

Extractive spectrophotometric determination of lead (II), cadmium (II), zinc (II) and vanadium (IV) with hexamethyleneiminedithiocarbamate

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A new method for the extraction and spectrophotometric determination of Pb(II), Cd(II), Zn(II) and V(IV) with hexamethyleneiminedithiocarbamate (HMICDT) at microgram levels is described. The TLC resolution of complex mixtures using the binary solvent, chloroform-toluene in the ratio (20:80) provided effective separation of the complexes, especially when surfactants such as tetrabutylammonium bromide and triton X-100 were used. The molar absorptivities and Sandell's sensitivities ($\mu\text{g cm}^{-2}$) for all these complexes are found to be in the ranges 0.5023×10^{-4} - 6.5446×10^{-4} and 0.0009-0.010 respectively, Beer's law is obeyed over the range 16.0-80.0 μg for Pb(II), 8.0-76.0 μg for Cd(II), 0.5-08.5 μg for Zn(II) and 12.0-95.0 μg for V(IV), per 10.0 ml of chloroform solution. This method has also been developed for the estimation of these metals in some alloys.

The biological importance¹⁻⁷ of dithiocarbamates has initiated tremendous interest in some metal complexes for their therapeutic importance for researchers. A literature survey reveals that the TLC analysis of the metal dithiocarbamates⁸⁻¹⁷, diacylglycerols¹⁸ and thiazolidinones¹⁹ has been reported, but attempts on achieving their resolution on various surfactants impregnated silica gel-G plates and quantitative isolation are scarce. This prompted us to undertake the title investigation.

Experimental

All the chemicals used were of AR grade and their solutions were always prepared afresh. The sodium salt of HMICDT was prepared by the method of Macrotrigiano *et al.*²⁰ and used as a 0.2% solution in distilled water. Stock solutions of the metal ions (1000 ppm) and copper sulphate (10^{-3} M) were prepared in doubly distilled water from their salts and standardised²¹. Naphthalene and chloroform were checked spectrophotometrically before use. A 20% naphthalene solution in acetone was used.

General procedure

To standard solutions containing either 64.0 μg of Pb(II), 48.0 μg of Cd(II), 08.5 μg of Zn(II) or 65.0 μg of V(IV), was added the reagent solution of sodium salt of HMICDT (2 ml, 0.2%). The volume was made upto 30 ml and pH adjusted at 3.5 for lead, 3.0 for cadmium, 6.0 for zinc and 3.0 for vanadium solutions. After thorough shaking, naphthalene solution (2 ml, 20%) was added in a fast stream with vigorous shaking. The complexes got adsorbed on microcrystalline naphthalene. The solid mass was filtered, washed several times with distilled water, then dried and dissolved in chloroform (10 ml). Since the resultant solutions were colourless, the Pb(II), Cd(II), Zn(II) and V(IV) ions were quantitatively replaced by cupric ions by shaking the respective chloroform-complex solutions with cupric nitrate solution (10 ml, 10^{-3} M). The resultant yellow coloured chloroform layer was then poured onto anhydrous sodium sulphate (2 g) to remove the last traces of water. The absorbance and λ_{max} of this solution against reagent blank was recorded.

The Pb(II), Cd(II), Zn(II) and V(IV)-HMICDT complexes were also analysed on surfactants impregnated silica gel-G plates by employing and ascending irrigation technique for the development of plates. The samples of each of these solutions in chloroform were spotted separately and the plates developed, dried and the spots made visible by placing the plates in iodine chamber for 40 sec. The $R_f \times 100$ values were calculated. The respective spots containing the complex, were then scraped off carefully after the iodine had evaporated, and dissolved in chloroform (10 ml). Since the resultant solutions were colourless, the Pb(II), Cd(II), Zn(II) and V(IV) ions were quantitatively replaced by cupric ions as described above.

Results and discussion

The lead, cadmium, zinc and vanadium-HMICDT complexes were quantitatively adsorbed onto microcrystalline naphthalene in the pH ranges 3.0-5.0, 1.5-6.0, 2.0-9.0 and 1.0-4.5 respectively, and showed absorption maxima (after replacement of the ions by cupric ions) at 435 nm. The reagent absorbed negligibly at this wavelength. The spectra obtained revealed the formation of only one type of complex in each instance. For 64.0 μg of lead, 48.0 μg of cadmium, 8.5 μg of zinc and 65.0 μg of vanadium, the

adsorption of the complexes were quantitative when a minimum of 1.0 ml, 0.5 ml, 0.5 ml and 1.0 ml respectively of reagent solution, and 1.0 ml, 0.8 ml, 0.5 ml and 1.0 ml respectively of naphthalene solution were used. So 2.0 ml each of 0.2% reagent solution and 20% naphthalene solution were preferred throughout the study. The quantitative recoveries were obtained when the volume of the aqueous phase did not exceed 80.0 ml. The adsorption is very rapid, which is complete in 10 sec and so a shaking time of 30 sec was found suitable. The formation of Pb(II), Cd(II), Zn(II) and V(IV) – HMICDT complexes is fairly rapid at room temperature; however, a 5 min digestion time was maintained throughout the present study. The final solution of Pb(II), Cd(II), Zn(II) and V(IV) complex in naphthalene chloroform were stable for 18, 20, more than 20 and 8 h respectively. Amongst the various organic solvents tried, the complexes were found to be insoluble in many of the non-aqueous and water miscible organic solvents, but dissolved easily in chloroform. A minimum of 2 min shaking time was required for quantitative replacement of lead, cadmium, zinc and vanadium ions by cupric ions.

