of Diverse Ion

In the determination of trace metals by the above procedure with iodide, three types of interferences are most frequently encountered. These are (i) Metal ions which form an ionic complex with iodide will be extracted into amine phase. (ii) Ions which form colored nonionic compound with iodide and extracted in neutral solvents because their solubility in these solvents (iii) Ions which oxidize and form colored soluble complex of indefinite composition.

With the exception of first type none of the remaining two types interfere in the determination of Cadmium by foregoing procedure. The first type also did not interfere seriously in the efficient extraction of Cadmium provided these ions are present in moderate amount.

The effect of iodide in Sulphuric acid on number of elements was examined. Bismuth interferes due to its yellow orange complex that absorbs at 460nm. The anion did not interfere seriously in the determination of Cadmium.

Comparative results are in Table-1.

Table-1: Determination of Cadmium (20 μg) in the presence of Diverse Ions.

Diverse Ion	Amount(μg)	Cd (μg) found	Error(%)
Ni^{2+}	500	19.99	-0.05
Co^{2+}	---	19.85	-0.75
Ca^{2+}	---	19.98	-0.1
Mg^{2+}	---	19.98	-0.1
Al^{3+}	1000	20.00	0.00
Ti^{4+}	2000	20.00	0.00
W^{6+}	500	20.10	+0.5
U^{3+}	---	19.90	-0.05
Pb^{2+}	---	19.89	-0.55
Cu^{2+}	---	20.2	+1.0
Bi^{4+}	1000	20.53	+2.65
Ag^+	---	20.12	+0.6
Sn^{2+}	500	22.5	+2.5
Sb^{3+}	---	20.8	+0.4
Na^+	1000	19.99	-0.05

K ⁺	----	19.99	-0.05
SO ₄ ²⁻	---	20.00	----
CO ₃ ²⁻	---	20.12	+0.6

Calibration, Sensitivity and Stability

Known concentrations of Cadmium were extracted by foregoing procedure. The absorbance measured at 480nm. Beer law was closely obeyed. Standard Curve was prepared (Fig: 6). The yellowish color of Cadmium Iodide CdI₂ extracted in organic phase allowed to stand for half an hour. No change was observed in the optical density. After that the solution begins to decompose.

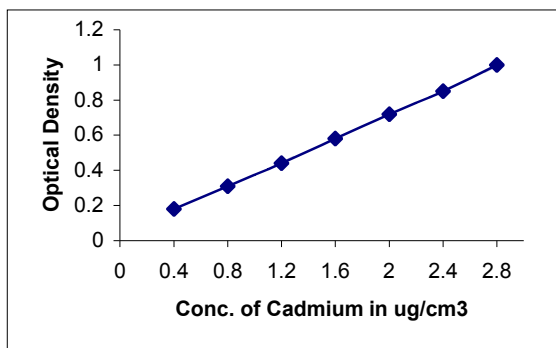


Fig. 6: Standard Graph for Cd(II)-I₂ system after extraction into organic amine phase.

Stability of organic solvent extract was found to be dependent on three factors, (a) concentration of KI, (b) concentration of acid, (c) type of solvent

Analysis of Unknown Mixture

As a final check on the method for the Spectrophotometric determination of Cadmium(II) Various unknown were also analyzed. The results shown in Table-2

Table-2: Analysis of Unknown Mixture.

S.No	Cd (μg) Added	Cd(μg) Found	Error (%)
1	8	7.94	-0.75
2	12	12.10	+0.83
3	16	15.99	-0.063
4	20	20.10	+0.50
5	27	27.19	+0.70
6	33	32.99	-0.03
7	43	43.05	0.12

Experimental

An instrument used for experimentation was Spectronic 21.

Reagents

The following solutions were prepared.

- Cadmium standard solution 1000 μg/cm³ as a stock solution.
- Standard solution of cadmium 20μg/cm³ (20ppm)
- Potassium Iodide solutions, 2M.
- Sulphuric acid, 2M
- Tribenzylamine, 1M in Chloroform

All other chemicals used were of analar grade.(E.Merck and BDH)

Application to the Analysis of Industrial Effluents

Transferred 2cm³ industrial effluents in a separating funnel, 2cm³ of (0.5M) Sulphuric acid and 2cm³ (0.35M) Potassium iodide was added. The yellow colored complex of Cadmium iodide was formed which was diluted to 10ml. After that 5ml of (0.2M) Tribenzylamine in chloroform was added and shaken for 60 seconds. Allow the phase to separate and after the equilibrium was attained, the organic phase caught the color complex completely which was extracted by filtering through small filter paper in 1cm cuvette to remove the suspended water droplets. and absorbance was measured at 480 nm. . Concentration was calculated from standard curve.

The investigated method was compared with already available conventional and atomic absorption Spectrophotometric method . The results were found favorable, shown in Table-3.

Table-3: Comparative analysis report of cadmium using iodide and other standard methods [13-15].

Sample No	Atomic absorption	Thiozone method	Present method
	methodCd (μg)	Cd(μg)	
1	0.19	0.18	0.19
2	0.21	0.20	0.22
3	0.23	0.22	0.24
4	0.25	0.24	0.25
5	0.28	0.27	0.29
6	0.30	0.29	0.33

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