Spectrophotometric Determination of Palladium(II), Osmium(VIII), and Iridium(III) with 2-Methyl-1,4-naphthoquinone 4-Oxime

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2-Methyl-1,4-naphthoquinone monoxime (MNQM) forms yellow-colored 1:1 (M:L) complex with palladium(II) and brown-colored 1:2 complex with osmium(VIII) and iridium(III). The complexes are insoluble in water but soluble in 1-butanol. The reagent has been used for the spectrophotometric determination of Pd(II), Os(VIII), and Ir(III). The palladium, osmium, and iridium complexes have maximum absorption at 460, 460, and 450 nm respectively with the sensitivity of 0.012 μg Pd/cm², 0.025 μg Os/cm², and 0.014 μg Ir/cm² for log I_0/I=0.001. The optimum concentration ranges for the determination of Pd(II), Os(VIII), and Ir(III) are 1.58—10.47, 3.02—23.99, and 1.6—11.5 ppm over the pH range 6.5—7.8, 6.5—7.7, and 5.9—7.3 respectively. The determinations have also been carried out in the presence of foreign ions. MNQM reacts with palladium(II) or osmium(VIII) or iridium(III) to form yellow- or brown-colored precipitates which are extractable in 1-butanol. These systems have been studied spectrophotometrically to determine the composition and other physical constants of the complexes. The possibility of determining Pd(II) or Os(VIII) or Ir(III) in presence of diverse ions has also been investigated. Palladium(II) and osmium(VIII) have been successfully determined in synthetic solutions corresponding to the alloys.

Experimental

Reagents and Apparatus. 2-Methyl-1,4-naphthoquinone monoxime (MNQM) was prepared by the method of Veldstra and Wiardi.[1] A 1×10^{-2} M (1 M=1 mol dm^{-3}) solution of the reagent was prepared in ethanol (95%).

1-Butanol (AnalaR) was distilled before use. Buffer solutions were prepared by mixing 0.2 M sodium acetate and 0.2 M acetic acid in requisite proportions. For higher pH, sodium hydroxide was added. Buffer solutions of potassium hydrogen phthalate–sodium hydroxide were prepared from solutions of the corresponding chemicals of reagent grade in doubly distilled water.

Palladium(II) Solution. Standard solution of palladium(II) was prepared by dissolving palladium dichloride (Johnson-Matthey) in dilute hydrochloric acid. The solution was standardized gravimetrically by precipitation with dimethylglyoxime.

Osmium(VIII) Solution. A 1 g ampouls of osmium tetraoxide (Johnson-Matthey) was dissolved in about 100 ml of 0.2 M sodium hydroxide in a glass stoppered flask as described by Ayres and Wells,[2] which was further standardized by the method of Klobbie.[3] Working solutions were prepared by diluting this stock solution, whenever required.

Iridium(III) Solution. A stock solution of iridium was prepared by dissolving iridium(III) chloride (Johnson-Matthey) in doubly distilled water containing 1 M hydrochloric acid. The iridium solution was standardized gravimetrically by precipitating iridium as the hydrated oxide, followed by careful ignition in air and then reduction to the metal in presence of hydrogen and cooling in air atmosphere of carbon dioxide. Subsequent dilutions were made by diluting the stock solution and keeping the acidity at 1 M.

Reagent grade chemicals were used in the study of interferences. Doubly distilled water was used throughout the work.

A Unicam SP 600 spectrophotometer was used for measuring absorbance and an ECIL expanded scale pH meter pH 821A was used for pH measurements.

Absorption Spectra and Effect of pH. Palladium, osmium, and iridium complexes show the maximum absorption at 460, 460, and 450 nm respectively (Figs. 1a, b, and c). This wavelength was chosen for subsequent measurements. A plot of absorbance vs. pH shows that the absorbances remain constant in the pH range 6.5—7.8, 6.5—7.7, and 5.9—7.3 for Pd(II), Os(VIII), and Ir(III), respectively. In subsequent studies the pH of the solutions was adjusted to 7.0, 6.9, and 6.7 for palladium, osmium, and iridium, respectively.

