Determination of Rhodium by Third-Derivative Spectrophotometry with *o*-Hydroxyhydroquinonephthalein in the Presence of *N*-Hexadecylpyridinium Chloride†

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Synopsis. A third-derivative spectrophotometric determination ($d^3A/d\lambda^3$) of rhodium with *o*-hydroxyhydroquinonephthalein (Qnph) in the presence of *N*-hexadecylyridinium chloride (HPC) was proposed by measuring the distance of $d^3A/d\lambda^3$ on the peak at 530 nm (λ_3) and the troughs at 500 nm (λ_2) and 560 nm (λ_4). Beer's law was valid for the range 0—10 μg rhodium 10^{-1} cm^3; the apparent molar $d^3A/d\lambda^3$ was 7.37×10^5 dm^3 mol^{-1} cm^{-1}.

The most popular spectrophotometric method for the determination of rhodium, one of the platinum metals, is based on reaction between rhodium(III) and tin(II) chloride in hydrochloric acid medium.[1-3] However, this method is not sensitive and lacks reproducibility. On the other hand, the derivative spectrophotometric method has recently been found to be more sensitive, selective, and reversible than classical zero-order derivative spectrophotometries.[4-6] In addition, we have recognized that *o*-hydroxyhydroquinonephthalein (Qnph) used as a xanthene dye is a most useful organic agent.[7-9] Also, the coexisting effect of such surfactants as *N*-hexadecylpyridinium chlorid (HPC) has been reported in various spectro- or fluoro-photometries.[10-12] Accordingly, for the purpose of establishing a sensitive and simple spectrophotometric determination of rhodium, a third-derivative spectrophotometric determination with Qnph was investigated in the surfactant micellar media.

Experimental

Apparatus and Reagents. Absorption and high-derivative spectra were recorded on a Shimadzu UV 160 spectrophotometer with a 1.0-cm matched cell. The third-derivative spectrum was recorded by a fixed third-order differentiation circuit of $\Delta\lambda$=31.5 nm with a scan speed of 1500 nm per min. A Hitachi-Horiba F-7AD glass electrode pH meter was used for pH measurements.

A Qnph solution, 1.0×10^{-3} mol dm^{-3} was prepared by dissolving Qnph in methanol. A 5.0×10^{-4} mol dm^{-3} rhodium(III) solution was diluted by using a standard atomic absorption spectroscopy solution (Wako chemical Co., Ltd.). A 1.0×10^{-2} mol dm^{-3} HPC solution was prepared by dissolving HPC in water; a Sörensen phosphate buffer solution (pH 6.4—7.2) was used for the pH adjustments. Deionized water was used throughout.

Standard Procedure. To a solution containing 0—10 μg rhodium(III) in a 10-cm^3 volumetric flask, 3.0 cm^3 of a 2.0×10^{-2} mol dm^{-3} buffer solution (pH 6.5), 1.0 cm^3 of a 1.0×10^{-2} mol dm^{-3} HPC solution and 0.8 cm^3 of 5.0×10^{-4} mol dm^{-3} Qnph solution were added; the mixture was diluted to volume with water (Solution A), kept at 75 °C for 30 min, then cooled to room temperature (10—25 °C) for 5 min. The $d^3A/d\lambda^3$ distances at 500 nm (trough λ_2), 530 nm (peak λ_3) and 560 nm (trough λ_4) were measured against a reagent blank (Solution B).

Results and Discussion

Absorption Spectra. Figure 1 shows the absorption spectra of the Qnph–rhodium(III) solution (Solution A) and the Qnph solution (Solution B) in the presence of HPC as a cationic surfactant (or absence). The color formation reaction in the presence of HPC was stable and exhibited a large absorbance in comparison with that in the absence of HPC. In addition, the derivative spectrum (third-derivative, $d^3A/d\lambda^3$) of Solution A against Solution B was most sharp and apparent. Figure 2 shows two peaks (λ_1 480 nm, λ_3 530 nm) and three valleys (λ_2 500 nm, λ_4 560 nm, λ_5 610 nm). The analytical response was obtained by measuring the absorbance distance between the peak at 530 nm (λ_3) and the valleys at 500 nm (λ_2) and 560 nm (λ_4); its value was large compared with the zero-order derivative absorption spectrum.

