Kinetic and Spectrophotometric Determination of Trace Zinc(II) in the Presence of a Large Amount of Lead(II) Using Ligand-Substitution Reactions of Their Metalloporphyrins with EDTA

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The formation constant of lead(II) complex of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine (H_2TPPS_4) ($\log K$) defined as $Pb^{2+} + H_2TPPS_4 \rightleftharpoons Pb(II)(TPPS_4) + 2H^+$ was found to be -9.97 ± 0.02 , which is approximately 10^9 times as small as that of $Zn(II)(TPPS_4)$. In addition, $Pb(II)(TPPS_4)$ was rapidly replaced with EDTA at a half-life time of 200 ms. On the other hand, $Zn(II)(TPPS_4)$ is stable and not replaced with EDTA even after 2 h. The large difference in the equilibrium and kinetic behavior between $Zn(II)$ - and $Pb(II)(TPPS_4)$ allows the determination of zinc(II) at as low as 10^{-7} mol dm $^{-3}$ concentration level in the presence of 10^{-2} mol dm $^{-3}$ lead(II). The molar absorptivity of $Zn(II)(TPPS_4)$ is 4.66×10^5 mol $^{-1}$ dm 3 cm $^{-1}$. The method was applied to the determination of zinc(II) in lead chemicals (lead(II) nitrate, lead(II) acetate and lead metal) and in tap and waste waters by measurement of the absorbance at 421 nm. The optimum conditions of the ligand-buffer solution containing aminopolycarboxylates and lead(II) are described to remove the interference of copper(II), cobalt(II) and manganese(II).

Keywords Zinc(II) determination, lead(II) chemicals, water, spectrophotometry, porphyrin

Most of colorimetric reagents for the determination of metals form stabler complexes with lead(II) than with zinc(II).^{1,2} Therefore, it is difficult to determine zinc(II) spectrophotometrically in the presence of a large amount of lead(II). However, we found that the formation constant of zinc(II) with tetrakis(4-sulfonatophenyl)porphine (H_2TPPS_4) is larger by about 10^9 times than that of lead(II). In addition, $Zn(II)(TPPS_4)$ is stable and is not replaced with ethylenediaminetetraacetic acid (EDTA) even after 2 h, while $Pb(II)(TPPS_4)$ is completely replaced with EDTA within 2 s. The large differences in the equilibrium and kinetic behavior between $Zn(II)$ - and $Pb(II)(TPPS_4)$ were applied to the determination of zinc(II) in the presence of a large amount of lead(II). The high molar absorptivity of $Zn(II)(TPPS_4)$ (4.66×10^5 mol $^{-1}$ dm 3 cm $^{-1}$) allows the determination of zinc(II) at as low as 10^{-7} mol dm $^{-3}$ concentration level in the presence of 10^{-2} mol dm $^{-3}$ lead(II). Zinc(II) complex with tetrakis(1-methylpyridinium-4-yl)porphine (H_2TMPyP) is also about 10^8 to 10^9 times as stable as lead(II).^{3,4}

The large equilibrium and kinetic differences between lead(II) and zinc(II) can be ascribed to the ionic radii difference (132 pm for Pb^{2+} ; 89 pm for Zn^{2+}). Large metal ions such as lead(II), mercury(II) and cadmium(II) can not incorporate well into porphyrin core and just sit on the porphyrin plane.⁵⁻⁸ Barkiga *et al.* called lead(II) porphyrin a "roof complex" after an X-ray