Rate of Color Development and Stability of the Complexes. Complex formation takes place instantaneously after the addition of the reagent to the palladium(II) or osmium(VIII) solution. With iridium(III) it was observed that rate of color development is slow at room temperature, but is accelerated by heating on a water bath. Solutions containing a fixed amount of iridium(III), reagent and buffer was heated on a water bath for different intervals of time and absorbances were measured at 450 nm. Results of this study show that full color development takes place on heating the contents for about 2 h.

The Pd-MNQM, Os-MNQM, and Ir-MNQM complexes were found to be quite stable and absorbances were found to remain unchanged upto 24, 72, and 48 h, respectively after which a slow decrease in absorbance take place.

Effect of Reagent Concentration. A plot of absorbance vs. moles of ligand shows that at least 10, 60, and 30 times molar excess of the reagent is required for maximum complexation for palladium, osmium, and iridium, respectively. In subsequent studies 20, 70, and 40 times molar excess of the reagent was used for Pd, Os, and Ir, respectively.

Adherence to Beer's Law, Optimum Range and Sensitivity. Beer's law is obeyed upto 11.91, 29.48, and 13.7 ppm (1 ppm=1 μg cm^{-1}) and the optimum concentration ranges for accurate determination, as determined from Ringbom plot (Fig. 2), are 1.58—10.47, 3.02—23.99, and 1.6—11.5 ppm for palladium, osmium, and iridium, respectively. The sensitivity, in terms of Sandell's definition, is 0.012 μg Pd/cm², 0.025 μg Os/cm², and 0.014 μg Ir/cm² for log I_0/I= 0.001 with molar absorptivity 8.6×10^3, 7.6×10^3, and 1.26×10^4 l mol^{-1} cm^{-1}, respectively.

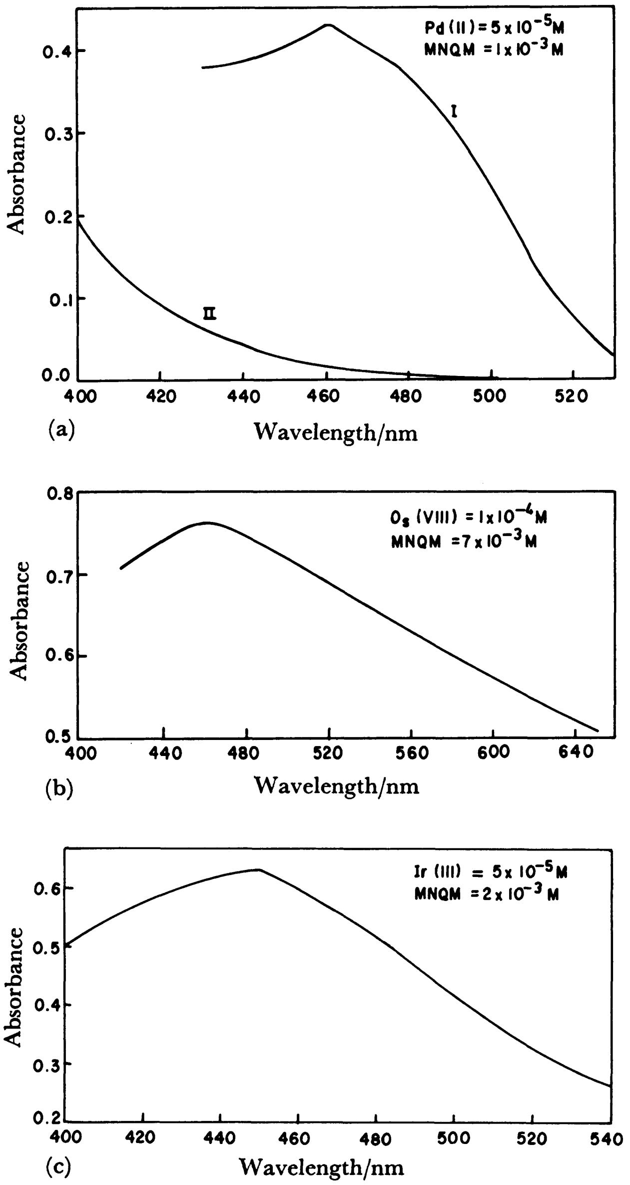

Fig. 1. Absorption spectra of:

(a): I. palladium(II) complex vs. reagent Pd(II), 5×10^{-5} M. II. reagent vs. 1-butanol, MNQM 1×10^{-3} M.

