Low-Temperature Phosphorimetric Determination of Traces of Palladium(II) with Water-Soluble Coproporphyrin III

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(Received June 1, 1995)

The characteristics of coproporphyrin III (Copro III) as a chelating agent, a chromogenic agent, and a luminescence agent for metal ions were studied. Copro III forms 1:1 complexes with Co(II), Cu(II), Mn(II), Ni(II), Pd(II), and Zn(II). Copper, palladium, and zinc complexes exhibit phosphorescence at liquid nitrogen temperature (77 K), and the intensity of the palladium complex ($\lambda_{\mathrm{Pd_{max}}}=659$ nm) is 10 and 13 times larger than that of the copper and zinc complexes ($\lambda_{\mathrm{Cu_{max}}}=685$ nm, $\lambda_{\mathrm{Zn_{max}}}=702$ nm), respectively. Based on these facts, a low-temperature phosphorimetric determination of the 10^{-8} mol dm^{-3} level of palladium was developed. The detection limit ($S/N=3$ using a 150 W xenon arc lamp as a light source) was 8×10^{-9} mol dm^{-3}, and the relative standard deviation was 2.8% for 6×10^{-7} mol dm^{-3} Pd(II) (7 determinations). Interference from many metal ions was avoided by selective extraction of palladium(II) as an ion-pair of the bromo complex with H_2SO_4-tetrabutylammonium bromide-methyl isobutyl ketone systems, followed by back extraction with acetate buffer solution (pH 5.0).

Extensive studies have been reported on the fluorescence[1)] and phosphorescence[2)] properties of naturally occurring porphyrin compounds. The determination of metal ions using the secondary emission of porphyrin derivatives was first reported by Solov'ev et al.[3)] They determined Cu(II) using water-insoluble etioporphyrin II at 77 K by phosphorimetry. We have demonstrated the usefulness of some water-soluble porphyrins as highly sensitive spectrophotometric reagents,[4,5)] as well as fluorimetric reagents for metal ions; for example, fluorimetric determination of 10^{-8} mol dm^{-3} Mg(II) with $\alpha,\beta,\gamma,\delta$-tetrakis(1-methylpyridinium-4-yl)porphine (TMPyP)[6)] and that of Zn(II) with the cadmium(II)-$\alpha,\beta,\gamma,\delta$-tetrakis(4-sulfophenyl) porphine (TPPS) complex.[7)] Also, Nishikawa et al. reported delayed fluorimetric determination of 10^{-8} mol dm^{-3} Zn(II) with TPPS.[8)]

In this paper, we report the characteristics of coproporphyrin III (Copro III) as a chelating agent and the properties of its absorption and luminescence spectra. Copper(II), palladium(II), and zinc(II) complexes emitted phosphorescence at 77 K and the palladium complex had the strongest intensity. The spectrum did not overlap with that of the copper and zinc complexes. Based on these findings, a method for the determination of 10^{-8} mol dm^{-3} Pd(II) was developed. This is the first use of a water-soluble porphyrin for low-temperature phosphorimetry.

Experimental

Reagents. Copro III (Fig. 1) was obtained as the sodium salt through the hydrolysis of coproporphyrin III tetramethyl ester (Nihon Sekiyu Co., Ltd.) using 1 mol dm^{-3} NaOH solution. It was then diluted with distilled water and used as a 10^{-4} mol dm^{-3} working solution. The working solution fades gradually at room temperature, but, it is stable for at least 90 d when stored in a refrigerator (4°C). A standard Pd(II) solution (1.0×10^{-2} mol dm^{-3}) was prepared by dissolving $PdCl_2$ (Wako Pure Chemical Co., Ltd.) in hydrochloric acid. The solution was standardized