analysis of tetrakispropylporphinatolead(II).⁹ The roof metalloporphyrin therefore dissociates easily to form free porphyrin in acid or is replaced with EDTA.^{3,10-12} On the other hand, zinc(II) incorporates well into porphyrin core^{13,14} and is so stable that $Zn(TPPS_4)$ is not replaced with EDTA. Noticing a difference of 10^{12} times in the acid-dissociation rate of zinc(II)- and cadmium(II)($TPPS_4$), we have proposed a kinetic method for the determination of zinc in a large excess of cadmium.¹⁰ After that, Ishii and Tsuchiai have reported a spectrophotometric and analogue derivative spectrophotometric determination of trace zinc in the presence of a high concentration of cadmium using ligand-substitution reaction with EDTA; but the extent of the different reactivity of zinc and cadmium has not been clear in both equilibrium and kinetics.¹² In the present paper, we clarify both the kinetic difference of 4×10^{11} times and the thermodynamic difference of 10^9 times between zinc(II)- and lead(II)-($TPPS_4$) in the ligand-substitution reaction of the metalloporphyrins with EDTA, and propose a kinetic spectrophotometric determination of zinc in a large excess of lead using the ligand substitution reaction of the metalloporphyrins with EDTA.

The reaction for the present study is

where M denotes zinc(II) or lead(II). The present method was applied to the determination of zinc(II) in lead chemicals and in tap and waste waters. The interference from copper(II) and cobalt(II) was removed by a ligand-buffer solution containing aminopolycarboxylate and lead(II).

Experimental

Reagents

5,10,15,20-Tetrakis(4-sulfonatophenyl)porphine (H_2TPPS_4) was synthesized and its sodium salt was purified by a published method.⁶ The purity was checked by thin layer chromatography and nuclear magnetic resonance spectroscopy. Solutions of zinc(II) and lead(II) were prepared from their nitrates, and the concentrations of zinc(II) and lead(II) in the stock solutions were determined by EDTA titration. EDTA, 3-carboxymethyl-6-(2-hydroxyethyl)-3,6-diaza-heptanedioic acid (HEDTA) and 3,12-bis(carboxymethyl)-6,9-dioxo-3,12-diaza-tetradecanedioic acid (EGTA) were purchased from DOJINDO Laboratories (Kumamoto, Japan). All other reagents were analytical reagent grade.

Procedure

A sample solution (25 cm³) containing zinc(II) (10^{-7} – 2×10^{-6} mol dm⁻³), lead(II) (2×10^{-3} – 2×10^{-2} mol dm⁻³) is taken in a brown 50 cm³ volumetric flask, and following solutions were added in the order as described: 5 cm³ of acetate buffer (pH 6.0; 5×10^{-1} mol dm⁻³), 2.5 cm³ of imidazole (1.0 mol dm⁻³; pH 6), 1 cm³ of H_2TPPS_4 (1.0×10^{-4} mol dm⁻³). The solution was allowed to stand for 30 min to complete the formation of Zn(II)(TPPS₄).

A 5 cm³ portion of EDTA (0.1 mol dm⁻³) was added to the solution to replace Pb(II)(TPPS₄) with EDTA and the solution was diluted to the mark (50 cm³). The absorbance was measured at 421 nm (λ_{max} of Zn(II)(TPPS₄)).

The formation constant of lead(II)(TPPS₄) was determined spectrophotometrically at pH 6.0 (*N,N'*-bis(2-sulfonatoethyl)piperazine: PIPES buffer (10^{-2} mol dm⁻³)), at an ionic strength of 0.1 mol dm⁻³ ($NaNO_3$) and 25°C. The absorption spectra were recorded by a Hitachi 323 UV-VIS spectrophotometer in a 1 cm cell with a thermostated water jacket. The pH values were determined by a Toa digital pH-meter HM-15A with a reference electrode (Metrohm EA 404) and a glass electrode (Metrohm EA 109). A 1.000×10^{-2} mol dm⁻³ nitric acid solution containing 0.09 mol dm⁻³ sodium nitrate was employed as a standard of hydrogen ion concentration ($-\log[H^+] = 2.000$).

