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Spectrophotometric Determination of Lead, Zinc, and Cadmium after Extraction of Their Diethyldithiocarbamates into Molten Naphthalene and Replacement by Copper

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A method is proposed for the extraction of lead, zinc, and cadmium as their diethyldithiocarbamates into molten naphthalene. These complexes are quantitatively extracted into molten naphthalene. After extraction, the solidified naphthalene containing the colorless complex of each of the above metals is dissolved in chloroform and the metal is replaced by copper(II) to develop a yellow color of copper(II) diethyldithiocarbamate. The absorbance is measured at 440 nm. Beer's law is obeyed in the concentration range of 5.0—130.0 μg for lead, 3.0—60.0 μg for zinc, or 5.0—100.0 μg for cadmium in 10 ml of the final solution. The molar absorptivities ($\mathrm{l\ mol^{-1}\,cm^{-1}}$) and Sandell sensitivities ($\mu\mathrm{g/cm^2}$) for lead, zinc, and cadmium are calculated to be 1.15×10^4, 0.0098, 1.11×10^4, 0.0059, and 1.15×10^4, 0.0098 respectively. Solutions containing 45.0 μg of lead, 40.0 μg of zinc, and 43.0 μg of cadmium separately gave mean absorbances of 0.250, 0.620, and 0.440 with standard deviations of 0.0027, 0.0059, and 0.0038, respectively. Conditions have been decided for the determination of lead, zinc, and cadmium in some alloys and synthetic mixtures.

Sodium diethyldithiocarbamate is one of the most popular and versatile organic reagents, which react with many metal ions.[1)] Studies of this reagent for use in solvent extraction have revealed that even with the proper control of pH, this reagent is not selective in extracting specific metals although many masking agents have been used.[2)] Liquid-liquid extraction no doubt is an excellent technique for the separation and concentration of metal ions. But it cannot be applied directly for those metal ions which form complexes with the chelating agents only at high temperature and form complexes having low solubilities at room temperatures.[3)] In such cases, the metal complex is first precipitated at high temperature and then it is extracted into a suitable organic solvent at room temperature.[3)] Thus the method is time consuming. Fujinaga and coworkers have developed a new method of extraction *i.e.* "Solid-liquid separation after liquid-liquid extraction" in which the above mentioned difficulty is overcome.[4,5)] The technique is especially useful for the extraction of those metal ions which form complexes with complexing agents at high temperature.[3)] In the present communication, conditions have been decided for the extraction of lead, zinc, and cadmium as their diethyldithiocarbamates into molten naphthalene and subsequent spectrophotometric determination after dissolution of the solid naphthalene containing the metal complex in chloroform and replacing the metal by copper(II) to develop a yellow color. The interference of various ions has been studied and the method is applied to the determination of lead, zinc and cadmium in some alloys.

Sodium diethyldithiocarbamate[6)] has also been used for the spectrophotometric determination of copper after extraction into molten naphthalene in the pH range of 2.0—8.0. The molar absorptivity was reported to be 1.20×10^4 $\mathrm{l\ mol^{-1}\,cm^{-1}}$. It was compared with the present method.

Experimental

Reagents. Solutions of lead nitrate, zinc sulfate, and cadmium sulfate were prepared in distilled water from their A. R. grade reagents and standardized by the known methods.[7)] A 1×10^{-3} M (1 M=1 mol dm^{-3}) solution of sodium diethyldithiocarbamate (Na ddtc) was prepared in distilled water.

Chloroform and naphthalene were tested for impurities spectrophotometrically before use.

Apparatus. An Elico pH meter and a Pye-Unicam SP-700 recording spectrophotometer were used.

General Procedure. An aliquot of each of the metal solution was taken in a beaker and 1 cm^3 of 1.0×10^{-3} M Na ddtc solution was added to it. The pH of the solutions was adjusted to 7.0 for lead, 4.5 for zinc, and 7.5 for cadmium with the buffer solution, perchloric acid (0.2 M) or sodium hydroxide (0.2 M) (Fig. 2). These solutions were transferred to 100 cm^3 round-bottom flasks and warmed in a water-bath at about 60 °C and then naphthalene (2.0 g) was added to each. The flask was stoppered and heating was continued until naphthalene melted. The mixture was stirred vigorously until the naphthalene solidified forming very fine crystals in all the cases. Once more the naphthalene was melted, shaken vigorously, and allowed to stand at room temperature. The naphthalene containing the colorless complex was separated by filtration, dried in the folds of a filter paper, and dissolved in chloroform. In each case, the solution was made exactly to 10 cm^3 in a volumetric flask. This 10 cm^3 extract in chloroform was treated with aqueous copper sulfate solution (10 cm^3 of 1×10^{-3} M) to develop a yellow color in the chloroform layer which was separated and dried with anhydrous sodium sulfate (2.0 g). A portion of this solution was taken in a 1-cm cell and the absorbance was measured at 440 nm in each case against the reagent blank.

