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The Extraction-spectrophotometric Determination of Lead with Bismuthiol II

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The solvent extraction-spectrophotometric determination of lead(II) with bismuthiol II was conducted in the presence of 1,10-phenanthroline(phen). Lead(II) was quantitatively extracted as ternary complexes into the chloroform phase over the pH range of 3.0—7.0. The composition of the extracted ternary complexes were confirmed to be Pb: bismuthiol II: phen=1 : 2 : 2 or 1 : 2 : 1, depending on the concentration of bismuthiol II added to the aqueous solution. The absorption maximum of the ternary complex (1 : 2 : 2) in chloroform was found to be at 342 nm, with a molar extinction coefficient of 3.5×10^4 dm^3 mol^{-1} cm^{-1}. Under optimum conditions, the absorbance follows Beer's law up to 300 μg of lead in 10 ml of chloroform. The coefficient of the variation was 1.3% for 30 μg of lead. Many elements interfered with the determination of lead(II). However, the interfering ions, with the exception of the indium and bismuth ions, were masked with a potassium cyanide solution. The proposed method was then applied to the determination of lead in standard zinc metals. A good agreement was observed between the results obtained by the proposed method and the standard values of the samples.

Bismuthiol II (3-phenyl-5-mercapt-1,3,4-thiadiazole-2-thione) has been used for the gravimetric determination of various metal ions, and it is well-known to be chelating reagent which is useful for the sensitive colorimetric determination of selenium[1] and tellurium.[2] The determination of lead(II) with bismuthiol II was made by gravimetry.[3,4] The spectrophotometric determination of lead(II) has not, however, been studied because of the insolubility in water of the complexes formed and because it is impossible to extract them into organic solvents.[5] From experiments employing synergistic extraction, we found that the lead–bismuthiol II chelate was extracted into chloroform to form a ternary complex with 1,10-phenanthroline (phen). In the present study, the fundamental conditions for the extraction of lead(II) as the lead–bismuthiol II–phen in chloroform, the composition of the ternary complex, and its application to the determination of lead(II) are discussed. As a result, a highly selective method for the spectrophotometric determination of small amounts of lead(II) has been established and then applied to the determination of lead(II) in zinc metals.

Experimental

Reagents. *A Lead(II) Standard Stock Solution (1.00 mg/ml)*: 0.2500 g of lead metal (Wako Pure Chemicals, 99.99%) was dissolved in a small amount of dilute nitric acid, and the solution was diluted with water in a 250-ml volumetric flask (nitric acid was added to make the final acidity 0.01 mol dm^{-3}). The solution was then diluted as required.

0.1% Phen Solution: 0.1 g of phen (Wako Pure Chemicals) was dissolved with a small amount of ethanol, after which the mixture was diluted to 100 ml with water.

Buffer Solution: An acetate buffer solution was prepared by mixing 0.5 dm^3 of 2 mol dm^{-3} acetic acid with 0.5 dm^3 of 2 mol dm^{-3} sodium acetate.

The other reagents used were all of an analytical reagent grade.

Standard Procedure. An aliquot of a standard lead(II) solution was transferred to a 100-ml beaker, and then the buffer solution and the phen solution were added. After the solution had been diluted to 50 ml with water, the pH of the solution was adjusted with diluted hydrochloric acid or ammonia and a 0.1% bismuthiol II solution was added. The resulting aqueous solution was then transferred into a separatory funnel. The lead complex thus formed was extracted with 10 ml of chloroform by shaking it vigorously for 2 min. After the separation of the mixture into two phases, the organic phase was transferred into a 10-mm quartz cell and the absorbance of the extract at 342 nm or 370 nm wasmeasured against the reagent blank or chloroform.