Results and Discussion

Formation of Pb(II)(TPPS₄)

The absorption spectrum of H_2TPPS_4 changed

considerably in the presence of lead(II): the absorbance at 413 nm decreased and that at 465 nm (absorption maximum of Pb(II)(TPPS₄)) increased. Under the present experimental conditions (pH 6.0), porphyrin is in its free base form and hydrolysis of lead(II) can be negligible. The equilibrium for the formation of Pb(II)(TPPS₄) is thus written by Eq. (2) (charges on porphyrin and metalloporphyrins are omitted throughout) with the equilibrium constant defined by Eq. (3)

$$K = [Pb(II)(TPPS_4)][H^+]^2/[Pb^{2+}]^1[H_2TPPS_4]^{-1} \quad (3)$$

Absorption spectra of solutions containing various concentrations of lead(II) (4×10^{-4} – 5×10^{-3} mol dm⁻³) and H_2TPPS_4 (2.0×10^{-6} mol dm⁻³) show a clear isosbestic point at 428 nm. The formation constant was determined from the change in absorbances: $\log K = -9.97 \pm 0.02$. The value is 10^9 times smaller than the corresponding value for zinc(II) (-0.43 ± 0.03).⁷

Ligand-substitution reaction of Pb(II)- and Zn(II)(TPPS₄) with EDTA

The very small formation constant of Pb(II)(TPPS₄) compared with Zn(II)(TPPS₄) indicates that lead(II) does not incorporate well into a porphyrin core and just sits on the porphyrin plane, as shown by an X-ray study of lead(II) porphyrin.⁹ The results also imply the rapid replacement of Pb(II)(TPPS₄) with EDTA. Figure 1 shows the kinetic runs for the ligand-substitution reaction of Pb(II)- and Zn(II)(TPPS₄) with EDTA (10^{-2} mol dm⁻³) at pH 6.0. Pb(II)(TPPS₄) is replaced with EDTA at a half-life time of 200 ms, but Zn(II)(TPPS₄) is not replaced even after 2 h. The conditional formation constants defined as $K' = [M(TPPS_4)][M^{2+}]^{-1} \times$

Fig. 1 Ligand-substitution reaction of Zn(II)(TPPS₄) and Pb(II)(TPPS₄) with EDTA ($C_{EDTA} = 10^{-2}$ mol dm⁻³) at 25°C and pH 6.0.

$[H_2TPPS_4]^{-1} = K[H^+]^{-2}$ ($M = Pb^{2+}$ and Zn^{2+}) are $10^{2.03}$ and $10^{11.5}$ at pH 6.0 for lead(II)- and zinc(II)(TPPS₄), respectively. The conditional formation constants of the Pb(II)- and Zn(II)(EDTA) complexes are $10^{13.55}$ and $10^{11.91}$ at pH 6.0.² Comparison of the conditional formation constants of Zn(II)(TPPS₄) with that of Zn(II)(EDTA) predicts that Zn(II)(TPPS₄) would be replaced thermodynamically with EDTA in a large excess of EDTA at pH 6.0 ($CH_2TPPS_4 = 2.0 \times 10^{-6}$ mol dm⁻³ and $C_{EDTA} = 10^{-2}$ mol dm⁻³). The rate of the ligand-substitution reaction of Pb(II)(TPPS₄) depends on both EDTA and hydrogen ion concentrations. In contrast, that of Zn(II)(TPPS₄) is independent of EDTA concentration and depends on only that of hydrogen ions. The half-life time of Zn(II)(TPPS₄) is 8.7×10^{10} s ($= 10^6$ d) at pH 6.0; this value was calculated from the acid-dissociation rate constant of Zn(II)(TPPS₄). Zn(II)(TPPS₄) dissociates 4×10^{11} times as slow as Pb(II)(TPPS₄) at pH 6.0 and at $C_{EDTA} = 10^{-2}$ mol dm⁻³. The large kinetic difference is comparable to the previous kinetic results concerning Cd(II)(TPPS₄) and Zn(II)(TPPS₄).¹⁰ The kinetic behavior also supports the qualitative observation of Cd(II)(TPPS₄) and Zn(II)(TPPS₄) reported by Ishii and Tsuchiai.¹² We will report the detail reaction mechanism for the ligand-substitution reaction of the metalloporphyrins with EDTA elsewhere.

