



EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM WITH 4-CHLOROISONITROSO- ACETOPHENONE THIOSEMICARBAZONE.

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ABSTRACT

A method has been proposed for the extraction and spectrophotometric determination of Cd (II) at microgram levels by using 4-chloroisoinitrosoacetophenone thiosemicarbazone (CINAPT) as an analytical reagent. Cd (II) forms yellowish complex with CINAPT, which can be extracted in chloroform in the pH range 8 to 9 under optimum conditions. The chloroform extract shows maximum absorbance at 395 nm. Beers law is obeyed over the range of 0.8 to 11 microgram per ml of Cd (II) and the molar absorptivity is $6.70 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. The composition of the extracted species is found to have 1 : 2 (metal : ligand) stoichiometry. Interference due to diverse cations and anions has also been investigated. The method has been successfully applied for the determination of cadmium in synthetic mixtures and industrial samples.

Key words : Spectrophotometric determination, Cadmium, 4-Chloroisoinitrosoacetophenone

INTRODUCTION

Cadmium is toxic¹ to all systems studied; man and animals. It exhibits a variety of toxic effects, which are closely related. Itai Itai kyo disease encountered in Japan mostly in woman aged 45–70 years is caused by cadmium intoxication². Being a toxic metal, its excessive use in industry has been a matter of great concern. It acts as a cumulative poison because of its bioaccumulating property. Literature survey reveals that various reagents are available for the extractive spectrophotometric determination of Cd (II). The proposed method is found to be simple, rapid and precise.

EXPERIMENTAL

The absorption measurements were carried out on a Shimadzu 1601 UV-Visible spectrophotometer. An Elico pH meter L1-120 model was used for pH measurements. The

chemicals used were of A.R. grade. Stock solution of cadmium was prepared by dissolving cadmium sulphate, which was standardized. The working solutions were prepared by appropriate dilutions as required. The reagent 4-chloroisnitrosoacetophenone thisemicarbazone was prepared as reported³⁻⁵.

To a suitable aliquot of Cd (II) solution was added an ethanolic solution of CINAPT (2 mL of 1% solution) and 2 mL of 1M sodium acetate in a beaker. The pH of the solution was adjusted to desired value using dilute solutions of NH_4OH / NaOH . The resulting mixture was shaken with 10 mL chloroform for 1 minute. The organic layer was separated and its absorbance was measured at 395 nm, against the reagent blank prepared under identical conditions. Amount of cadmium in unknown solutions was determined from the standard calibration curve. To study the interference, the foreign ions were added to the aqueous phase before the extraction and pH adjustment. The precision and accuracy of the present method was tested by multiple analysis of the solution containing a known amount of Cd (II).

RESULTS AND DISCUSSION

A comparison of the absorption spectra of the yellow coloured solution of cadmium (II)–CINAPT complex in chloroform and the reagent blank showed that the cadmium complex has a λ_{max} at 395 nm, where the reagent has relatively low absorbance. The study of effect of variation in pH on the extraction of cadmium (II) indicated that the extraction is quantitative in the pH range 8.0–9.0. All the interactions were therefore carried out at pH 8.0 by using sodium acetate buffer (Fig. 1).

The result of extraction of Cd (II) with varying amount of CINAPT showed that 1 mL of 1% solution of it was sufficient for quantitative extraction. The extraction was found to be quantitative for equilibration time of 1 minute or more.

The complex system confirms to the Beer's law over the range of 0.8–11.0 microgram per mL of cadmium (II) (Fig. 2). The molar absorptivity of the extracted species was found to be $6.70 \times 10^3 \text{ Lit mol}^{-1} \text{ cm}^{-1}$ at 395 nm while the Sandell's sensitivity was $0.0016 \mu\text{g cm}^{-2}$.