Results and Discussion

Absorption Spectra. Bismuthiol II reacts with lead(II) to form a pale yellow complex. The absorption spectra of the Pb–bismuthiol II–phen complex and the Pb–bismuthiol II chelate extracted are shown in Fig. 1. The ternary complex has an apparent absorption maximum at 342 nm, whereas the Pb–bismuthiol II chelate gives hardly any absorbance because it is

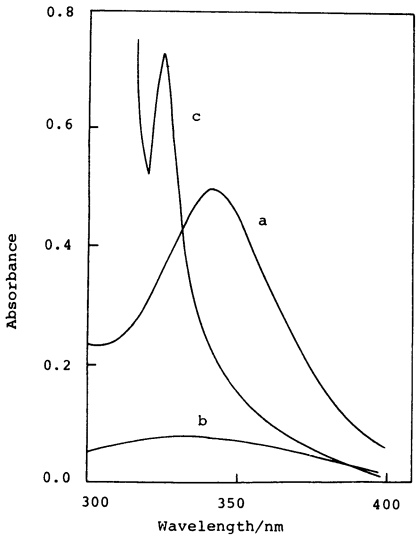

Fig. 1. Absorption spectra.
a): 0.1% phen 2 ml; Pb 30 μg, b): 0.1% phen none; Pb 30 μg, c): 0.1% phen 2 ml; Pb none. 0.1% bismuthiol II: 2 ml; pH: 4.0, reference: reagent blank (a, b); chloroform (c).

unextractable into chloroform.

Effect of pH. After the pH of solutions containing 30 μg of lead(II) and 2 ml of a 0.1% phen solution had been controlled to the desired values with aqueous ammonia and hydrochloric acid, 2 ml of a 0.1% bismuthiol II solution was added to the solution and the extraction was carried out by the above procedure. The results are shown in Fig. 2. Since the absorbance of the reagent blank increased remarkably below pH 2.5, the measurement of the absorbance at 342 nm became impossible below pH 2.5; therefore, the absorbance of the organic phase was measured at 370 nm, where the effect of absorption due to the reagent blank was less than at 342 nm. The extraction of the ternary complex starts at pH 0, reaches a maximum at pH 3.0, and thereafter remains constant over the range of pH 3.0—7.0. When a dilute reagent solution (0.2 ml of a 0.1% bismuthiol II solution) and 0.2 ml of 0.1% phen were used to examine the optimum pH over the range of 3.0—7.0, the absorbance of the extract showed a maximum at pH 3.5. All the extraction, however, was carried out at pH 4.0 in consideration of the effect of the reagent blank.

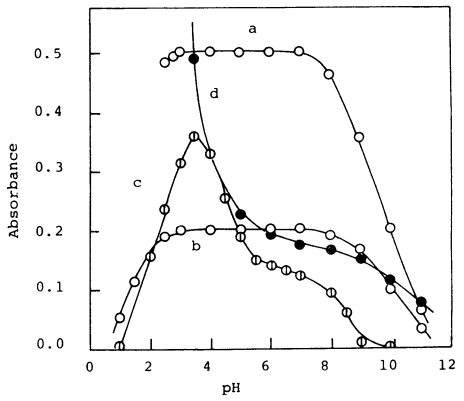

Fig. 2. Effect of pH on absorbance.
a, b): 0.1% bismuthiol II 2 ml; 0.1% phen 2 ml; Pb 30 μg, c): 0.1% bismuthiol II 0.2 ml; 0.1% phen 0.2 ml; Pb 30 μg, d): 0.1% bismuthiol II 2 ml; 0.1% phen 2 ml; Pb none, wavelength: 342 nm (a, c, d), 370 nm (b), reference: reagent blank (a, b, c); chloroform (d).