The large difference between Pb(II)- and Zn(II)(TPPS₄) in their equilibrium and kinetic behavior allows the determination of zinc(II) in the presence of a large amount of lead(II). Figure 2 shows absorption spectra observed after the ligand-substitution reaction

Fig. 2 Absorption spectra observed after the addition of EDTA to solutions of Zn(II)- and Pb(II)(TPPS₄) mixture. CH_2TPPS_4 , 2.0×10^{-6} mol dm⁻³; C_{EDTA} , 1.00×10^{-3} ; pH 6.0. Concentrations of Zn(II)/ 10^{-7} mol dm⁻³: 0 (a); 2.97 (b); 5.91 (c); 8.87 (d); 11.8 (e); 14.7 (f).

with EDTA at various concentrations of zinc(II) (1.0×10^{-7} – 1.5×10^{-6} mol dm⁻³; 6 – 100 ppb Zn) in the presence of lead(II) (1×10^{-3} mol dm⁻³). The absorbance change at 421 nm is linearly correlated to the concentration of zinc(II) against the reagent blank. The molar absorptivity is 4.66×10^5 mol⁻¹ dm³ cm⁻¹.

Rate of formation of Zn(II)(TPPS₄)

The rate of formation of metalloporphyrin is very slow except for mercury(II), cadmium(II) and lead(II).⁶ The reaction, however, is accelerated 10^3 to 10^4 times in the presence of mercury(II), cadmium(II) or lead(II). Their metalloporphyrins make it easy for the medium size of metal ions to attack the porphyrin plane from the back.^{6,15} Figure 3 shows the catalytic effect of lead(II) on the formation of Zn(II)(TPPS₄). Pyridine, imidazole and amino acids also catalyze the formation of Zn(II)(TPPS₄) by about 10 to 100 times, as reported by Ishii and Tsuchiai¹², and Kawamura *et al.*¹⁶ The catalysts (L) form the molecular complexes as a reaction intermediate of $ZnL \cdot H_2TPPS_4$ through a hydrophobic interaction between the catalysts (L) and the porphyrin plane.¹⁷ Zn(II)(TPPS₄) is completely formed within 20 min in the presence of lead(II) (10^{-3} mol dm⁻³) and imidazole (5×10^{-2} mol dm⁻³) (Fig. 3).

Fig. 3 Rate of the formation of Zn(II)(TPPS₄) at 25°C, pH 6.0, $CH_2TPPS_4 = 1.00 \times 10^{-6}$ and $C_{Zn} = 3.87 \times 10^{-6}$ in the absence (1, ○) and presence (2, ▲ – 6, ⊙) of lead(II) and catalysts (L). $C_{Pb} = 9.80 \times 10^{-4}$ for (2) to (6). Catalysts and their concentrations are pyridine = 9.81×10^{-3} (3, □), imidazole = 9.79×10^{-3} (4, ●), pyridine = 9.81×10^{-3} and imidazole = 9.79×10^{-3} (5, △), imidazole = 4.89×10^{-2} (6). Unit of concentration is mol dm⁻³ for all solutions.

Table 1 Effect of foreign ions on the determination of zinc(II) in the presence of lead(II)

Ion	Concentration/mol dm ⁻³	Recovery, %
Ca ²⁺	1.00×10 ⁻³	106
Mg ²⁺	1.00×10 ⁻³	97
Sr ²⁺	1.00×10 ⁻⁴	100
Ba ²⁺	1.00×10 ⁻⁴	96
Mn ²⁺	9.98×10 ⁻⁶	87
Fe ³⁺	9.90×10 ⁻⁶	106
Al ³⁺	1.00×10 ⁻⁵	100
Co ²⁺	1.00×10 ⁻⁵	78
Ni ²⁺	1.00×10 ⁻⁵	102
Cu ²⁺	1.01×10 ⁻⁵	56
Hg ²⁺	1.01×10 ⁻⁵	104
Cd ²⁺	1.00×10 ⁻³	105
Cl ⁻	1.00×10 ⁻⁴	102
Br ⁻	9.96×10 ⁻⁴	96
I ⁻	1.00×10 ⁻³	102
SCN ⁻	1.00×10 ⁻⁴	101
SO ₄ ²⁻	1.00×10 ⁻⁵	100
S ₂ O ₃ ²⁻	1.00×10 ⁻⁴	99
SiO ₃ ²⁻	9.95×10 ⁻⁵	102
H ₂ PO ₄ ⁻	1.00×10 ⁻⁵	97