Results and Discussion

Absorption Spectra. It has already been established that copper is extracted quantitatively into molten naphthalene as a diethyldithiocarbamate complex in the pH range of 2—11 and has an absorption maximum at 440 nm. The stability constant of copper(II) diethyldithiocarbamate as indicated in the literature is two times more than those of lead, zinc, and cadmium diethyldithiocarbamates.[8)] Obviously these metals can be quantitatively replaced by copper from the chloroform layer into the aqueous layer after their extraction as diethyldithiocarbamates.

The absorption spectra of sodium diethyldithiocarbamate and lead, zinc, and cadmium complexes in naphthalene and chloroform solution were recorded against water and reagent blank after replacing the metal by copper(II). It was observed that copper complex absorbed strongly at 440 nm, where the reagent blank absorbed negligibly (Fig. 1).

Effect of pH. Extractions were carried out at different pH's keeping other conditions constant. It was found that the extractions were quantitative in the pH range of 6.2—8.3 for lead, 4.8—9.3 for zinc, and 6.6—11.5 for cadmium (Fig. 2).

Effect of Reagent Concentration. At optimum pH, extractions were carried out at varying reagent concentrations. It was observed that the extractions were quantitative for 0.5—4.0 cm^3 of the reagent in all the cases (Fig. 3). So 1.0 cm^3 of the reagent was used throughout the experiments in all the cases.

Effect of Electrolytes. Various electrolytes such as sodium chloride, sodium nitrate, sodium acetate, and sodium perchlorate (0.01—1.0 M) caused no improvement in extraction, indicating no salting-out effect.

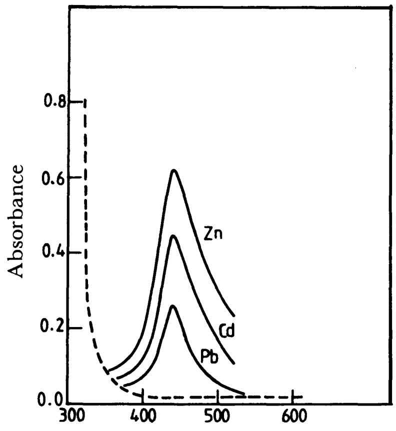

Fig. 1. Absorption spectra of Na ddtc and Cu complex in naphthalene-chloroform solution. Pb: 45.0 mg; Zn: 40.0 mg; Cd: 43.0 mg; Na ddtc (1×10^{-3} M); 2.0 ml in each case; pH : 8.3; naphthalene: 2.0 g. Reference: Water and reagent blank.

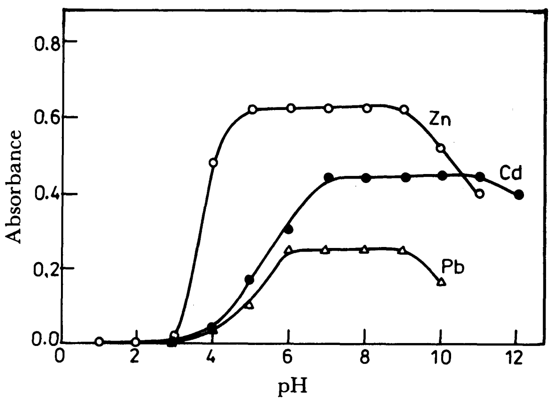

Fig. 2. Effect of pH. Pb: 45.0 mg; Zn: 40.0 mg; Cd: 43.0 mg; Na ddtc (1×10^{-3} M): 2.0 ml in each case; naphthalene: 2.0 g. Wavelength: 440 nm. Reference: Reagent blank.

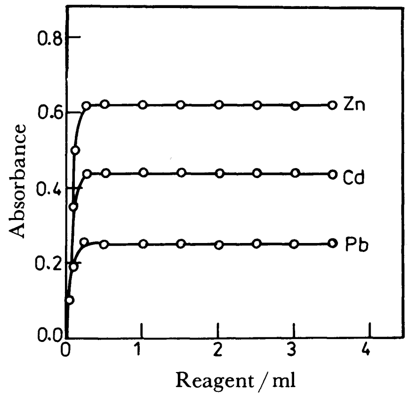

Fig. 3. Effect of reagent concentration. Conditions were same as in Fig. 2. Reference: Reagent blank.