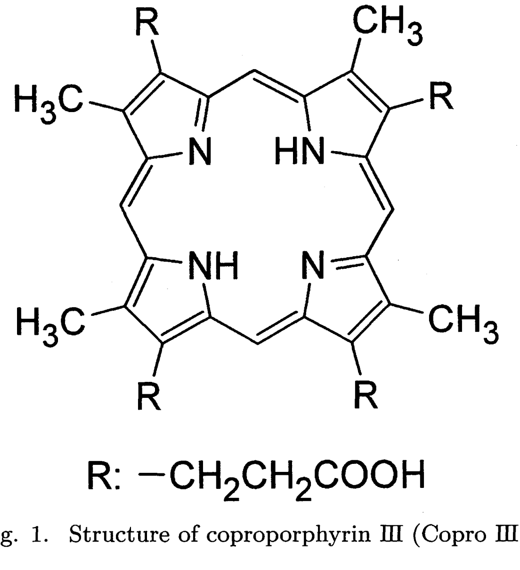

Fig. 1. Structure of coproporphyrin III (Copro III).

using chelatometric titration.[9] All other reagents were of guaranteed reagent grade.

Apparatus. Luminescence measurements were performed with a Hitachi 850 fluorescence spectrophotometer equipped with a phosphoroscope attachment, a 150 W xenon arc lamp excitation light source, and an R-928F photomultiplier detector tube.

Extraction and Back Extraction of Palladium(II). A 10 cm^3 aliquot of sample solution containing 0.05 to 3.2 μg of Pd(II) was placed in a 30 cm^3 cylindrical glass vial fitted with a plastic cap. One cm^3 of 0.5 mol dm^{-3} H_2SO_4 and 0.5 cm^3 of 0.1 mol dm^{-3} tetrabutylammonium bromide solution were added. The mixture was shaken for 5 min with 5 cm^3 of methyl isobutyl ketone and then centrifuged for 5 min at 2500 rpm. The aqueous phase was discarded and 5 cm^3 of 0.5 mol dm^{-3} CH_3COOH–CH_3COONa buffer solution (pH=5.0) was added. This mixture was shaken for 5 min and then centrifuged for 5 min at 2500 rpm. The aqueous phase was used for determining Pd(II) by the following procedure.

Analytical Procedure. A sample solution, not more than 10 cm^3, containing 0.05 to 3.2 μg of Pd(II) was placed in a 50 cm^3 Erlenmeyer flask. A half cm^3 of 10^{-4} mol dm^{-3} Copro III solution, 1 cm^3 of 1 mol dm^{-3} CH_3COOH–CH_3COONa buffer solution (pH 5.0), and 0.5 cm^3 of 10^{-2} mol dm^{-3} L-ascorbic acid solution were added. The mixture was boiled for 2 min and then allowed to cool to room temperature. The solution was transferred to a 25 cm^3 volumetric flask and 10 cm^3 of ethanol were added. The apparent pH of the solution was adjusted to 2.0 with 2 cm^3 of 1 mol dm^{-3} HNO_3 and the solution was then diluted to the mark with water. The low-temperature phosphorescence intensity was measured at 659 nm at 77 K using an excitation wavelength of 390 nm.

Results and Discussion

Absorption Spectra and Acid Dissociation Constants of Copro III. The absorption spectra of the free base (H_2L) form and the dication (H_4L^{2+}) form of Copro III are shown in Fig. 2. The spectral properties {maximum absorption wavelength (λ_{max}) and molar absorptivity (ε)} and acid dissociation constants, obtained through analysis of absorbance–pH plots, are shown in Table 1. The absorption bands of Copro III as a whole were located in a shorter wavelength region than those of the *meso*-substituted water-soluble porphyrins (such as TPPS and TMPyP), and the H_4L^{2+} species did not have any absorption band in the wavelength region 600 to 700 nm.