Zinc(II), 8.87×10⁻⁷ mol dm⁻³; lead(II), 1×10⁻³ mol dm⁻³; 25°C; pH 6.0; C_{H₂TPPS₄}, 2.00×10⁻⁶ mol dm⁻³; C_{imidazole}, 0.05 mol dm⁻³.

Effect of foreign ions

Table 1 shows the effect of the various cations and anions usually encountered in the determination of zinc(II). Most substances do not interfere with the determination of 8.87×10⁻⁷ mol dm⁻³ zinc(II), but copper(II), cobalt(II) and manganese(II) do. Such interference was removed by using a ligand-buffer solution consisting of aminopolycarboxylates (Y=EDTA, HEDTA and EGTA) and lead(II).

Optimum composition of ligand-buffer solution

Nakagawa and Tanaka have proposed the use of a ligand-buffer solution for the porlarographic determination of zinc(II) in the presence of cadmium.¹⁸ We determined the optimum composition of ligand-buffer solution to mask copper(II), cobalt(II) and manganese(II) for the determination of zinc(II) in a sample containing a large amount of lead(II), as follows.

In order to mask N (Cu(II), Co(II), Mn(II)) as completely as possible, most of N should be the form of NY:

$$[NY]/[N] = K_{NY}[Y] \gg 1, \quad (4)$$

and zinc(II) should be free ions:

$$[ZnY]/[Zn^{2+}] = K_{ZnY}[Y] \ll 1 \quad (5)$$

where K_{NY} and K_{ZnY} refer the formation constants of metal ion N and zinc(II) with Y, respectively. Lead(II) to be added as a component of the ligand buffer for masking the metal N should satisfy the condition:

Table 2 Effect of components of ligand buffer on the determination of zinc(II) by the present method

Y	C _Y /mol dm ⁻³	C _{Pb} /mol dm ⁻³	Recovery of Zn, %
EDTA	1.00×10 ⁻³	2.00×10 ⁻³	103
	1.00×10 ⁻³	3.00×10 ⁻³	104
	1.00×10 ⁻³	4.00×10 ⁻³	102
	5.00×10 ⁻⁴	1.00×10 ⁻³	101
	5.00×10 ⁻⁴	2.00×10 ⁻³	103
HEDTA	1.00×10 ⁻³	2.00×10 ⁻³	100
	1.00×10 ⁻³	3.00×10 ⁻³	103
	1.00×10 ⁻³	4.00×10 ⁻³	104
	5.03×10 ⁻⁴	1.00×10 ⁻⁴	98
	5.03×10 ⁻⁴	2.00×10 ⁻⁴	102
EGTA	1.01×10 ⁻³	2.00×10 ⁻³	96
	1.01×10 ⁻³	3.00×10 ⁻³	104
	1.01×10 ⁻³	4.00×10 ⁻³	102
	1.01×10 ⁻⁴	2.00×10 ⁻³	100
	2.02×10 ⁻⁴	2.00×10 ⁻³	101
	3.03×10 ⁻⁴	2.00×10 ⁻³	99

C_{Zn}, 8.87×10⁻⁷ mol dm⁻³; C_{H₂TPPS₄}, 2.00×10⁻⁶ mol dm⁻³; pH 6.0.