(b): Osmium(VIII) complex vs. reagent, Os(VIII) 1×10^{-4} M.

(c): iridium(III) complex vs. reagent, Ir(III) 5×10^{-5} M.

Recommended Procedure. Palladium and Osmium. A suitable aliquot containing 15.8—104.7 μg of palladium(II) or 30.2—239.9 μg of osmium(VIII) is taken and an excess of reagent in ethanol is added. pH is adjusted in the range 6.5—7.8 for palladium with potassium hydrogen phthalate-sodium hydroxide or 6.5—7.7 for osmium with sodium acetate-sodium hydroxide. The volume is made upto 10 ml with doubly distilled water. 10 ml of 1-butanol is added, the contents are shaken on a shaking machine and set aside for equilibration. The nonaqueous layer is separated, centrifuged to remove water droplets and the absorbance is measured against a reagent blank prepared under identical conditions. Knowing the absorbance, the amount of palladium is deduced from the calibration curve.

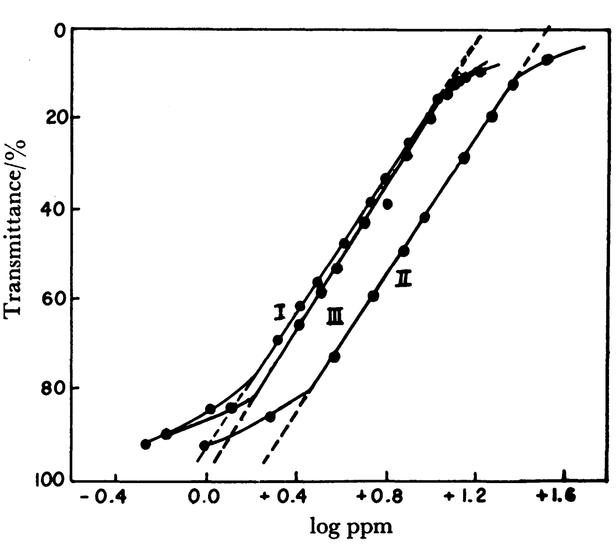

Fig. 2. Ringbom plot for:
I: Pd(II)-MNQM complex.
II: Os(VIII)-MNQM complex.
III: Ir(III)-MNQM complex.

Iridium(III). To the solution containing 16—115 μg of iridium is added an excess of reagent and pH of the solution is adjusted in the range 5.9—7.3 with acetate buffer and dilute solution of sodium hydroxide. The total volume is made upto 10 ml with doubly distilled water. The contents are heated on a boiling water bath for about 2 h, then cooled to room temperature (30±5 °C) and extracted in 10 ml of 1-butanol. The mixture is shaken on a shaking machine and kept aside for equilibration. The nonaqueous layer is separated, centrifuged and the absorbance is measured at 450 nm. The iridium concentration is then deduced from the calibration curve.

Molar Composition of the Complexes. The composition of the complexes were determined by Job's method of continuous variations,[4,5] which shows that the stoichiometric ratio of metal to MNQM in the complex is 1:1 (Pd:MNQM) or 1:2 (Ir:MNQM) (Figs. 3a and b).

The ratio of osmium to MNQM was determined by logarithmic method of Bent and French,[6] which shows that molar ratio of metal to ligand in the complex is 1:2 (Fig. 3c).

Absorbance Deviations. Measured under optimum conditions, the solutions containing 5.32 ppm of Pd(II) gave absorbance readings with average relative deviation of ±0.46%. The standard deviation was found to be 0.003. 9.51 ppm of Os(VIII) gave an average relative deviation of ±0.44% with standard deviation of 0.0024. 6.4 ppm of iridium the standard deviation comes out to be 0.0024 with an average absorbance of 0.42.