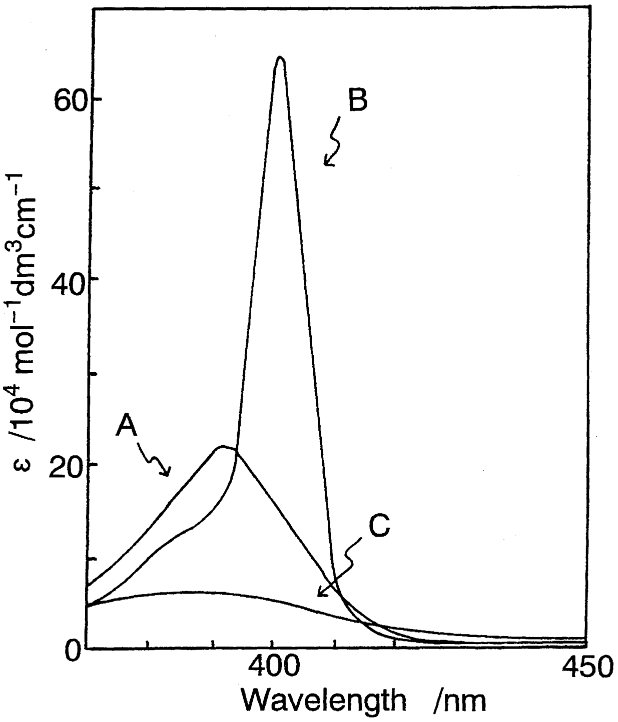

Fig. 2. Absorption spectra of Copro III (H_2L, A; H_4L^{2+}, B) and palladium complex (C). The spectra of H_4L^{2+} and palladium complex were measured at pH 1.0 and that of H_2L was measured at pH 9.2.

There was an extremely large difference in acid dissociation constants between K_{a4} and K_{a3} (i.e., pK_{a4}=2.76, pK_{a3}=7.13, ΔpK_a=pK_{a3}−pK_{a4}=4.37), compared with those of TPPS (pK_{a4}=4.86, pK_{a3}=4.95, ΔpK_a=0.09)[10] and TMPyP (pK_{a4}=0.80, pK_{a3}=2.06, ΔpK_a=1.26).[11] Statistical analysis of the absorbance–pH plots (Fig. 3) showed that protons of the propionic acid groups at the 2, 4, 6, and 7 positions of the porphine ring dissociate between pH 3 to 6 in very close proximity to each other. Therefore, the large difference in K_{a4} and K_{a3} of Copro III was attributed to the electrostatic effect of the ionized propionic acid groups.

Complex Formation. The reactions of Copro III with Co(II), Cu(II), Mn(II), Ni(II), Pd(II), and Zn(II) were examined. The solutions of Copro III and metal ion were mixed so as to all have the same concentration (1×10^{-6} mol dm^{-3}). This mixture was adjusted to pH 6.0 with CH_3COOH–CH_3COONa buffer solu-

Table 1. Absorption Spectral Data and Acid Dissociation Constants of Copro III

	Free base form (H_2L)[a]					Dication form (H_4L^{2+})[b]			Acid dissociation constant[c]	
	Soret	I	II	III	IV	Soret	I	II	pK_{a4}	pK_{a3}
λ_{max}/nm	392	499	536	557	606	400	548	590	2.76	7.13
$\varepsilon/10^4$ mol^{-1} dm^3 cm^{-1}	22.2	1.7	1.5	1.3	0.9	64.3	2.5	1.3		

a) Dication form of Copro III in the acid solution (pH 1.0). b) Free base form of Copro III in the alkaline solution (pH 9.2). c) $K_{a4}=\frac{[H^+][H_3L^+]}{[H_4L^{2+}]}$, $K_{a3}=\frac{[H^+][H_2L]}{[H_3L^+]}$, here, H_3L^+ indicates mono protonated form. The pK_{a4} and pK_{a3} were determined by successive approximation method and least squares method. Ionic strength (I)=0.1 (NaCl) at 20 °C.