Effect of pH. The maximum and constant $d^3A/d\lambda^3$ was obtained within limited ranges of pH 6.4—7.2,

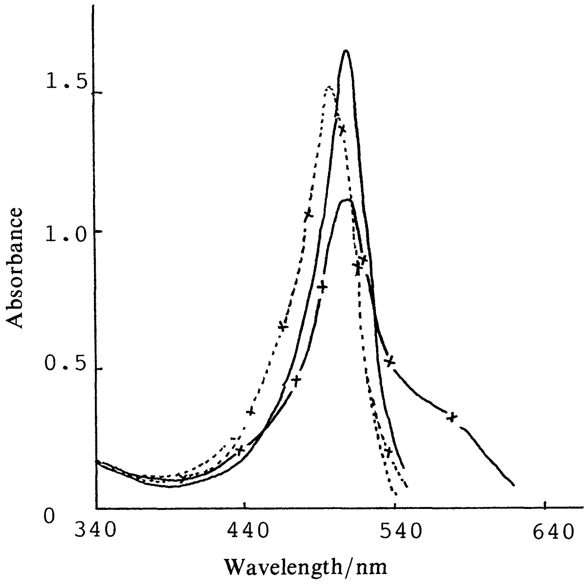

Fig. 1. Absorption spectra of Qnph–rhodium(III) solution (Solution A) and Qnph solution (Solution B) in the presence or absence of HPC at pH 7.0. Rhodium(III), 2.5 ppm, Qnph, 2.5×10^{-5} mol dm^{-3}; HPC, 1.0×10^{-3} mol dm^{-3}; Reference, water -------, Qnph; ----X----, Qnph–rhodium(III); ———, Qnph–HPC (Solution B); ——X——, Qnph–HPC–rhodium(III) (Solution A).

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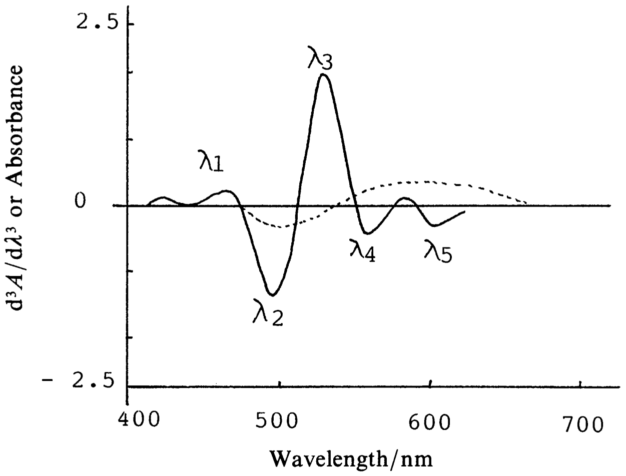

Fig. 2. Zero-order and third-derivative spectra of Qnph–rhodium(III) solution (Solution B) in the presence of HPC. Rhodium(III), 5.0×10^{-6} mol dm^{-3}; Qnph, 4.0×10^{-5} mol dm^{-3}; HPC, 1.0×10^{-3} mol dm^{-3}; pH 6.5; Reference, reagent blank (Solution B). ------, Zero-order spectrum; ———, Third-derivative spectrum.

Table 1. Effect of Various Surfactants on Zero-Order and Third-Derivative Spectrophotometries

Surfactant	Zero-order		$d^3A/d\lambda^3$
	max	Absorbance	
—	535	0.105	b) 0.50
HPC	572	0.540	3.70
SLS	532	0.115	b) 0.80
LS	532	0.117	b) 0.80
Brij 35	532	0.135	b) 0.85
HPC+Brij 35	570	0.390	2.90
HPC$^{a)}$+Brij 35	530	0.132	b) 0.85
SLS+Brij 35	504	0.09	b) 0.65

Rhodium(III) 5.0 μg 10 cm^{-3}; Qnph, 5.0×10^{-4} mol dm^{-3}; pH, 6.5; HPC, 1.0×10^{-3} mol dm^{-3}; other surfactants, 0.01%. a) HPC, 1.0×10^{-4} mol dm^{-3}. b) Insufficiency.

using 2.0—3.0 cm^3 of a 2.0×10^{-1} mol dm^{-3} phosphate buffer solution. Accordingly, 3.0 cm^3 of a buffer solution (pH 6.5) was used for pH adjustments in all further work.