Effect of Diverse Ions. The effect of diverse ions was studied in the determination of palladium, osmium, and iridium following the recommended procedure. The amounts (in ppm) of ions which do not cause any interference with 5.32 ppm of palladium, are given below in parentheses. Masking agents, wherever used, have been mentioned against each:

Chloride or citrate or tartrate (800), bromide or fluoride or

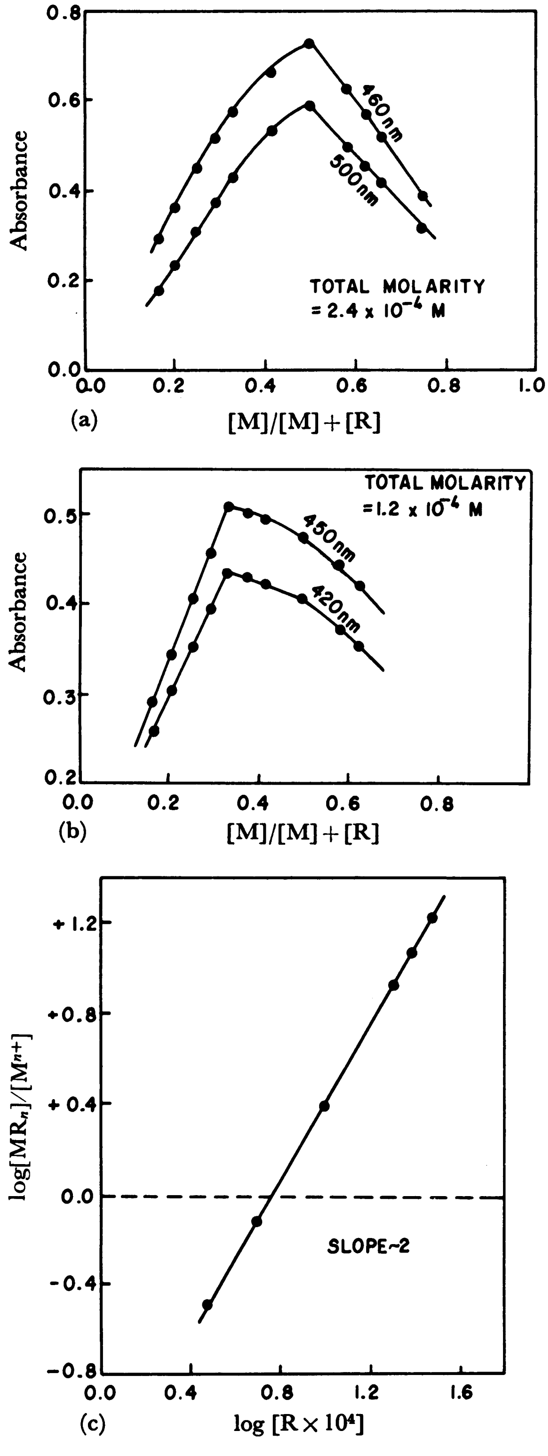

Fig. 3(a). Composition of Pd-MNQM complex by Job's method.

(b): Composition of Ir-MNQM complex by Job's method.

(c): Composition of Os-MNQM complex by Bent and French method.

Table 1. Determination of Pd(II) in Synthetic Solutions

Alloy	Pd present ppm	Amount of foreign ion taken ppm	Pd found ppm	Error/%
1. Pd-Cu (40% Cu, 60% Pd)	6.0	4.0	6.02	+0.33
	6.0	4.0	6.01	+0.16
	6.0	4.0	6.02	+0.33
2. Pd-Ag (40% Ag, 60% Pd)	6.0	4.0	6.01	+0.16
	6.0	4.0	5.99	−0.16
	6.0	4.0	6.03	+0.5
3. Pd-Au (50% Au, 50% Pd)	6.0	6.0	6.0	0.00
	6.0	6.0	6.03	+0.5
	6.0	6.0	6.0	0.00
4. Pd-Ru (Jewellary alloy) (4.5% Ru, 95.5% Pd)	2.00	0.09	1.98	−1.0
	4.24	0.20	4.24	0.00
	3.00	0.14	3.01	+0.33

nitrite (100), nitrate (1500), sulfate or oxalate or phosphate (2500), Ca(II) or Ba(II) or Sr(II) or Cd(II) or La(III) (200), Mg(II) or Ir(III) (20), Al(III) or Sn(II) or Th(IV) (100, F$^-$), Zn(II) or Hg(II) or Cu(II) or Mo(VI) or U(VI) or V(IV) or Zr(IV) or Li(I) or Y(III) or Pb(II) (100), Fe(II) or Ru(III) (10), Co(II) or Mn(II) (50), Ni(II) or As(III) (70), Cr(III) (50, tar), Ag(I) (70), Rh(III) (8), Pt(IV) (25).