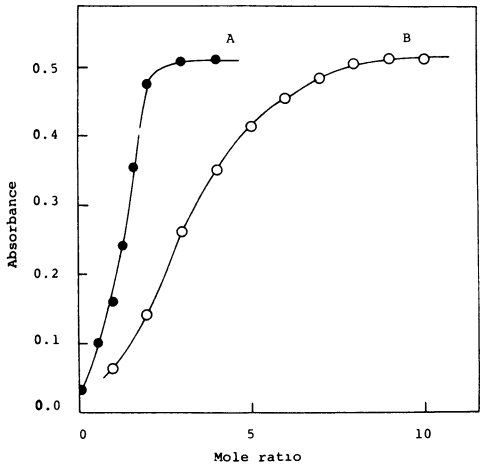

Fig. 3. Effect of amount of reagents.
A) Effect of amount of phen: 0.1% bismuthiol II 2 ml, B) effect of amount of bismuthiol II: 0.1% phen 2 ml, Pb: 30 μg, pH: 4.0, wavelength: 342 nm.

Effect of Bismuthiol II and Phen Concentrations. The extraction of lead(II) from aqueous solutions containing bismuthiol II in varying concentrations was examined, the phen concentration (2 ml of a 0.1% solution in 50 ml of an aqueous solution), the amount of lead (30 μg), and other variables being kept constant. The results are shown in Fig. 3. The absorbance of the extract was found to be constant above 2.9×10^{-5} mol dm^{-3} (mole ratio of lead : bismuthiol II = 1 : 10, Curve B). In the same way, the effect of the phen concentration is shown by Curve A, more than three-fold excess of phen over the lead concentration is necessary in order to obtain the maximum absorbance. The absorbance at a mole ratio of zero in Curve A corresponds to that of the binary Pb–bismuthiol II chelate.

Effect of Shaking Time. A 10 ml portion of chloroform was added to a solution containing the ternary complex, and the mixed solution was shaken vigorously. The ternary complex was completely extracted into chloroform by vigorous shaking for 30 s. Shaking for 1 min was found to be satisfactory for complete extraction.

Effect of Standing Time. The absorbance of the ternary complex in a closed quartz cell was measured at 5 min intervals. The absorbance was constant until 30 min, past which it decreased gradually. On the other hand, the absorbance of the ternary complex extracted from an aqueous solution containing 2 ml of 5% ascorbic acid remained unchanged, even after 2 h at room temperature.

Effect of Volume of Aqueous Phase. For the investigation of the effect of the volume of the aqueous solution, the volume of the aqueous phase was changed between 20 and 200 ml, the other factors being kept constant. The absorbance of the extract gradually increased in proportion to the volume of the aqueous phase.

Organic Solvents. Several kinds of organic solvents were tested in order to achieve a quantitative extraction of the lead complex. The ternary complex was extracted only in chloroform, not quantitatively in such solvents as benzene, toluene, xylene, carbon tetrachloride, isobutyl methyl ketone, ethyl acetate, and diisopropyl ether.

Calibration Curve and Molar Extinction Coefficient. A calibration curve for the determination of lead was made under optimum conditions. A good linear relationship was obtained over the concentration range from 3 μg to 300 μg of lead per 10 ml of chloroform. The molar extinction coefficients were 3.52×10^{4} dm^{3} mol^{-1} cm^{-1} (at 342 nm) and 3.72×10^{3} dm^{3} mol^{-1} cm^{-1} (at 400 nm), the sensitivity being 5.9×10^{-3} μg per cm^{2} for an absorbance of 0.001 (at 342 nm). Thirty replicate determinations of a sample solution containing 30 μg of lead(II) gave the coefficient of the variation of 1.3%. The extractability of the lead complex was larger than 99% under optimum conditions.