Effect of Surfactants. The complex formation reactions between Qnph and rhodium(III) were systematically investigated by using the $d^3A/d\lambda^3$-method in the absence or presence of only a surfactant, or its combination; cationic-, anionic, nonionic-, and amphoteric-surfactants—HPC, sodium dodecylsulfate (SDS), Tween 20, sodium *N*-lauroylsarcosine (LS). The coexistence of only the cationic surfactant was most effective, and its color was stable and abundant regarding reproducibility. In tested cationic surfactants such as hexadecyltrimethylammonium chloride (HTAC), benzyldimethyltetradecylammonium chloride (Zephiramine, Zp), benzyltriethylammonium chloride (TBBAC), and HPC, the presence of 5.0×10^{-3} mol dm^{-3} HPC was most effective.

Table 2. Effect of Foreign Ions

Foreign ions	Added		$d^3A/d\lambda^3$	Error
	as	μg/10 cm^3		%
—	—	—	3.80	—
Co(II)	Nitrate	0.30	3.81	+0.3
Ni(II)	Nitrate	4.40	3.83	+0.8
Zn(II)	Nitrate	3.27	3.82	+0.6
Bi(III)	Nitrate	0.52	3.88	+2.1
Th(IV)	Nitrate	1.16	3.81	+0.3
S^{2-}	Sodium	0.80	3.79	−0.3
$S_2O_3^{2-}$	Sodium	0.28	3.80	+0
$C_2O_4^{2-}$	Sodium	6.6	3.79	−0.3
Citrate	Sodium	14.10	3.78	−0.6
F^-	Potassium	144.50	3.80	±0

Rhodium(III) taken, 5.0 μg 10 cm^{-3}; Qnph, 5.0×10^{-4} mol dm^{-3}; HPC, 1.0×10^{-3} mol dm^{-3}; pH, 6.5; Reference, reagent blank (Solution B).

Accordingly, final 1.0×10^{-3} mol dm^{-3} HPC was used for a further investigation.

Effect of Concentration of Qnph. The recommended concentration of Qnph was final 0.4—1.0×10^{-4} mol dm^{-3}, and final 5.0×10^{-5} mol dm^{-3} Qnph was used for subsequent procedures.

Effect of Stability. The effects of the temperature and heating time were examined at 10—80 °C for 2—60 min. The optimum heating condition was at 70 °C for 5—20 min; further work was carried out at 70 °C for 5 min.

Calibration Graph and Reproducibility. Beer's law held at lower than 10 μg of rhodium(III) per 10 cm^3, and apparent molar $d^3A/d\lambda^3$ was 7.37×10^5 dm^3 mol^{-1} cm^{-1}. The reproducibility for 5 μg/10 cm^3 rhodium(III) (5 experiments) was 1.5%.

Interferences. Although nickel(II), zinc(II), bismuth(III), thorium(IV), and other platinum metals, such as palladium, gave a positive error, and citrate, oxalate, thiocyanate ions gave negative errors, the infuluence of foreign ions on the proposed $d^3A/d\lambda^3$-method was reduced to about half, compared with zero-order spectrophotometry. For a mixture of rhodium and other platinum metals, pre-separation by other techniques, such as ion exchange chromatography,[13,14] was necessary.

Composition of Complex. The molar ratio of rhodium(III) to Qnph in a color formation reaction in the presence of HPC was determined by continuous variation (Job's) and molar-ratio methods to be 2:3; the molar ratio of rhodium(III) to HPC, however, was not investigated.

Conclusion. The complex formation reaction between Qnph and rhodium(III) in the presence of a cationic surfactant alone, such as HPC at pH 6.5, was very stable and abundant regarding reproducibility. Accordingly, this Qnph-rhodium(III) complex was newly used for a sensitive and simple third-derivative spectrophotometry of rhodium(III). The $d^3A/d\lambda^3$-method was compared with zero-order spectrophotometry; the calibration graph was linear over the range 0—10 μg rhodium(III) per 10 cm^3. The proposed method was 5-times more sensitive, and the influence of foreign ions was reduced by half compared with the zero-order method. Also, the method was 10-fold more sensitive than Chromazurol S, and 30-fold more sensitive than the Eriochrome Cyanine R and 4-(2-pyridylazo)resorcinol methods.[15,16]

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