Derivative spectrophotometry for determination of zinc(II) and cadmium(II) using diphenylcarbazone in presence of Triton X-100

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Diphenylcarbazone has been used for the simultaneous and individual determination of zinc(II) and cadmium(II) at trace levels. The carbazone complexes of zinc(II) and cadmium(II) at pH 7–10 are pink in color, and are soluble in TX-100 micellar media. Under optimum conditions, calibration graphs for individual and simultaneous determination by first, second, third and fourth derivative spectrophotometry has been obtained. A zero crossing method using fourth derivative at 493.5 nm and 448.5 nm has been used for simultaneous determination of Zn(II) and Cd(II) respectively. To investigate the selectivity of the method, the effects of diverse ions on the determination of zinc and cadmium have also been studied. The recommended procedure has been applied to synthetic binary alloys and pharmaceutical samples.

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Zinc and cadmium exist together in several real environmental and food samples. Zinc is the second most prominent trace metal in human body after iron. Zinc is involved in a large number of enzymatic functions, fulfilling both structural and catalytic roles[1]. Cadmium improves the mechanical properties of zinc alloys, which are used as sacrificial anodes in corrosion protection of structural steelwork immersed in seawater. An increasing use of zinc and toxicity of cadmium necessitates the development of simple, sensitive and reliable method for their simultaneous determination in different samples. A survey of literature reveals that anodic stripping voltammetry[2,3,4], flow injection diode array[5], alternating current stripping voltammetry[6], oscillopolarography[7], total X-ray fluorescence[8], optical fiber sensor[9], UV-vis absorption spectrophotometry[10], high performance liquid chromatography[11], flame AAS[12] and

electrothermal integrated coupled plasma-mass spectrometry/atomic emission spectrometry[13] have been used for the determination of zinc(II) and cadmium(II). These techniques have various limitations of high cost, requirement of tedious preliminary separation techniques and excessive use of organic solvents. These techniques require large volumes of solvents which are expensive, health hazards and harmful to the environment. Also, use of multi-step procedures, lead to loss of analytes during the extraction.

Simultaneous determination of these metals in diverse matrices is difficult due to spectral overlap of their complexes (Fig. 1). In such cases, derivative spectrophotometry in a suitable micellar medium is useful for analyzing the complex matrix. In this method, zero crossing technique is used for the determination of metal concentration. Derivative spectrophotometry has been used for the simultaneous determination of Zn and Cd, by using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in the presence of cetylpyridinium chloride[14].

We report herein a new method for the simultaneous determination of zinc(II) and cadmium(II) on the basis of formation of colored complexes with diphenylcarbazone (DPC) using
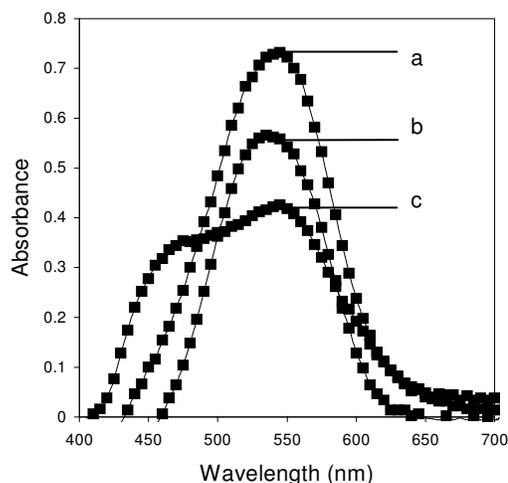

Fig. 1—Absorption spectra of (a) mixture of Zn(II)-DPC and Cd(II)-DPC complex in TX-100; (b) Cd (II)-DPC complex in TX-100; (c) Zn (II)-DPC complex in TX-100 [Cd(II) = 1.0 µg ml⁻¹, Zn(II) = 1.0 µg ml⁻¹, DPC = 4.16 X 10⁻⁴ M, TX-100 = 1 ml of 1% (v/v)].

derivative spectrophotometry. The proposed method does not require tedious and expensive processes of solvent extraction; hence use of toxic, expensive and carcinogenic solvents can be avoided. The proposed method is applied for the determination of zinc(II) and cadmium(II) in alloys and pharmaceutical samples. The detection limits are very low for both metal ions. These are comparable to other sensitive and expensive methods such as FAAS[15].