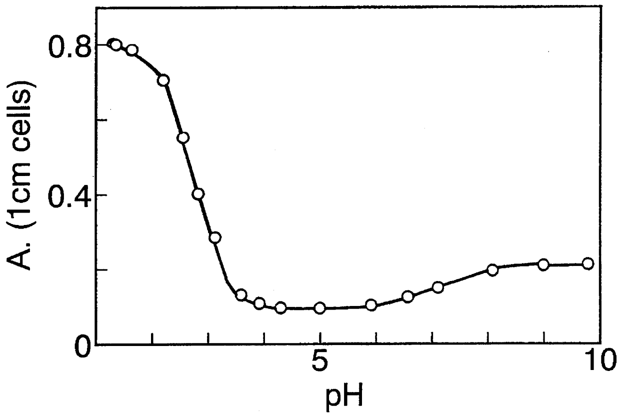

Fig. 3. Absorption–pH plots of 1×10^{-6} mol dm^{-3} Copro III. Absorbance was measured at 400 nm at 20 °C. Ionic strength: 0.1 mol dm^{-3} (NaCl).

tion and was brought to a boil using a heater. Copro III quantitatively reacted with Zn(II) within 3 min, and 90% of Co(II), 60% of Mn(II), and 5% of Ni(II) formed complexes within 15 min. Though 95% of Cu(II) and 50% of Pd(II) reacted with Copro III within 1 min and 10 min, respectively, their degree of complexation rarely increased from these values even though the solutions were boiled for a longer time. However, in the case of the Pd(II)–TPPS system,[12] 2×10^{-4}—8×10^{-3} mol dm^{-3} L-ascorbic acid accelerated the complexation of Pd(II) and Cu(II) with Copro III to quantitatively form the complexes within 1 min under boiling conditions. The stoichiometry of the metal : ligand ratio of these complexes was 1 : 1, based on the molar ratio method.

Absorption and Luminescence Spectra of Copro III Complexes. The spectral data of some metal complexes in the Soret band are summarized in Table 2. The molar absorptivities, ε, of the complexes, except for the cobalt(II) and zinc(II) ones, were less than 1×10^{5} mol^{-1} dm^{3} cm^{-1}. The spectra of some metal complexes extensively overlapped that of Copro III. The luminescence spectra data at room temperature and at 77 K are shown in Table 3 and in Fig. 4. At room temperature, Copro III (H_2L and H_4L^{2+}) and the zinc complex have a red color fluorescence; however, the fluorescence of Copro III is quantitatively quenched by complexation with Co(II), Cu(II), Mn(II), Ni(II), and Pd(II). At 77 K, Copro III produced only fluorescence, however, the zinc(II) complex produced both fluorescence and phosphorescence, while the copper(II) and palladium(II) complexes exhibited phosphorescence. The palladium(II) complex had the strongest phosphorescence and its spectrum did not overlap that of the copper(II) and zinc(II) complexes. Though it overlapped the fluorescence spectrum of Copro III, this did not hinder the determination of Pd(II), because the fluorescence disappeared by the time the long-lived luminescence of more than 1 ms was measured. The relative phosphorescence intensity (R.P.I.) of the Pd–Copro III complex was 1.1 and 5.3 times larger than those of the Pd–TPPS and Pd–TMPyP complexes, respectively (see Fig. 5).

Table 2. Absorption Spectral Data in Soret Band for Some Metal–Copro III Complexes

Copro III (L)	pH	λ_{max}/nm	$\varepsilon/10^4$ mol^{-1} dm^3 cm^{-1}
Zn–L	9.2	404	40.1
Co–L	1.0	409	21.2
Ni–L	1.0	383	6.5
Mn–L	1.0	458	5.6
Cu–L	1.0	387	3.9
Pd–L	1.0	387	3.1

Table 3. Fluorescence Spectral Data for Copro III and Zn–Copro III at Room Temperature

Copro III (L)	pH	Excitation λ_{max}/nm	Emission λ_{max}/nm	Relative fluorescence intensity
H_4L^{2+}	1.0	400	594	1.0
H_2L	9.2	392	612	0.59
Zn–L	9.2	404	578	0.42