Composition of the Ternary Complexes. By the use of the equilibrium-shift method, lead: bismuthiol II

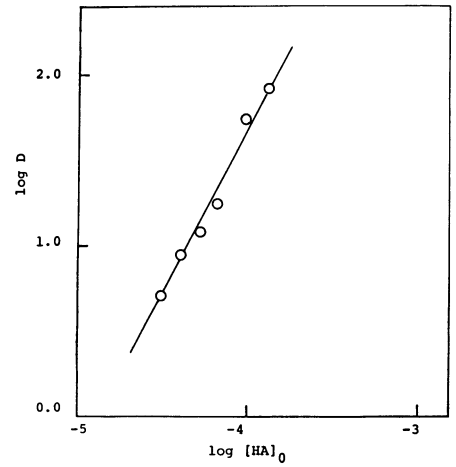

Fig. 4. Determination of the mole ratio of Pb: bismuthiol II in the ternary complex by equilibrium-shift method. Reference: reagent blank, 0.1% phen: 2 ml, Pb: 30 μg, pH: 4.0, aqueous phase: 50 ml, D: distribution ratio, $[HA]_0$: concentration of bismuthiol II in chloroform phase.

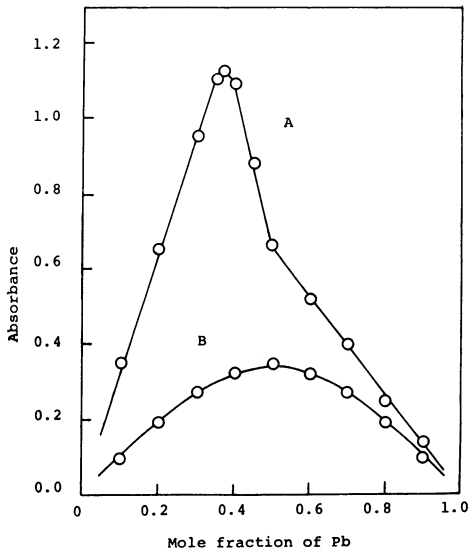

Fig. 5. Determination of the mole ratio of Pb: phen in the ternary complex by the continuous variation method.
Reference: reagent blank, pH: 4.0, 0.1% bismuthiol II: 2 ml (A), 0.2 ml (B), $[Pb]+[phen]=9.66\times10^{-6}$ mol dm^{-3} (50 ml).

Table 1. Effects of foreign ions

Ions	Amount (μg)	Added as	Pb found (μg)	Tolerance limits (μg)
Ag(I)	10	$AgNO_3$	36.7	0.4
Al(III)	1000	$Al(NO_3)_3\cdot9H_2O$	30.0	1000
As(III)	1000	As_2O_3+NaOH	30.0	1000
Au(III)	10	$HAuCl_4\cdot4H_2O$	38.2	0.3
Ba(II)	1000	$BaCl_2\cdot2H_2O$	30.0	1000
Bi(III)	10	Bi+HNO_3	37.8	0.3
Ca(II)	1000	$CaCl_2$	30.0	1000
Cd(II)	10	Cd+HNO_3	43.2	0.2
Co(II)	10	Co+HNO_3	92.3	0.1
Cr(III)	1000	$Cr(NO_3)_3\cdot9H_2O$	30.0	1000
Cu(II)	10	Cu+HNO_3	48.1	0.1
Fe(III)	10	Fe+HNO_3	62.4	0.1
Ga(III)	1000	Ga+HCl	30.0	1000
Hg(II)	10	$HgCl_2$	35.3	0.5
In(III)	10	In+HNO_3	59.1	0.1
Mg(II)	1000	MgO+HCl	30.0	1000
Ni(II)	10	Ni+HCl	52.5	0.1
Pd(II)	10	$PdCl_2$+HCl	44.2	0.2
Sb(III)	1000	Sb+H_2SO_4	30.0	1000
Sn(II)	1000	Sn+HCl	30.0	1000
Tl(I)	1000	$TlNO_3$	30.0	1000
V(V)	50	V+Aqua regia	39.1	5
W(VI)	100	$Na_2WO_4\cdot2H_2O$	28.0	15
Zn(II)	10	Zn+HCl	45.1	0.2

Pb taken: 30.0 μg. Wavelength: 342 nm.