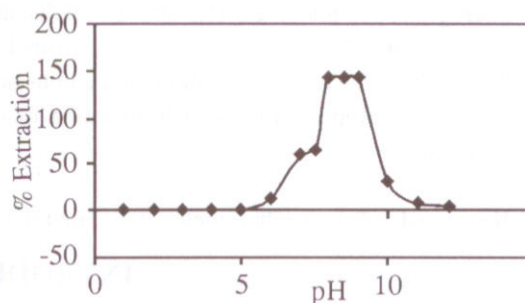


Fig. 1 Extraction of cadmium (II) as a function of pH

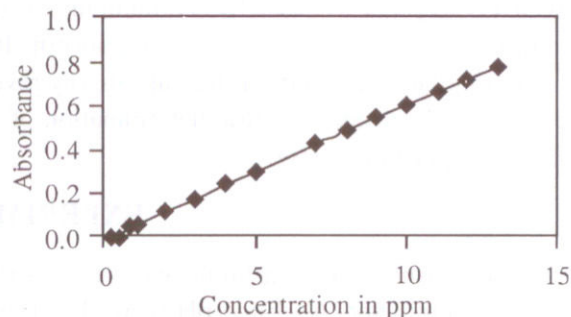


Fig. 2 Calibration plot for cadmium (II)

The average of 7 determinations of 10 µg of cadmium (II) in 10 mL aqueous solution was found to be 10.05 µg per mL, which varied between 10.01 – 10.09 µg per mL of cadmium at 95% confidence limit. Standard deviation and variance were found to be 0.05 and 0.0025, respectively. The composition of the extracted species, determined from a plot of log D Vs. log R, as also by mole ratio and Job's continuous variation methods, was found to be 1 : 2 (metal : ligand) for Cd (II)–CINAPT system.

The following ions, when present in amounts indicated do not interfere in the spectrophotometric determination of Cd (II). 10 mg each of Na (I), K (I), Sr (II), Mn (II); 5 mg each of Li (I), Ba (II), Ca (II), Mg (II) Hg (II), Al (III), Bi (III), As (III), V (V), W (VI); 10 mg each of oxalate, phosphate, sulphate, thiosulphate, fluoride; 20 mg each of persulphate, sulphate, chloride, bromide, iodide, chlorate, bromate, iodate, nitrate, nitrite, cyanate, acetate, pyrophosphate, perchlorate and thiourea. The interference by ions Ag (I), Ni (II), Co (II), Pb (II), Zn (II), cyanide, tartarate and EDTA can be removed by using appropriate masking agents.

The developed method was applied for the determination of cadmium in synthetic mixtures and in water samples. The results obtained (Table 1) were found to be in good agreement with those reported or obtained by atomic absorption spectroscopy.

Table 1. Determination of Cd (II) in synthetic mixtures and water samples

S. No.	Sample	Cadmium found*	
		By AAS	Present method
1.	Synthetic mixtures		
	(a) Cd (50) Mn (50) Fe (50)	50 ppm	49.70 ppm
	(b) Cd (50) Zr (50) Zn (50) #	50 ppm	49.30 ppm
	(c) Cd (50) As (50) Cu (50) ##	50 ppm	49.50 ppm
2.	Environmental water samples		
	(a) Certified value	Cd added	Cd measured
	0.16 ± 0.008	2.00	2.163 ppm
	(b) 0.21 ± 0.005	3.00 ppm	3.11 ppm

* Average of 5 determinations

masked by sodium thiosulphate

masked by sodium fluoride

In conclusion, the present method is simple, selective, rapid and accurate and though, it has relatively lower molar absorptivity, but offers advantages for determination of Cd (II) in terms of simplicity, rapidity or wider range of pH and speed over the known reagents⁶⁻¹⁰.

REFERENCES

1. E. Browning, Toxicity of Industries Metals, Appleton Century Crofts, New York, 2nd Edition, (1969) p. 98.
2. Sec. Annual report on carcinogens (NTP 81-43), 68 (1981).
3. A. I. Vogel "A Text Book of Practical Organic Chemistry" Longman Green and Co. Ltd., London (1954).
4. H. Muller and H.V. Pechman, J. Chem. Soc., **58**, 51 (1890).
5. Beilsteins Handbuch, Der Organischen, p. 614, 680, Band 7 (1948).
6. S. B. Padgaonkar, R. B. Pawar and A. D. Sawant, Samyak J. Chem., **23**, 16 (1998).
7. Ashok Kumar, Arti Asolkar and Pratibha Pandey, Ind. J. Chem., **32**, 644 (1993).
8. Kate Grudpan, Talanta, **36**, 1005 (1989).
9. X. Z. Fan and Z. P. Liu, Analytical Laboratory (China), **13**, 39 (1994).
10. W. Q. Jiang and Y. R. Zhu, Anal Lett., 25 (1992).

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