Analysis of Metals by Solid-Liquid Separation after Liquid-Liquid Extraction. Spectrophotometric Determination of Some Metals by Extraction of Metal Complexes with Molten Naphthalene

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A procedure is described for the spectrophotometric determination of metals after extraction with molten naphthalene. Some metal ions react in aqueous solution with complex-forming reagents such as oxine, 2-methyloxine, dimethylglyoxime or α-benzil dioxime to form water-insoluble complexes in certain pH ranges, the complexes being easily extracted into molten naphthalene. The extracted mixture of metal complex and naphthalene is dissolved in dimethylformamide and the amount of each metal is determined spectrophotometrically. The working range of metal ion concentration and effect of various factors such as pH, amount of reagent and naphthalene were studied, and the molar absorptivity, sensitivity and relative standard deviation evaluated.

Spectrophotometric determination of metals in aqueous solution after extraction of their complexes with organic solvent have been widely employed in the analysis of trace amount of metal ions. However, the method is not applicable when the solubility of the complexes in the solvent is small.

We have developed a new method "solid-liquid separation after liquid-liquid extraction," and have applied it to the determination of copper,[1,2] zinc,[3] magnesium,[4] and cadmium[5] with oxine as the complex-forming reagent, and to that of nickel[6] and palladium[7] with dimethylglyoxime. The method is based on the formation of metal complex which is extractable quantitatively with molten naphthalene. After the mixture of solidified complex and naphthalene have been cooled, it is dissolved in adequate organic solvent and the amount of metal in the solution is determined spectrophotometrically. The method is useful for the determination of metals such as zinc, magnesium or cadmium, since direct extraction of the complex with conventional solvents such as benzene or chloroform is very difficult owing to its hydrated structure. Each complex is easily extracted at high temperature merely by being put in contact with molten naphthalene. The extract is easily dissolved in dimethylformamide to develop intense coloration of the stable complex. In the present paper, successful extraction of the following complexes into molten naphthalene is presented: oxine complex of copper, zinc, magnesium and cadmium, 2-methyloxine complex of copper, dimethylglyoxime complex of nickel, and α-benzildioxime complex of nickel.

Experimental

Reagents. Standard 0.01 M metal solutions. Stock solutions of copper, zinc, magnesium, cadmium and nickel were prepared by dissolving copper sulfate, zinc sulfate, magnesium chloride, cadmium chloride and nickel sulfate of reagent grade in water weakly acidified with a few drops of concentrated sulfuric acid or hydrochloric acid and standardized chelatometrically. It was diluted suitably before use.

1% oxine and 2-methyloxine solutions. Prepared by dissolving 1.0 g of oxine or 2-methyloxine in 2 ml of glacial acetic acid on a water bath and diluting to 100 ml with water.

0.5% dimethylglyoxime and 0.02% α-benzil dioxime solutions in ethanol.

Buffer solutions. Mixtures of 1 M acetic acid and 1 M sodium acetate, 0.5 M disodium hydrogen phosphate and 0.5 M potassium dihydrogen phosphate, or 1 M ammonia water and 1 M ammonium chloride.

Redistilled demineralized water was used.

Naphthalene, dimethylformamide and all other reagents were of analytical reagent grade and used without further purification.

Apparatus. A Hitachi Model 124 spectrophotometer was used for the absorbance measurements with matched 10 mm glass cells. A Toa-Dempa HM-6A pH meter equipped with combined glass and calomel electrodes was used for pH measurements.

Procedure. Transfer an aliquot of standard metal solution to a tightly stoppered 80 ml Erlenmeyer flask and