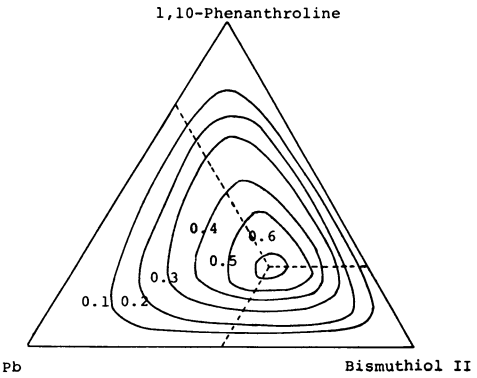

Fig. 6. Continuous variation method applied to three component system of Pb–bismuthiol II–phen complex. $[Pb]+[bismuthiol\ II]+[phen]=2.86\times10^{-5}$ mol dm^{-3}.

was found to be 1 : 2, as is shown in Fig. 4. On the other hand, lead : phen was obtained to be 1 : 1 or 1 : 2, depending on the concentration of bismuthiol II added to the aqueous solution. The 1 : 1 complex was formed in lower concentrations of bismuthiol II (6-fold of the Pb concentration), while the other complex was formed in a higher concentration of the reagent (60-fold) (Fig. 5). A triangular coordinate method extended to the three-component system of the continuous-variation plot was applied to the determination of the ternary complex. The results are shown in Fig. 6. The maximum absorbance is obtained at the mole ratio of lead: bismuthiol II: phen=1 : 2 : 1.

Effects of Diverse Ions and of Masking. The experimental results are summarized in Table 1. Each 10 μg of silver, gold, bismuth, cadmium, cobalt, copper, iron, mercury, indium, nickel, palladium, vanadium, and zinc interferes with the determination of lead. The interference of such ions as silver (up to 10 mg), gold (up to 8 mg), cadmium (up to 1 mg), cobalt (up to 100 μg), copper (up to 10 mg), mercury (up to 1 mg), nickel (up to 10 mg), vanadium (up to 10 mg), iron (up to 20 μg), and zinc (up to 10 mg) can be masked by the use of 20 ml of a 2% potassium cyanide solution. Zinc in the determination of lead in a metal was confirmed to be masked up to 0.5 g with 20 ml of 20%

TABLE 2. ANALYTICAL RESULTS OF ZINC-METAL STANDARD SAMPLES[a)]

Sample	Sample taken (mg)	Pb found (μg)	Pb found (%)
H-501	497.2	23.5	0.00473
Pb 0.0048%	497.2	24.3	0.00489
	497.2	24.1	0.00485
	497.2	24.5	0.00493
	497.2	24.0	0.00483
		Average	0.00485
H-502	15.43	31.1	0.202
Pb 0.21%	15.43	33.0	0.214
	15.43	31.4	0.203
	15.43	31.2	0.202
	15.43	31.9	0.207
		Average	0.206
H-503	2.969	32.3	1.088
Pb 1.11%	2.969	33.2	1.118
	2.969	32.5	1.095
	2.969	32.0	1.078
	2.969	32.9	1.108
		Average	1.097

a) Japanese standard samples (Kagaku Gijutusha Co.).

potassium cyanide. Indium and bismuth were not masked.

Determination of Lead in the Zinc Metal. The proposed method was applied to the analysis of lead in zinc metal. A sample solution was prepared as follows : Take less than 5 g of a sample in a beaker and dissolve the sample with 60 ml of nitric acid (2+1). Then dilute the solution to 100 ml in a volumetric flask.

A 10 ml aliquot (3—300 μg Pb) of this sample solution was taken for analysis, a 20 ml portion of a 20% potassium cyanide solution was used as a masking reagent in a draft chamber, and the pH of the sample solution was adjusted to pH 7. Two ml of a 0.1% phen solution and 2 ml of a 0.1% bismuthiol II solution were used as reagents.

The lead in standard samples of zinc metal was determined by the proposed method. The analytical results are shown in Table 2. Good agreement was observed between results obtained by the proposed method and the standard values of the samples. The present method is rapid and accurate enough for the determination of lead in zinc metal.

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