For 9.51 ppm of osmium(VIII), the limits of tolerance are: chloride or bromide or fluoride (250), nitrate (150), nitrite or citrate or sulfide or borate (50), oxalate or thiocyanate (100), phosphate (300), sulfate or sulfite (400), Ca(II) or Hg(II) (100), Ba(II) or Sr(II) or Ni(II) (70), Mg(II) or V(IV) or Pb(II) (40), Al(III) (20, F$^-$), Mn(II) (10, F$^-$), Ag*(I) (30, Cl$^-$), Co(II) or As(III) or Pt(IV) (20), Fe(II) (30), Cu(II) or Ir(III) (10), U(VI) (100, PO$_4^{3-}$), Ru(III) or Rh(III) (20). Thiosulfate, iodide, and palladium(II) interfere in the determination.

For 6.4 ppm of iridium(III), the limits of tolerance are: chloride (450), bromide or iodide or sulfate or oxalate or tartrate or phosphate (500), nitrate (2500), nitrite or borate or thiocyanate (100), sulfite (1500), citrate (250), fluoride (1000), Ca(II) or Ba(II) (200), Sr(II) (150), Fe(II) or Zn(II) (10), As(III) (70), Mo(VI) (50), Sn(II) (10, F$^-$), Os(VIII) or Pd(II) (20) (extracted in cold), U(VI) (20, C$_2$O$_4^{2-}$), Hg(II) (5, I$^-$), Th(IV) (20, F$^-$), Cu(II) (5, SCN$^-$), Al(III) (50, F$^-$), Mg(II) (20), Ag*(I) (100, Cl$^-$), Co(II) or Ni(II) (50), Mn(II) (30), V(IV) (60), Pb(II) (80). Ru(III), Rh(III), and Pt(IV) interfere and attempts to mask these cations were unsuccessful.

Determination of Palladium in Synthetic Solutions. To ascertain the selectivity of the reagent the method was successfully used for the determination of palladium in alloys. Synthetic solutions similar to those of the alloys of palladium were prepared and the amount determined following the recommended procedure. Results obtained are summarised in Table 1.

Determination of Osmium in Osmiridium. Osmiridium can be analyzed successfully after decomposition by attack with chlorine and dissolution of platinum metal salts in hydrochloric acid. No distillation is required unless the amounts of interfering elements are above the tolerance

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* Removed by centrifugation.

limit. For a synthetic sample of osmiridium results obtained are shown in Table 2.

Discussion

Various chromogenic reagents used for the determination of palladium have been reviewed.[7,8] *N,N*-Dimethyl-*p*-nitrosoaniline[8,9] and *p*-nitrosodiphenylamine[9] have been extensively used for the spectrophotometric determination of palladium. The disadvantage is that both of them cannot be used in presence of large amount of natural salts such as sodium chloride and other platinum metals and several base metals interfere. MNQM is more selective than these methods. As compared to dimethylglyoxime.[8] MNQM is more selective and sensitive. Absorption maximum does not lie in the UV region as in the case of phenyl 2-pyridylketone oxime[10] (340 nm) and triphenylphosphine[11] (346 nm). Methylglyoxime and salicylaldehyde oxime[12] have also been used, but sensitivity of both is low. Palladiazo[13] is less selective than MNQM, since most of the base metals and noble metals interfere. Tropolone[14] method is sensitive but suffers from interference due to many metals. The sensitivity of 2-hydroxy-1-naphthaldehyde oxime[15] is also high but molybdenum(IV) and osmium(III) interfere seriously. The chief advantage of the present method is that palladium can be determined successfully in presence of other metals, especially eighth group metals and platinum metals except osmium.