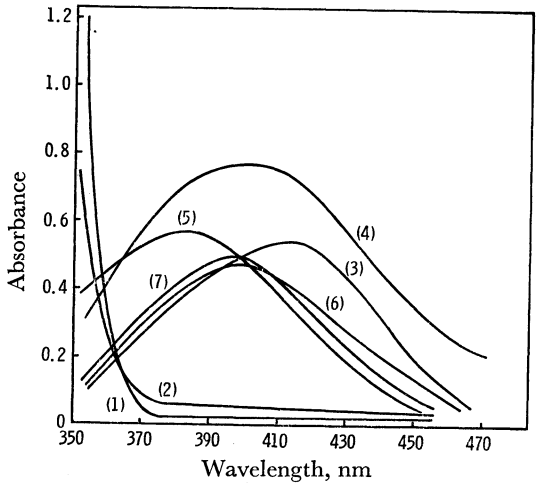

Fig. 1. Absorption spectra of oxine, 2-methyloxine and metal complexes in naphthalene–dimethylformamide solution.
(1) 1% oxine: 1.0 ml; pH: 5.0; against water
(2) 1% 2-methyloxine: 1.5 ml; pH: 5.5; against water
(3) Cu: 64 μg; 1% oxine; 1.0 ml; pH: 5.0
(4) Zn: 262 μg; 1% oxine: 1.0 ml; pH: 8.9
(5) Mg: 73 μg; 1% oxine: 2.0 ml; pH: 9.9
(6) Cd: 100 μg; 1% oxine: 1.5 ml; pH: 7.5
(7) Cu: 64 μg; 1% 2-methyloxine: 1.5 ml; pH: 5.5
Reference: Reagent blank

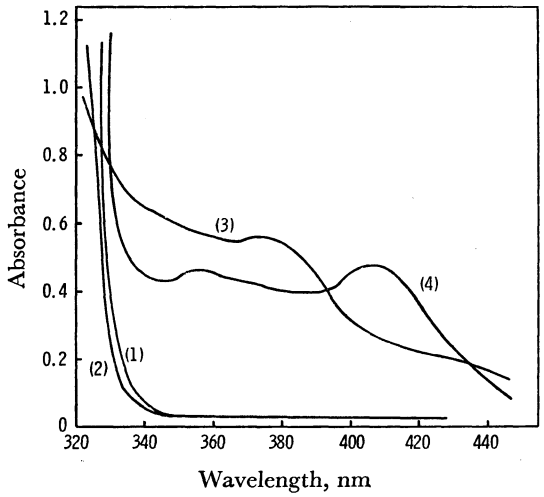

Fig. 2. Absorption spectra of dimethylglyoxime, α-benzil dioxime and metal complexes in naphthalene–dimethylformamide solution
(1) 0.5% dimethylglyoxime: 0.5 ml; pH: 8.6; against water
(2) 0.02% α-benzil dioxime: 3.0 ml; pH: 9.0; against water
(3) Ni: 117 μg; pH: 8.6; 0.5% dimethylglyoxime: 0.5 ml
(4) Ni: 29.4 μg; pH: 9.0; 0.02% α-benzil dioxime: 3.0 ml
Reference: Reagent blank

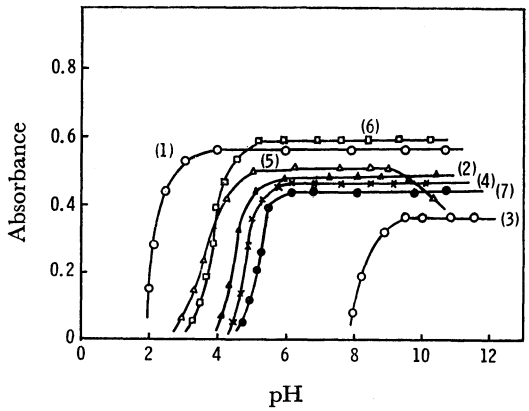

Fig. 3. Effect of pH on absorbance
(1) Cu: 64 μg; 1% oxine: 1.0 ml; Wavelength: 412 nm
(2) Zn: 163 μg; 1% oxine: 1.0 ml; Wavelength: 400 nm
(3) Mg: 49 μg; 1% oxine: 2.0 ml; Wavelength: 384 nm
(4) Cd: 100 μg; 1% oxine: 1.5 ml; Wavelength: 400 nm
(5) Cu: 64 μg; 1% 2-methyloxine: 1.5 ml; Wavelength: 400 nm
(6) Ni: 117 μg; 0.5% dimethylglyoxime: 0.5 ml; Wavelength: 374 nm
(7) Ni: 29 μg; 0.02% α-benzil dioxime: 3.0 ml; Wavelength: 406 nm
Reference: Reagent blank