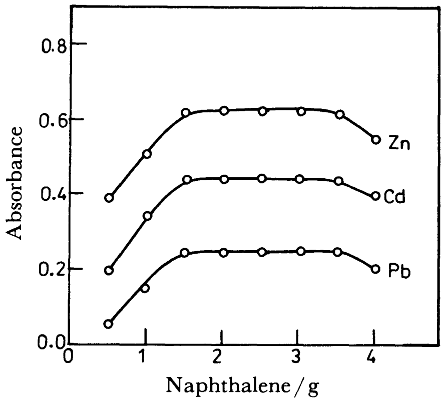

Fig. 4. Effect of amount of naphthalene. Conditions were same as in Fig. 2. Reference: Reagent blank.

Effect of Amount of Naphthalene. The amount of naphthalene was varied from 0.25—4.0 g. The absorbance remained constant when the naphthalene used was in the range of 1.4—3.5 g (Fig. 4).

Effect of Volume of Aqueous Phase. Since the volume of the aqueous phase is very large as compared to that of naphthalene (2.0 g), it was necessary to study the effect of the volume of the aqueous phase on the extraction on these metal ddtc complexes. The volume of the aqueous phase was varied from 10 to 70 cm^3. The extraction was quantitative when the volume of the aqueous phase did not exceed 40 cm^3 for lead and 50 cm^3 for zinc and cadmium. Above these volumes of the aqueous phase the extraction was not quantitative (Fig. 5).

Effect of Digestion and Shaking Times. The complex was digested at high temperature on a boiling water-bath (81 °C) between 1—10 min before extraction into naphthalene. It was observed that the constant absorbance was obtained by digesting between 2—10 min for cadmium, zinc, and lead. Therefore, 5 min of digestion time was selected. The effect of shaking time on the absorbance was also examined. It was observed that the extraction of the complex into molten naphthalene was very fast and no change was seen in the degree of the extraction when shaking time was varied from 1—20 min. Therefore, 2

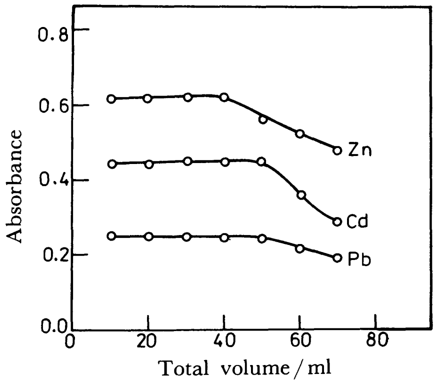

Fig. 5. Effect of volume of aqueous phase. Conditions were same as in Fig. 2. Reference: Reagent blank.

min of shaking time was chosen in all the cases for the further work.

Beer's Law and Sensitivity. Under the optimum conditions described above, calibration curves were constructed at 440 nm in each case. Beer's law held in the concentration range of 5.0—130.0 μg for lead, 3.0—60.0 μg for zinc, and 5.0—100.0 μg for cadmium in 10 cm^3 of the chloroform solution. The molar absorptivities (l mol^{-1} cm^{-1}) and Sandell sensitivities (μg/cm^2) were calculated to be 1.15×10^4, 0.0098; 1.11×10^4, 0.0059; and 1.15×10^4, 0.0098, respectively (for lead, zinc, and cadmium). Solutions containing 45.0 μg of lead, 40.0 μg of zinc, and 43.0 μg of cadmium gave mean absorbances of 0.250, 0.620, and 0.440 with standard deviations of 0.0027, 0.0059, and 0.0038, respectively. The percentage of the extraction was established in each case by back-extracting the metal from the chloroform layer (before replacing by copper) with 20 cm^3 of 4 M HNO_3 and then determining the metals by atomic absorption spectrophotometry. It was 95.75, 92.40, and 95.80% respectively. These values are consistent with those obtained spectrophotometrically after metal ion exchange with copper(II).