Table 2. Determination of Osmium(VIII) in Synthetic Mixture Corresponding to Osmiridium

Metals present/ppm				Os Found	Error/%
Os	Ir	Ru	Pt		
6.0	6.0	6.0	2.0	6.01	+0.16
4.0	4.0	4.0	1.0	4.02	+0.5
2.0	0.05	0.3	0.1	1.99	−0.5

Out of the several reagents suggested for spectrophotometric determination of osmium, thiourea[16] is one of the most useful and recommended reagent for osmium. Despite the lack of sensitivity, the chief disadvantage is that the quantity of thiourea required for a fixed amount of osmium depends on the volume of the solution. 1,5-Diphenylcarbohydrazide[17,18] is an extremely sensitive reagent for osmium, but the associated platinum metals and base metals (iron, cobalt, nickel, copper) interfere. The color development is dependent on temperature, time of standing in aqueous phase, the period of extraction of the complex into $CHCl_3$ and subsequent absorbance measurement, the concentration of perchloric acid

Table 3. Sensitivities of Reagents for Pd, Os, and Ir

Reagent	Sensitivity μg Pd/cm^2	Reagent	Sensitivity μg Os/cm^2	Reagent	Sensitivity μg Ir/cm^2
8-Quinolinethiol	0.024/272 nm 0.003/286 nm	1,5-Diphenylcarbohydrazide	0.00127/560 nm	Leucocrystal violet	0.004/590 nm
N,N-Dimethyl-*p* nitrosoaniline	0.0015/510—525 nm	2-Aminophenol-4-sulfonic acid	0.1/440 nm	4,4′-Bi-*o*-anisidine	0.016/530 nm
Methylglyoxime	3.0/427 nm	Tiron	0.033/470 nm	*N,N*-Dimethyl-*p*-nitrosoaniline	0.010/530 nm
Palladiazo	0.0032/540 nm	7-Amino-1-naphthol-3,6-disulfonic acid	0.2/480 nm	Cerium(IV) sulfate sulfuric acid	0.12/510 nm
Acenaphthenequinone monoxime	0.0084/385 nm	Acenaphthenequinone monoxime	0.0323/430 nm	Acenaphthenequinone monoxime	0.021/385 nm
2-Hydroxy-1-naphthaldehyde oxime	0.0097/402 nm				
2-Methyl-1,4-naphthoquinone 4-oxime (MNQM) (Present method)	0.012/460 nm	2-Methyl-1,4-naphthoquinone 4-oxime (Present method)	0.025/460 nm	2-Methyl-1,4-naphthoquinone 4-oxime (Present method)	0.014/450 nm

and even the order of addition of the reagents. In case of 7-amino-1-naphthol-3,6-disulfonic acid,[19] sensitivity is very low, though the other platinum metals do not interfere. In acenaphthenequinone monoxime[20] 90 min heating of solution is needed and sensitivity is also low. In phenanthrenequinone monosemicarbazone[21] sensitivity is low and 5 min of heating is required.

Very few satisfactory reagents are available for the spectrophotometric determination of iridium. In Leucocrystal Violet[22] method, Rh and Fe(III) interfere seriously and this method depends upon a specific composition of the dissolved iridium salt and aged iridium solutions give green solutions of lower absorbance than those which are freshly prepared. Tin bromide method[23,24] is not selective. This method is sensitive to certain variation in the procedure such as time of contact, temperature, quantity of reagent and hydrobromic acid. In 4,4′-bi-*o*-anisidine[25] method, there is interference from associated metals from oxidants and sulfuric acid solution cannot be used. The absorbance is sensitive to the amount of reagent and to the acidity of the medium. In *N*,*N*-dimethyl-*p*-nitrosoaniline method,[26] composition of the complex is not known and the method offers no specificity among platinum metals and there is interference from nonvolatile acids. The method is sensitive to changes in the conditions. In acenaphthenequinone monoxime method,[27] most of the platinum metals interefere and prior separation of iridium is necessary and sensitivity is also low.

The present method for the determination of Pd(II), Os(VIII), and Ir(III) using 2-methyl-1,4-naphthoquinone 4-oxime, involves simple technique. The method is selective and the complexes are stable for a long time. Effect of pH, buffer, heating time, amount of reagent do not have any effect on the absorbance. Most of the associated metals do not interfere. The sensitivities of the present method are promising and compare well with other known reagents in Table 3.

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