$K_{NY} > K_{PbY} > K_{ZnY}$. The concentration of free Y in the ligand buffer is calculated from the following equation:

$$[Y] = C_Y(C_{Pb} - C_Y)^{-1} K_{PbY}^{-1} \quad (6)$$

where C_Y and C_{Pb} denote the total concentrations of Y and lead(II), respectively.

EDTA, HEDTA and EGTA satisfying the condition of $K_{ZnY} < K_{PbY} < K_{NY}$ were used to mask copper(II), cobalt(II) and manganese(II) as the components of the ligand buffer. Cobalt(II) and manganese(II) complexes were oxidized to the corresponding trivalent metal complexes by hydrogen peroxide. The formation constants (logarithmic values) of zinc, lead and copper with EDTA, HEDTA and EGTA are 16.4, 17.9 and 18.7 for EDTA, 14.6, 15.5 and 17.5 for HEDTA, and 12.6, 14.5 and 17.6 for EGTA, respectively.² Table 2 summarizes the recovery of zinc(II) in the ligand-buffer solution containing aminopolycarboxylates and lead(II) in different portions. When C_{Pb}/C_Y is >2, the recovery of zinc(II) is quantitative for all three aminopolycarboxylates. Thus the following conditions were used to remove the interference of copper, cobalt and manganese: $C_{Pb}=2 \times 10^{-3}$ mol dm⁻³ and $C_Y=1 \times 10^{-3}$ mol dm⁻³ for the ligand buffers of Pb-EDTA and Pb-HEDTA components, and $C_{Pb}=2 \times 10^{-3}$ mol dm⁻³ and $C_Y=2 \times 10^{-4}$ mol dm⁻³, for that of Pb-EGTA component, respectively. The results are listed in Table 3. It was easy to mask cobalt(II) by oxidation to cobalt(III) complexes, but manganese was not sufficiently masked by the present method. This is because manganese(III)aminopolycarboxylate complex would undergo a slow decomposition.¹⁹ Lead chemicals contain copper as a major impurity, at an extent of ≤0.001%. Thus EGTA

Table 3 Masking of copper(II), cobalt(II) and manganese(II) by the ligand buffer ($C_{Zn}=8.87 \times 10^{-7} \text{ mol dm}^{-3}$; $C_{H_2TPPS_4}=2.0 \times 10^{-6} \text{ mol dm}^{-3}$)

Ion	Concentration/ mol dm^{-3}	Recovery of Zn, %		
		EDTA ^a	HEDTA ^a	EGTA ^a
Cu ²⁺	2.01×10^{-6}	86	96	96
	5.05×10^{-6}	69	85	97
	1.01×10^{-5}	50	69	96
	5.05×10^{-5}	11	27	72
Co ²⁺	2.00×10^{-6}			96
	5.00×10^{-6}	99	102	94
	1.00×10^{-5}	98	100	91
	5.00×10^{-5}	94	96	60
Mn ²⁺	1.97×10^{-6}			90
	5.02×10^{-6}	79	90	79
	9.98×10^{-6}	72	75	71

a. Components of the ligand buffers are $C_{Pb}=2.00 \times 10^{-3} \text{ mol dm}^{-3}$ and $C_Y=1.0 \times 10^{-3} \text{ mol dm}^{-3}$ for EDTA and HEDTA, and are $C_{Pb}=2.00 \times 10^{-3} \text{ mol dm}^{-3}$ and $C_Y=2.02 \times 10^{-4} \text{ mol dm}^{-3}$ for EGTA.

was chosen for the selective masking of copper in the presence of lead(II), because the difference of the formation constants between Pb(II)(EGTA) and Cu(II)(EGTA) complexes is larger than that of the corresponding EDTA and HEDTA complexes. Experimental results (Table 3) also reveal that copper was more masked by EGTA than EDTA or HEDTA.