Table 1. Effect of diverse anions
Pb: 45.0 μg, Zn: 40.0 μg, and Cd: 43.0 μg

Alkali salt added	Anion added (mg)	Absorbance at 440 nm		
		Pb	Zn	Cd
—	—	0.250	0.621	0.440
Sodium chloride	5.0	0.250	0.622	0.442
Potassium bromide	5.0	0.245	0.620	0.444
Potassium iodide	5.0	0.200	0.615	0.445
	0.5	0.244	0.620	0.440
Sodium acetate	5.0	0.240	0.620	0.442
Sodium sulfate	5.0	0.100	0.622	0.440
	0.2	0.200	0.620	0.436
	0.1	0.240	0.622	0.440
Sodium perchlorate	5.0	0.250	0.620	0.440
Potassium sodium tartrate	5.0	0.245	0.618	0.440
Sodium citrate	5.0	0.155	0.520	0.390
	0.5	0.240	0.615	0.440
Potassium thiocyanate	5.0	0.250	0.615	0.440
Sodium thiosufate	5.0	0.250	0.615	0.442
EDTA (disodium)	5.0	0.002	0.005	0.003
	0.1	0.014	0.015	0.012

Composition of the Metal Complex. The nature of lead, zinc, and cadmium diethyldithiocarbamates extracted into molten naphthalene was studied by the Job's method of continuous variation and the mole ratio method. A sharp peak at 0.33 mole fraction in Job's curve and a clear break at 1:2 (metal:Na ddtc) ratio in the mole-ratio plot suggested the extraction of $Pb(C_5H_{10}NS_2)_2$, $Zn(C_5H_{10}NS_2)_2$, and $Cd(C_5H_{10}NS_2)_2$ into the molten naphthalene.

Effect of Diverse Ions. The interference of various ions has been studied in detail. Generally, 5.0 mg of the anions and 1.0 mg of the cations were added, individually to the solutions containing 45.0 μg of lead, 40.0 μg of zinc, or 43.0 μg of cadmium before

Table 2. Effect of diverse cations
Pb: 45.0 μg, Zn: 40.0 μg, and Cd: 43.0 μg

Alkali salt added	Anion added (mg)	Absorbance at 440 nm		
		Pb	Zn	Cd
—	—	0.250	0.621	0.440
Sodium arsenite	1.0	0.250	0.625	0.440
Silver(I) nitrate	1.0	0.240	0.610	0.430
Cobalt(II) chloride	1.0	0.310	0.700	0.520
	0.4	0.255	0.625	0.450
Copper(II) chloride	1.0	0.270[a]	0.650[a]	0.460[a]
	0.5	0.255[a]	0.630[a]	0.445[a]
Chromium(III) nitrate	1.0	0.250	0.620	0.442
Iron(III) chloride	1.0	0.265[b]	0.635[b]	0.460[b]
	0.5	0.252[b]	0.620[b]	0.436[b]
Mercury(II) chloride	1.0	0.245	0.610	0.440
Iridium(III) chloride	1.0	0.255	0.628	0.445
Nickel(II) chloride	1.0	0.290	0.685	0.510
	0.5	0.255	0.620	0.445
Osmium tetraoxide	1.0	0.252	0.624	0.444
Palladium(II) nitrate	1.0	0.340[c]	0.750[c]	0.560[c]
	0.5	0.255[c]	0.640[c]	0.450[c]
Rhodium(III) chloride	1.0	0.250	0.622	0.444
Potassium tellurite	1.0	0.240	0.615	0.430
Ruthenium(III) chloride	1.0	0.254	0.620	0.442
Thallium(I) nitrate	1.0	0.254	0.620	0.442
Sodium tungstate	1.0	0.250	0.622	0.440
Tartar emeric	1.0	0.260	0.624	0.450
Lead(II) nitrate	1.0	—	0.624[d]	0.445[d]
Zinc(II) chloride	1.0	0.256[e]	—	0.650[f]
	0.5	0.254[e]	—	0.580[f]
	0.2	0.252[e]	—	0.550[f]
Cadmium(II) chloride	1.0	0.254[e]	0.757	—
	0.5	0.252[e]	0.680[g]	—
	0.2	0.250[e]	0.680[g]	—
Indium(III) sulfate	1.0	0.260	0.630	0.450

a) Copper was eliminated by preextraction at pH 2.5. b) Interference of iron(III) was eliminated after masking with 10 ml of 5% NaF. c) Extraction of Pb, Zn, and Cd were carried out at pH 9.0 to eliminate Pd. d) Lead was eliminated as lead sulfate. e) Interference of zinc and cadmium was eliminated by masking with 10 ml of 5% NaCN. f) Extraction of cadmium was carried out at pH 11.5 to reduce extraction of zinc up to some extent. g) Extraction of zinc was carried out at pH 4.8 to eliminate cadmium.