Experimental

An Elico SL-164 double beam UV-vis spectrophotometer utilizing quartz cells was used to record the spectra. It was loaded with Spectra Treatz software to calculate their derivatives and interfaced to a computer in conjunction with an HP Laserjet 1010 printer. A Century CP 901 digital pH meter was used to adjust the pH.

Stock solutions of metal ions were prepared by dissolving requisite amounts of $ZnSO_4.7H_2O$ or $CdSO_4.8H_2O$ in acidulated triply distilled water. These were standardized with EDTA [16] and diluted as required for further work. A methanolic solution of 0.1% DPC was prepared. Solutions of triton X-100 (TX-100, 1%), sodium laurylsulphate (SLS), cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB) were prepared by dissolving the requisite amounts in triply distilled water. To study the effect of pH, 0.1 N solutions of NaOH and CH_3COOH acid were prepared. The final pH was adjusted to 9 with sodium acetate/acetic acid buffer prepared by literature method[16].

Procedure

For simultaneous determination, 0.5–10 µg each of Zn(II) and Cd(II) was taken in a 10 ml volumetric flask. DPC reagent (1 ml), TX-100 (1 ml) and sodium acetate/acetic acid buffer (pH 9, 2 ml) were added to the flask. The volume was adjusted to 10 ml with triply distilled water. A portion of the solution was transferred into a spectrophotometer cell and its spectrum was recorded against blank solution. First, second, third and fourth derivative spectra were evaluated by using Spectra TreatZ software.

Instrumental parameters such as $\Delta\lambda$ and scan speed were optimized to give a constant position of isodifferential/zero cross-over points. The optimum $\Delta\lambda$ for first and second- order derivative was found to be 0.5 nm. A scan speed of 300 nm (lowest) was found suitable for simultaneous determination of zinc(II) and cadmium(II). Response time was automatically selected by the spectrophotometer in accordance with the optical energy and scan speed.

The positions of isodifferential (zero cross-over) points of zinc(II) and cadmium(II) complexes were determined by recording first, second, third and fourth derivative spectra of the two sets of solutions containing varying concentrations of Zn(II)/Cd(II) (from 0.5–10 µg) ions at constant concentrations of Cd(II)/Zn(II) ions (1 µg). The concentrations of DPC, TX-100 and buffer were kept constant for both sets. The calibration curve for the determination of Zn(II) in the presence of Cd(II) was prepared by measuring the derivative amplitude at isodifferential point of the Cd-DPC complex and plotting against the concentration of analyte (in µg ml^{-1}), and vice versa for Cd(II) ions.

Analysis of real samples

Pharmaceutical samples and alloys such as Supradyn, Vimgran and Brass were treated with conc. HNO_3 acid on a hot plate at low temperature. Then temperature was increased to 250-300°C for a few seconds. The residue was again treated with conc. HNO_3 till all brown fumes were removed. Then, it was treated with aqua regia if required and dried to get a white residue. The residue was cooled and dissolved in triply distilled water in a 100 ml measuring flask. Weighed amounts of cadmium sulphate and zinc sulphate were added and the total volume was made up to 1000 ml. An aliquot of 0.1 ml was taken and with recommended procedure, spectra were recorded. Since iron, manganese and copper ions cause serious interference in the determination, 1.0 ml each of 10% NaF and 10% sodium thiosulphate was added to the working solution to mask these interferences. The absorbances were recorded at isodifferential points and concentrations were calculated with reference to their calibration graphs.

Results and discussion

The influence of nature and concentration of different micellizing agents such as SLS, CTAB, CPB and TX-100 on absorbance of both metal complexes have been studied. The absorbance was found maximum in TX-100 for both complexes. The effect of concentration of TX-100 on sensitivity of the method was studied by varying its concentration from 0.00–0.02%. In the concentration range 0.005–0.01%, absorbance was found to be high and stable for both the complexes. Hence, a 0.01% solution of TX-100 was used for further studies.

The effect of *p*H was studied by using 0.1 *N* NaOH and 0.1 *N* HCl solutions. It was observed that complexes of both metals were unstable in acidic media. Maximum absorbance was observed in 7-10 *p*H range for both complexes. Therefore, sodium acetate buffer of *p*H 9 was used to adjust the *p*H.