Determination of zinc in lead chemicals and tap and waste waters

The present method was applied to the determination of zinc(II) in lead(II) nitrate, lead(II) acetate and lead metal, and in tap and waste waters. Lead chemicals were analyzed as follows. A sample of lead chemicals (10–200 mg Pb) was taken into a brown 50 cm³ volumetric flask; then 5 cm³ of acetate buffer (pH 6; $5 \times 10^{-1} \text{ mol dm}^{-3}$), a half equivalent of EGTA to lead(II), 2.5 cm³ of imidazole ($10^{-1} \text{ mol dm}^{-3}$), and 1 cm³ of H₂TPPS₄ ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$) were added. The solution was allowed to stand for 30 min to complete the formation of Zn(TPPS₄). A 2 cm³ portion of EDTA ($2.5 \times 10^{-1} \text{ mol dm}^{-3}$) was added to the solution to replace the formed Pb(II)(TPPS₄) with EDTA. Concentration of zinc was determined from measurement of the absorbance at 421 nm. For the determination of zinc in waters, 2 cm³ of lead(II) nitrate ($5 \times 10^{-2} \text{ mol dm}^{-3}$) and 2 cm³ of EGTA ($5 \times 10^{-3} \text{ mol dm}^{-3}$) were added to a sample solution before adding imidazole. The other procedure was the same as for the analysis of zinc in lead chemicals. The results for the determination of zinc in lead chemicals and waters are collected in Table 4. A few ppm level of zinc was found in these samples. Concentrations of zinc in lead(II) nitrates were also checked by an atomic absorption spectrophotometric method: zinc concentrations found in lead nitrates purchased from A Co. Ltd., B Co. Ltd. and C

Table 4 Determination of zinc(II) in lead chemicals and waters by the present method

Sample	Taken ^a / g or cm ³	Zinc(II) found	
		μg	ppm
Lead nitrate (G.R)			
A. Co. Ltd.	0.166	0.569	3.4
	0.332	1.080	3.3
B. Co. Ltd.	0.166	0.092	0.6
	0.332	0.245	0.7
Lead nitrate (E.R)			
C. Co. Ltd.	0.166	0.268	1.6
	0.332	0.507	1.5
B. Co. Ltd.	0.166	0.575	3.5
	0.332	1.080	3.3
Lead acetate (G.R)			
B. Co. Ltd.	0.190	0.062	0.3
	0.380	0.170	0.4
Lead metal (G.R) ^b			
A. Co. Ltd	0.104	0.434	4.2
	0.208	0.905	4.4
Tap water	1.0	0.791	0.79
	2.0	1.590	0.80
Waste water	10.0	1.020	0.10
	20.0	2.000	0.10

a. Units are g for lead chemicals and cm³ for waters, respectively.

b. Lead metal of 2.08 g was dissolved by nitric acid and dried, and followed by dissolving in a 100 cm³ volumetric flask. A 5 or 10 cm³ aliquot of the solution was analyzed.

Co. Ltd. were 3.3 ppm, 0.6 ppm and 1.6 ppm, respectively. The values are sufficiently in agreement with those obtained by the present method (see Table 4).

The present method is based on a kinetic difference of 4×10^{11} times and an equilibrium difference of 10^9 times in the reactivity of Pb(II)- and Zn(II)(TPPS₄). The proposed method is so selective and sensitive that $10^{-7} \text{ mol dm}^{-3}$ zinc(II) can be determined in the presence of 10^5 times excess of lead in water. Molar absorptivity of Zn(TPPS₄) is $4.66 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. The calibration curve is linear in the range of 0–100 ng Zn/cm³. Determination limits were 1 ng Zn/cm³ in waters and 20 ng Zn/g in lead chemicals. Recoveries were 96.5–104.6%.

The authors wish to express their thanks Dr. Motoharu Tanaka (an Honorary Professor of Nagoya University) for his helpful comments. We also gratefully acknowledge the financial support of this study by a Grant-in-Aid for Scientific Research (No. 01470030) from the Ministry of Education, Science and Culture.

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(Received July 8, 1989)

(Accepted September 4, 1989)