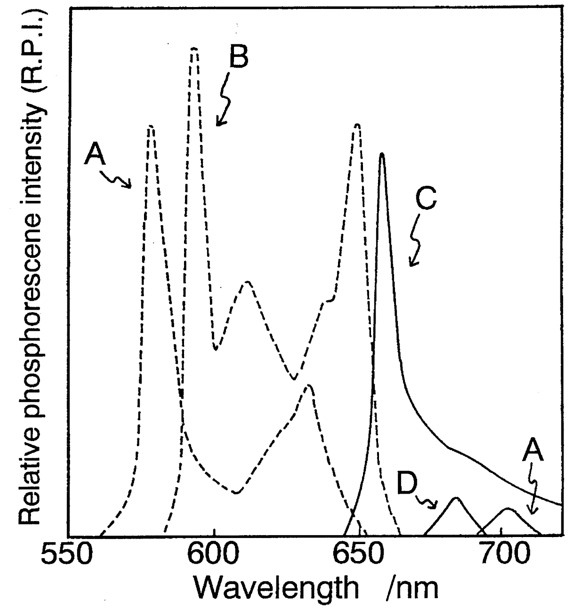

Fig. 4. Low temperature fluorescence (dashed line) and phosphorescence (solid line) spectra of H_4L^{2+} (B), Zn–L (A), Pd–L (C), and Cu–L (D) at 77 K. Curve A: at apparent pH 6.0, curve B, C, and D at apparent pH 2.0 in ethanol–water mixture (ethanol 40 v/v%), respectively. Excitation wavelength: (A) 408 nm, (B) 405 nm, (C) 390 nm, (D) 396 nm. [Copro III]=1×10^{-6} mol dm^{-3}, [metal]=2×10^{-6} mol dm^{-3}.

Other Conditions for the Low-Temperature Phosphorimetric Determination of Pd(II). Palladium(II) quantitatively formed a complex with Copro III in the pH range 4.5 to 6.5 (Fig. 6), and the complex once formed did not dissociate even under acidic conditions such as pH=1.0. The phosphorescence in-

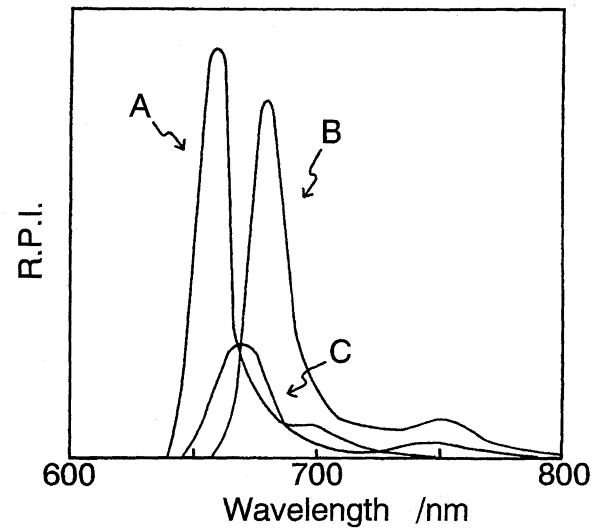

Fig. 5. Low temperature phosphorescence spectra of Pd–Copro Ⅲ (A), Pd–TPPS (B), and Pd–TMPyP (C) at 77 K at apparent pH 2.0 in ethanol–water mixture (ethanol 40 v/v%). Excitation wavelength: (A) 390 nm, (B) 414 nm, (C) 416 nm. [porphyrin] = 1×10^{-6} mol dm^{-3}, [palladium(Ⅱ)] = 2×10^{-6} mol dm^{-3}.