dilute to about 30 ml with water. Add the complex-forming reagent and then adjust the pH with a buffer solution. Mix the solution well and allow it to stand for 15 min and then warm gently on a water bath at 60 °C until a precipitate of the metal complex appears. Add 2.0 g of naphthalene and heat the mixture to 90 °C. Shake it vigorously till naphthalene solidifies forming fine crystals. Melt it again and shake well, then allow it to cool to room temperature. Warm it again and slowly melt the very fine solidified crystals suspended in the solution, letting them grow to a larger crystalline deposit. After cooling it at room temperature, separate the solidified deposit on a filter paper, wash with water and blot the surplus water with a dry filter paper. Dissolve the deposit with dimethylformamide. Transfer the solution to a 25 ml volumetric flask, fill with dimethylformamide up to 25 ml, and measure the absorbance of the solution in a 10 mm cell against the reagent blank.

Results and Discussion

Figures 1 and 2 show the absorption spectra of metal complexes in naphthalene–dimethylformamide solution against the reagent blank. These complexes have their absorption maxima in the range 370—410 nm, whereas the reagent shows no absorption above 370 nm.

Figure 3 shows the effect of pH on the absorbance of metal complexes in naphthalene–dimethylformamide

TABLE 1. SPECTROPHOTOMETRIC DETERMINATION OF METALS IN NAPHTHALENE-DMF

Metal complexes	Max. wavelength (nm)	pH of extraction	Amount of reagent (ml)	Calibration curve (ppm)	Molar absorptivity ($l \cdot mol^{-1} \cdot cm^{-1}$)	Sensitivity (g/cm^2)	Relative standard deviation (%)
Cu–oxinate	412	3.5—	1% oxine, 0.3—1.5	0.6—10	5.4×10^3	0.012	1.16
Zn–oxinate	400	5.5—10.5	1% oxine, 0.3—3.0	0.7—14	4.6×10^3	0.013	0.45
Mg–oxinate	384	9.5—	1% oxine, 1.5—2.0	0.3— 5	4.5×10^3	0.006	1.40
Cd–oxinate	400	6.0—	1% oxine, 1.0—2.0	1.0—16	5.5×10^3	0.020	1.01
Cu–2-methyl-oxinate	400	5.5—9.0	1% 2-methyloxine, 1.0—3.0	0.6—10	5.2×10^3	0.012	1.06
Ni–dimethyl-glyoximate	374	5.5—	1% dimethylglyoxime, 0.2—1.0	1.0—23	3.0×10^3	0.020	0.92
Pd–dimethyl-glyoximate	370	1.1—7.8	1% dimethylglyoxime, 1.0	3.0—53	1.7×10^3	0.062	0.64
Ni–α-benzil dioximate	406	6.0—	0.02% α-benzil dioxime, 1.5—	0.4— 6	9.0×10^3	0.006	0.88

Naphthalene: 2.0 g, Solvent: Chloroform for Pd, Dimethylformamide for other metals

solution against the reagent blank. The pH values of the aqueous solution after extraction were measured at room temperature. The pH values were adjusted with acetate, phosphate or ammonia buffer solution except for the extraction of cadmium.

The amounts of naphthalene were varied from 0.5 to 3.0 g, extraction operation being carried out by the recommended procedure. Addition of naphthalene above 1.5 g gave no effect on the results. 2.0 g of naphthalene was adequate for complete extraction of each metal complex.

Variation of absorbance with the amount of complex-forming reagent was relatively small over the large amount of the reagent. The amount of buffer solution, 0.5—5 ml, had no effect on the absorbance. Acetate and ammonium salts gave considerable error, both positive and negative, for cadmium determination. Since the speed of extraction of metal complexes into molten naphthalene is great owing to high temperature, extraction is completed merely by contact with molten naphthalene or by slight shaking. It is not necessary to remove water on naphthalene crystals with anhydrous sodium sulfate, since dimethylformamide is miscible with water. The results obtained are summarized in Table 1. The calibration curve for each metal was derived at a proper wavelength against the reagent blank. The molar absorptivity, sensitivity and relative standard deviation on each metal were also calculated for ten determinations.

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