The Job's method confirms the ML_2 complexation in all the cases. The TLC resolution data exhibited more satisfactory results when 1% tetrabutylammonium bromide and 1% triton-X were used as an adsorbent, and, chloroform: toluene (20:80) as the solvent for the development of plates.

The interference of several ions in the determination of Pb(II), Cd(II), Zn(II) and V(IV) was studied and the results are presented in Table 1.

Analysis of alloys

In order to assess the analytical applicability of the proposed method, lead, zinc and vanadium contents in certain alloys such as gun metal (Pb: 6.3%, Zn: 4.4%), aluminium alloy (Zn: 0.80%, Pb: 0.10%) and carbon steel (V: 0.06%) were determined by the recommended procedure. The alloys were dissolved separately in HCl (30 ml) containing a few drops of conc. HNO_3 acid. The mixture was gently heated and the excess acid was evaporated and the requisite volume made up with distilled water.

The various interfering radicals were either masked by suitable masking agents or effectively eliminated as a result of the difference in the $R_f \times 100$ values, by the TLC method of separation and resolution. The latter method proved to be more convenient, highly selective and sensitive, yielding more accurate results.

Table 1—Effect of diverse ions in the determination of lead, cadmium, zinc and vanadium

[Pb: 64.0 μ g; Cd: 48.0 μ g; Zn: 8.5 μ g; V: 65.0 μ g; HMICDT = 2 ml, 0.2%; naphthalene solution = 2 ml, 20%; pH for Pb = 3.5, Cd = 3.0, Zn = 6.0 and V = 3.0]

Amount of ions added = 500 μ g

Ion	Absorbance at 435 nm			
	Lead	Cadmium	Zinc	Vanadium
	0.341	0.582	0.851	0.641
Bromide	0.342	0.581	0.853	1.212*
Chloride	0.350	0.581	0.852	0.708
Iodide	0.348	0.583	0.852	0.641
Thiocyanate	0.253*	0.587	0.851	0.641
Dihydrogen				
Ortho-phosphate	0.343	0.580	0.851	0.642
EDTA	0.240*	0.508*	0.632*	0.758*
Thiosulphate	0.250*	0.580	0.602*	0.640
Sulphate	0.353	0.582	0.852	0.643
Carbonate	0.355	0.580	0.855	0.958*
Acetate	0.341	0.586	0.857	0.661
Citrate	0.339	0.580	0.850	0.752*
Cobalt (II)	1.000	0.580	1.000	0.950
	0.331 ^a		0.848 ^a	0.641 ^a
Nickel (II)	1.500	1.500	1.380	1.510
	0.333 ^a	0.581 ^a	0.852 ^a	0.652 ^a
Iron (III)	—*	—*	—*	1.328
	0.338 ^b	0.582 ^b	0.850 ^b	0.650 ^b
Zinc (II)	—*	—*	—	—*
	0.342 ^a	0.582 ^a	—	0.661 ^a
Bismuth (III)	1.512	1.508	1.410	0.752
	0.340 ^c	0.581 ^c	0.848 ^c	0.640 ^c
Mercury (II)	0.343	0.582	0.848	0.643
Magnesium (II)	0.340	0.581	0.852	0.666
Molybdenum (VI)	0.348	0.588	0.855	0.656
Lead (II)	—	0.841	0.952	—*
	—	0.581 ^d	0.850 ^d	0.652 ^d
Cadmium (II)	—*	—	—*	—*
	0.348 ^b	—	0.851 ^b	0.640 ^b
Vanadium (V)	0.347	0.587	0.850	—
Chromium (III)	0.341	0.583	0.852	0.642
Ruthenium (III)	0.339	0.585	0.850	0.640
Rhodium (III)	0.340	0.580	0.852	0.642
Manganese (II)	0.341	0.589	0.854	0.632
Palladium (II)	0.308	0.512	0.642	0.592
	0.341 ^a	0.583 ^a	0.850 ^a	0.640 ^a
Tellurium (IV)	0.336	0.581	0.850	0.643

*Interfered seriously.

^aAfter masking with 5 ml of 10% sodium cyanide solution.

^bAfter masking with 5% triethanolamine solution.

^cBismuth extracted at pH 10.0.

^dAfter masking with sodium sulphate solution.

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