The effect of reagent concentration was studied by keeping the amount of metal ion constant (10 µg) at constant *p*H 9, containing different concentrations of reagent varying from 0.5–4 ml of 4.16×10^{-4} *M* DPC solution. The absorbance of metal complexes remains constant over the range of 1.2–3 ml of reagent. The composition of complexes was studied by molar ratio method. The M: L ratio was found to be 1:2 in each case. In all further studies therefore, concentration of ligand was kept within the above-mentioned limits wherever possible.

Normal spectra of Zn(II) and Cd(II) complexes show maximum absorption values at 511 nm and 547 nm, respectively, whereas free ligand has λ_{max} at 490 nm. The closeness of overlapping absorption spectra of the Zn(II) and Cd(II) complexes (Fig. 1) prevents use of zero order absorption measurements for the simultaneous determination of Cd(II) and Zn(II). For this reason derivative spectrophotometric methods have been applied. To select the derivative order, first, second, third and fourth order derivative spectra of Cd(II) and Zn(II) complexes were studied. Study revealed that fourth derivative spectra gave results of highest accuracy and lowest detection limits. Calibration graphs for first, second, third and fourth derivative spectra were obtained by using zero-cross over/isodifferential point method. Two sets of mixtures were studied; one with increasing amounts of Cd(II) from 0.5–10 µg at constant concentration of Zn(II) and second with increasing amounts of Zn(II) from 0.5–11 µg at constant concentration of Cd(II). The heights for the peaks were measured at isodifferential points of the other metal complex. In first derivative, heights were measured at 491 nm and 533.5 nm for preparing the calibration curve of Cd(II) and Zn(II) complexes, respectively. For second derivative heights were measured at 466 nm for Zn(II) and 421 nm for Cd(II), respectively. Similarly, for third derivative amplitudes were measured at 481 nm for Cd(II) and at 531 nm for Zn(II), respectively. The measurements for fourth derivative were done at 448.5 nm for Cd(II) and 466 nm and 493.5 nm for Zn(II) (Figs 2 and 3). The statistical data is given in Tables 1 and 2.
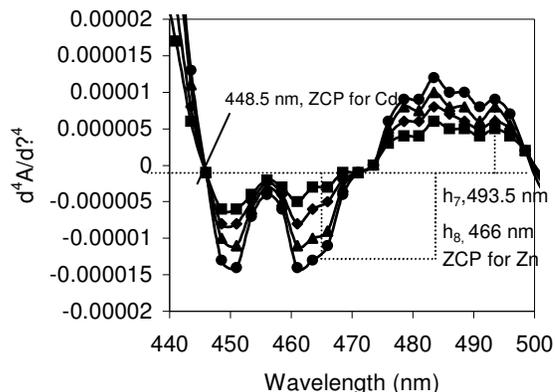

Fig. 2—Fourth derivative absorption spectra of mixture of Zn(II)-DPC and Cd(II)-DPC complex. [Zn(II); (a) 0.1 µg ml^{-1}; (b) 0.15 µg ml^{-1}; (c) 0.20 µg ml^{-1}; (d) 0.25 µg ml^{-1}; (e) 0.3 µg ml^{-1}, Cd(II); 0.1 µg ml^{-1}, DPC = 4.16×10^{-4} *M*, *p*H = 9, TX-100 = 1 ml of 1% (*v/v*)].
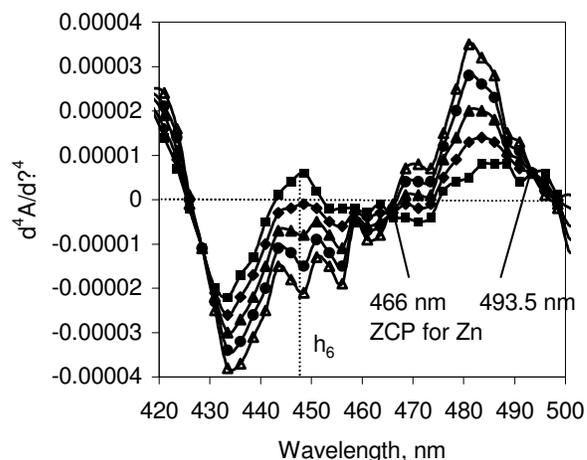