TABLE 3. DETERMINATION OF LEAD, ZINC, AND CADMIUM IN ALLOYS AND SYNTHETIC MIXTURES

Alloy/Synthetic mixture	Composition (%)	Metal present (μg)	Metal found (μg)	Average μg	Error %	Metal found by AAS method (μg)
Aluminium brass C NBS-C1120	Cu: 80.1, Zn: 18.1 Al: 1.5	Zn: 18.0	17.8, 17.7, 17.8, 17.8, 17.8	17.78	1.22	18.2
Phosphor bronze NBS-63C	Cu: 80.5, Pb: 9.4 Zn: 9.0, P: 0.2	Pb: 37.6	37.5, 37.0, 37.2, 37.0, 37.2	37.18	1.11	37.5
	As: 0.02	Zn: 36.0	35.5, 35.6, 35.8, 35.7, 35.6	35.62	1.05	35.8
Bronze BCS-182/1	Cu: 84.8, Sn: 5.0, Zn: 5.2, Pb: 3.5,	Pb: 35.0	34.5, 34.4, 34.6, 34.8, 34.7	34.60	1.14	34.8
	P: 0.5, As: 0.14	Zn: 10.4	10.3, 10.3, 10.3, 10.2, 10.3	10.28	1.15	10.5
Gun metal BCS-183/3	Cu: 84.5, Sn: 6.7, Zn: 3.3, Pb: 3.4,	Pb: 34.0	33.8, 33.6, 33.7, 33.6, 33.5	33.64	1.06	34.0
	Ni: 1.5, As: 0.15	Zn: 9.9	9.8, 9.7, 9.8, 9.8, 9.8	9.8	1.01	9.9
Synthetic mixture	Cd: 50.0, Pb: 5.0, Cu: 45.0,	Pb: 50.0	49.5, 49.4, 49.3, 49.4, 49.5	49.42	1.16	49.8
		Cd: 25.0	24.8, 24.7, 24.8, 24.8, 24.6	24.74	1.04	25.0
Synthetic mixture	Pb: 20.0, Cd: 5.0, Ni: 50.0, Co: 25.0	Pb: 40.0	39.5, 39.6, 39.7, 39.5, 39.5	39.52	1.11	40.2
		Cd: 30.0	29.7, 29.8, 29.6, 29.7, 29.7	29.7	1.10	29.9

extraction. Among the anions examined (Table 1), only iodide and sulfate interfered with the determination of lead, but their relatively low concentration can be tolerated. Citrate and Na_2H_2 edta interfered in all the cases, the extraction being impossible in the presence of Na_2H_2 edta in all the cases obviously due to higher stability constant of metal edta complex than that of the metal ddtc complex.[9] Citrate can be tolerated in a relatively low concentration (Table 1). Among the cations examined (Table 2), Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Pd^{2+} seriously interfered, but Co^{2+} and Ni^{2+} can be tolerated if present in a relatively low concentration. The interference of copper was eliminated by preextraction (chloroform extraction) at pH 2.5 and from the aqueous solution these metal ions (Pb, Zn, and Cd) can be extracted at their respective pH range. To eliminate the effect of palladium the extraction of lead, zinc, and cadmium were carried out at about pH 9 where palladium does not form complexes with Na ddtc. In all the cases Fe^{3+} was masked by adding 10 cm^3 of 5% NaF before extraction. The interference from Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Pd^{2+}, Zn^{2+}, and Cd^{2+} in the determination of lead can also be eliminated by adding 10 cm^2 of 5% NaCN solution before extraction (Table 2).

Determination of Lead, Zinc, and Cadmium in Alloys and Synthetic Mixtures. A Sample of 100 mg of the alloy of known composition was taken in a beaker and 15—20 cm^3 of concentrated nitric acid were added. When the vigorous reaction was over, the solution was evaporated on a hot plate to about 5 cm^3. It was diluted with 50 cm^3 of distilled water, heated again for 20—25 min, filtered through a Whatman No.42 filter paper and the filtrate was collected in a 1 liter volumetric flask. The residue was washed ten times with dilute HNO_3 (1:1000) and the volume was made upto the mark with distilled water. An aliquot of this sample solution was taken and analyzed by the general procedure already stated. Five replicate determinations were made for each sample. The interference of various ions have been eliminated as stated in Table 2.

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