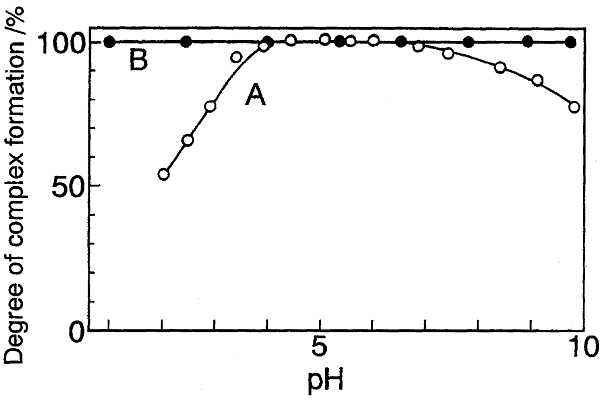

Fig. 6. Effect of pH on degree of complex formation. Curve A: Pd(Ⅱ)–Copro Ⅲ–L-ascorbic acid mixture after boiling for 2 min, curve B: Pd(Ⅱ)–Copro Ⅲ complex at room temperature. [Copro Ⅲ] = 1×10^{-6} mol dm^{-3}, [palladium(Ⅱ)] = 1.2×10^{-6} mol dm^{-3}, [L-ascorbic acid] = 2×10^{-4} mol dm^{-3}.

tensity of the reaction mixture remained constant for at least one day. The use of an aqueous solution for low-temperature phosphorimetry is liable to break a sample tube due to the considerable volume expansion while freezing the sample solution. To avoid this difficulty, the addition of a variety of water miscible organic solvents was tested. Ethanol gave a good result, and was freely mixed with water to give a translucent solid upon freezing. An ethanol content of 40% v/v was used.

The relative phosphorescence intensity of the Pd–Copro Ⅲ system, shown in Fig. 7, sharply decreased at an apparent pH value around 3. Thus, the apparent pH for measurement was decided to be 2.0.

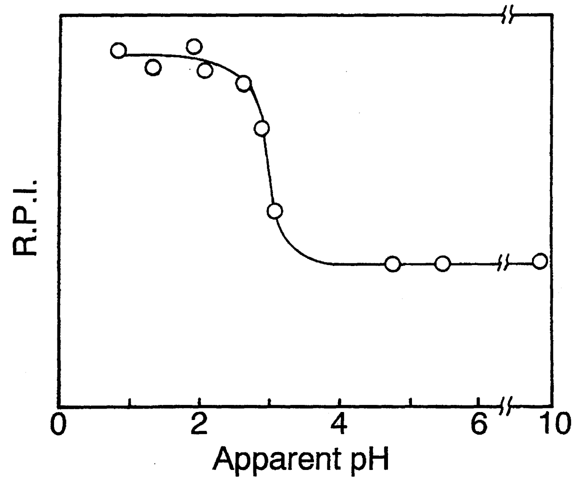

Fig. 7. Effect of apparent pH on relative phosphorescence intensity of Pd–Copro Ⅲ. Excitation wavelength: 390 nm, emission wavelength; 659 nm. [Copro Ⅲ] = 1×10^{-6} mol dm^{-3}, [palladium(Ⅱ)] = 6×10^{-7} mol dm^{-3}.

Calibration Curve and Reproducibility. A linear relationship between the concentration of Pd(Ⅱ) and the relative phosphorescence intensity was observed over the concentration range 2×10^{-8} mol dm^{-3} to 1.2×10^{-6} mol dm^{-3}. The detection limit ($S/N=3$) was as low as 8×10^{-9} mol dm^{-3}. The relative standard deviation was 2.8% for 6×10^{-7} mol dm^{-3} Pd(Ⅱ) (7 determinations).

Effects of Other Ions. The effects of other metal ions on the determination of Pd(Ⅱ) were examined (Table 4). Vanadium was added as its ammonium salt and other metal ions were added as their chlorides, nitrates, sulfates, or acetates. Deviations of ±5% were allowed for the relative phosphorescence intensity. A thousand µg of Mn(Ⅱ), Ni(Ⅱ), and alkali metals, and 100 µg of Pt(Ⅱ) did not interfere with the determination, but the tolerance limit for Cu(Ⅱ) was not very high.

