4-(2-Quinolylazo)phenol as a Spectrophotometric Reagent for Palladium(II), Osmium(VIII), and Gold(III)

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Reaction behavior of 4-(2-quinolylazo)phenol (*p*-QAP) is established with three noble metals, i.e. palladium(II), osmium(VIII), and gold(III), under various conditions. Palladium(II) forms a 1 : 1 greenish violet complex at pH 8—10 (absorption maximum at 580 nm), while osmium(VIII) forms a 1 : 1 violet compex at pH 8—9.5 (absorption maximum at 550 nm) with the ethanolic solution of *p*-QAP. Color reaction with gold(III) with ethanolic solution of *p*-QAP is instantaneous, but fades away with time. However, a 4 :4 : 2 mixture of water, ethanol, and cyclohexanol stabilizes this color for 45 min. Thus a 1 : 1 red gold(III) complex formed at pH 8—9.5 absorbs maximum at 550 nm. The Sandell's sensitivities (ng cm^{-2}) of the color reactions are 2.7, 3.9, and 9.8 with palladium(II), osmium(VIII), and gold(III) respectively. Other physicochemical characteristics of the complexes are established. A number of foreign ions tested for their interferences and use of masking agents wherever necessaty it tabulated. Synthetic solutions identical in composition to some palladium(II) and gold(III) alloys are estimated to ascertain the suitability of the reagent.

4-(2-Quinolylazo)phenol (*p*-QAP) was used as an analytical reagent for copper in blood serum[1] and in milk;[2] and for silver[3] and the silver-(*p*-QAP) complex for the indirect determination of iodide.[3] This reagent showed further good analytical potentialities against the micro determination of some other noble metals. Whereas, a very limited number of heterocyclic azo dyes find their uses for the determination of noble metals,[4-19] comparatively this reagent has been found a potential reagent for palladium(II), osmiun(VIII), and gold(III).

Experimental

Apparatus. A Unicam SP 600 spectrophotometer with matched 10-mm glass cells was used for recording the spectra. A Beckman Expandomatic SS-2 pH meter was used for the pH adjustments.

Reagents. *p*-QAP Solution. *p*-QAP was synthesized[1,3] as described earlier, and used as a 1×10^{-3} mol · cm^{-3} solution prepared by dissolving 0.249 g in 1 dm^3 of ethanol. The dark red solid (*p*-QAP) synthesized was quite stable for several months however, *p*-QAP solution more than a week old were discarded, as the older soutions gave slightly less absorbances with metal ions in comparison to freshly prepared solutions.

Palladium(II) Solution. A stock solution of palladium(II) was prepared by dissolving appropriate amount of palladium chloride (Johnson and Mathey, U.K.) in 2 mol · cm^{-3} hydrochloric acid. The solution was standardized gravimetrically with dimethylglyoxime.[20]

Osmium(VIII) Solution. A 1-g ampoule of osmium tetraoxide (Johnson and Mathey, U.K.) was broken beneath the surface of about 100 ml of normal sodium hydroxide solution, contained in a glass-stoppered flask, as described by Ayres and Wells.[21] The orange-red solution was washed into a one litre volumetric flask and made upto volume with doubly distilled water. The solution was standardized iodometrically by the method of Klobbie.[22]

Gold(III) Solution. A stock solution of gold(III) was prepared by dissolving appropriate amount of gold(III) chloride (Johnson and Mathey, U.K.) in doubly distilled water. The solution was 1 mol · dm^{-3} with respect to hydrochloric acid. The solution was standardized iodometrically.[23]

All other reagents were of analytical grade and doubly distilled water was used throughout.

Determination of Palladium(II). To a suitable volume of sample containing 4.7—25.7 μg of palladium(II) add 2 ml of 1×10^{-3} mol · dm^{-3} *p*-QAP solution followed by 1 ml of borate/HCl buffer. Dilute to 10 ml with water and ethanol keeping 50% (v/v) ethanol concentration. Heat on a boiling water bath for 5 min, cool and add ethanol to compensate the loss of volume on heating. Measure the absorbance at 580 nm against a corresponding reagent blank prepared under identical conditions.

Determination of Osmium(VIII). To a suitable volume of sample containing 7.9—32.4 μg of osmium(VIII) add 1 ml of 1 mol · dm^{-3} sodium acetate solution and 2 ml of 1×10^{-3} mol · dm^{-3} *p*-QAP. Raise the volume to 10 ml keeping 50% (v/v) ethanol concentration. Measure the absorbance at 550 nm against a reagent blank and deduce the amount of osmium(VIII) present from the calibration curve.

Determination of Gold(III). To a suitable volume of sample containing 17.4—58.9 μg of gold(III) add 3 ml of 1×10^{-3} mol · dm^{-3} *p*-QAP solution. Add 2 ml of cyclohexanol and 1 ml of aqueous solution 0.05 mol · dm^{-3} $Na_2B_4O_7$. Dilute to 10 ml with water and ethanol, adjusting water, ethanol and cyclohexanol in the ratio 4 : 4 : 2(v/v) in the final solution. Measure the absorbance of the solution at 550 nm against a corresponding reagent blank.