Fig. 3—Fourth derivative absorption spectra of mixture of Zn(II)-DPC and Cd(II)-DPC complex [Cd(II); (a) 0.1 µg ml^{-1}; (b) 0.15 µg ml^{-1}; (c) 0.20 µg ml^{-1}; (d) 0.25 µg ml^{-1}; (e) 0.3 µg ml^{-1}, Zn(II); 0.1 µg ml^{-1}, DPC = 4.16×10^{-4} *M*, *p*H = 9, TX-100 = 1 ml of 1% (*v/v*)].

The calibration graphs obtained by recommended methods were linear over a range of 0.05–1 µg ml^{-1} for cadmium(II) in the presence of 0.1 µg ml^{-1} of zinc(II) and 0.05–1.1 ml^{-1} of zinc(II) in the presence of 0.1 µg ml^{-1} of cadmium(II). Sensitivity was calculated by S/N=3 for first second, third and fourth derivatives. The high values of correlation coefficients and intercepts on the axes (close to zero) indicate the good linearity of all the calibration graphs and correspondence to Beer's law for the derivative measurements.

Table 1—Simultaneous determination of Cd(II) and Zn(II) in pharmaceutical samples and alloys

Sample	Composition	Amount present (mg) in sample		Found (mg)		RSD (%)	
		Cd(II)	Zn(II)	Cd(II)	Zn(II)	Cd(II)	Zn(II)
Pharmaceutical samples (a) Vimgran Sarabhai Chemi-cals	Zn = 15 mg Cu[a] = 2 mg Selenium dioxide = 50 mcg Chromium picolinate = 200 mcg	10[c]	15	9.9	14.8	1.1	1.2
(b) Supradyn (solution prepared in 100 ml distilled water) Nicholas Piramal India Limited	CuSO$_4$[a] = 3.39 mg ZnSO$_4$ = 2.20 mg Sodium molybdate dihydrate = 0.25 mg Sodium borate = 0.88 mg	1.0[c]	0.89	1.1	0.85	1.2	1.3
Alloys (a) Brass alloy Alfa Aesar	Copper[a] = 58.18 % Lead = 2.56 % Zinc = 38.99 % Iron[b] = 0.09 % Tin = 0.12 %	15[c]	26	14.8	24.99	1.0	1.1
(b) Wood's metal Alfa Aesar	Bismuth = 50 % Lead = 25 % Tin = 12.5 % Cadmium = 12.5 %	0.125	0.20[c]	0.123	0.21	1.1	1.2

[a]masked with 2 ml of 10% sodium thiosulphate
[b]masked with 2 ml of 5% sodium fluoride
[c]amount added before analysis

Table 2—Determination of Cd(II) and Zn(II) in synthetic binary mixtures

S. No.	Metal ion (µg ml^{-1})				Recovery (%)	
	Taken		Found			
	Cd(II)	Zn(II)	Cd(II)	Zn(II)	Cd(II)	Zn(II)
1	0.165	0.896	0.163	0.886	98.78	98.83
2	0.455	0.784	0.450	0.770	98.90	98.72
3	0.390	0.560	0.383	0.556	98.20	99.28
4	0.585	0.224	0.573	0.222	97.94	99.10
5	0.650	0.672	0.643	0.671	98.92	98.95

Amongst the methods utilized for the determination of cadmium(II) and zinc(II), the most sensitive seems to be the fourth derivative because of lower values of detection limit utilizing the regression line. Also it can be seen that the fourth derivative values of zinc and cadmium complexes at 493.5 nm and 448.5 nm, respectively have a better precision and sensitivity than first second and third derivative values.

Application to real samples

The proposed method was validated by the analysis of Zn(II) and Cd(II) ions in alloys and pharmaceutical samples. An aliquot of the sample solution was analyzed by the procedure described above after adding a suitable masking agent. The concentrations of Cd(II) and Zn(II) were determined from the plots of the fourth derivative amplitudes at 493.5 nm and 448.5 nm respectively (isodifferential points of Zn(II) and Cd(II) complexes). The results for the simultaneous determination and certified amount present in the sample are given in Tables 1 and 2.

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