Removal of Interfering Metal Ions. The removal of interfering metal ions by solvent extraction was attempted. Maeck et al. already reported that Pd(Ⅱ) was selectively extracted as the halide complex using H_2SO_4–tetrabutylamine–methyl isobutyl ketone systems.[13] Both 1 mol dm^{-3} nitric acid solution and 0.5 mol dm^{-3} CH_3COOH–CH_3COONa buffer solution (pH = 5.0) gave good results for the stripping solution, however, the pH of the latter solution was suitable for complexation of Pd(Ⅱ) with Copro Ⅲ.

Application of Proposed Method. A synthetic solution containing 10 ppm each of eleven kinds of metal ions {Al(Ⅲ), Cd(Ⅱ), Co(Ⅱ), Fe(Ⅱ), Mn(Ⅱ), Cu(Ⅱ), Ni(Ⅱ), Pd(Ⅱ), VO^+, VO_3^-, and, Zn(Ⅱ)} and 100 ppm each of four kinds of metal ions {Na(I), K(I), Ca(Ⅱ), and Mg(Ⅱ)} was prepared. To the solution, 1.60 µg Pd(Ⅱ) (0.064 ppm) was added and then determined after

Table 4. Tolerance Limits of Foreign Metal Ions for the Determination of Palladium(II) [a,b]

The method without pretreatment		The method with pretreatment		
Tolerance limits[c] μg/25 cm^3	Metal ions	No.	Synthetic solution[d] added/cm^3	Relative phosphorescence intensity
1000	Mn(II), Ni(II)	1	0	100
100	Ag(I), Ba(II), Ca(II), Hg(II),	2	1	93.9
	Mg(II), Pt(II)	3	1	95.7
10	Cr(III), Ga(III), VO^{2+}, VO_3^-,	4	1	96.4
	Zn(II)	5	1	99.9
1	Al(III), Ca(II), Co(II), Fe(II),	6	1	100.6
	In(III), Pd(II), Sn(II), Sr(II)			
<1	Cu(II)			av. 97.3 r.s.d. 2.9%

a) Palladium(II), 1.60 μg. b) Total sample volume, 15 cm^3. c) Deviations of ±5% were allowed for relative phosphorescence intensity. d) Synthetic solution contains each 10 ppm of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn, and each 100 ppm of Na, K, Ca, Mg.

Table 5. Sensitivities and Interfering Metal Ions for Determination of Palladium(II)

Method	Reagent	Detection limit/ppm	Interfering ion
Spectrophotometry	Dithizone[14]	0.1	None
	5-Cl-PADAB[15]	0.02	Cr(VI)
	TPPS[12]	0.002[a]	Cu(II), Hg(II)
	TPPS_4[16]	0.002[a]	Cu(II), Zn(II)
Spectrophotometry with HPLC	PAR[17]	0.1	None
	MNT[18]	0.001	Rh(III)
Flame A. A.		0.01	
I. C. P.		0.006	
Flameless A. A.		0.002[b]	
This method without pretreatment	Copro III	0.0009	Cu(II)

a) This is calculated value from ε against absorbance 0.005. b) Sample size, 0.01 cm^3, A. A.; Atomic absorption spectrophotometry.

the pretreatment procedure described above. Satisfactory recovery (97.3%, relative standard deviation 2.9%, 5 determinations) of Pd(II) was obtained.

Comparison with Other Methods. This is the first method for the determination of Pd(II) using the luminescence of the palladium complex itself, and it appears to be one of the most sensitive methods for Pd(II) (Table 5). This method is superior to a spectrophotometric method with other water-soluble porphyrins[12,16] because Hg(II) and Zn(II) did not seriously interfere. This new technique will be useful for the determination of trace amounts of Pd(II).

Conclusions

Low temperature phosphorimetry with Copro III was proven to be a rapid method for the determination of 10^{-8} $\mathrm{mol\,dm^{-3}}$ Pd(II). Copper and zinc complexes of Copro III also produce phosphorescence, hence the determination of these metals by phosphorimetry may be established. Water-soluble porphyrins are useful as a phosphorimetric reagent.

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