Results and Discussion

Among platinum metals, palladium is the easiest to determine and a number of organic reagents are known. Heterocyclic azo dyes are an important class of sensitive reagents for palladium. But very few are known for other noble metals. 4-(2-Quinolylazo)phenol forms a greenish violet complex with palladium at higher pH's. Full colour development takes place when the mixture is heated on a boiling water bath for about 5 min. Under the appropriate condi-

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Table 1. Physicochemical Characteristics of the Metal-*p*-QAP Complexes

Characteristic	Pd(II)-*p*-QAP comlex	Os(VIII)-*p*-QAP complex	Au(III)-*p*-QAP complex
λ_{max}/nm	580	550	550
pH range	8.0—10.0	8.0—9.5	8.0—9.5
Reagent required for full complexation (mol)	4	4	5
Beer's law range (ppm)	0.0—2.75	0.0—3.80	0.0—6.30
Optimum concentration range (ppm)	0.47—2.57	0.79—3.24	1.74—5.89
Sandell's sensitivity ($\mu g \cdot cm^{-2}$)	0.0027	0.0039	0.0098
Molar absorptivity (ε) ($l \cdot mol^{-1} \cdot cm^{-1}$)	3.98×10^{4}	4.9×10^{4}	2.0×10^{4}
Composition(M : L) by job's method	1 : 1	1 : 1	1 : 1

tions found for palladium(II), complexes of zinc, cadmium, mercury, cobalt, and gold decompose and therefore can be tolerated in varying amounts. Platinum metals, except osmium, do not form complexes and thus 50-fold of each are tolerated. A fair amount of EDTA does not interfere and has been used to mask many common metals. On the other hand, *p*-QAP forms violet complex with osmium(VIII) in alkaline medium and no warming is required for the color development. However formation of this complex can be obviated by nitrite and thus palladium can be determined selectively. However palladium(II) interferes in the determination of osmium(VIII).

Preliminary investigations on the colour reaction of gold(III) with ethanolic solution of *p*-QAP showed instantaneous red colour formation at higher pH's. The color, however, fades away with time. To stabilise the colour developed different solvents, singly of their mixtures have been tried and found that a mixture of water, ethanol and cyclohexanol in the ratio 4 : 4 : 2 can be used conveniently since the complex has maximum absorbance and is quite stable for 45 min. The effect of different solvents on the stability of gold(III)-*p*-QAP complex with time has been shown in Fig. 1.

Physicochemical Characteristics. In Fig. 2 are the spectra recorded for the complexes of *p*-QAP with the three metals. The optimum conditions and other physicochemical constants established for the complexes have been given in Table 1.

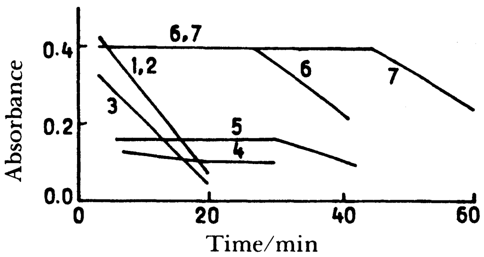

Fig. 1. Effect of different solvents on the stability of Au(III)-(*p*-QAP) complex with time (curves 1 and 2, 50% ethanol and 50% dioxane; 3, 50% DMF; 4, DMF : BuOH : water=5 : 2 : 3; 5, DMF : *c*-$C_6H_{11}OH$: BuOH: water=5 : 1 : 1 : 3; 6, ethanol : *c*-$C_6H_{11}OH$: water= 5 : 1 : 4 and 7, ethanol : *c*-$C_6H_{11}OH$: water=4 : 2 : 4).

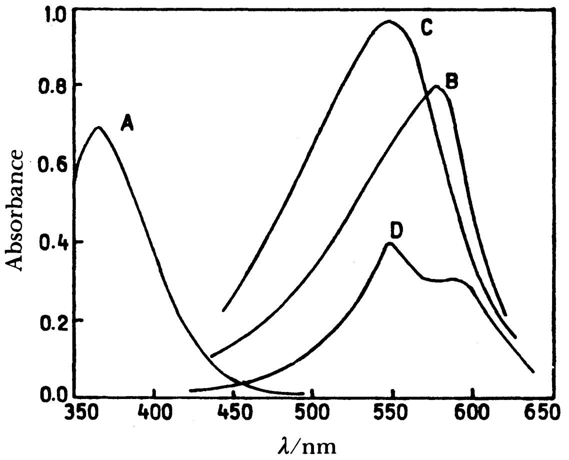

Fig. 2. Absorption spectra of *p*-QAP and its metal complexes at pH 8.0(A) 2.5×10^{-5} mol dm^{-3} *p*-QAP in 50% ethanol (v/v), (B) 2×10^{-5} mol dm^{-3} Pd(II)+1×10^{-4} mol dm^{-3} *p*-QAP[in 50% ethanol (v/v)], (C) 2×10^{-5} mol dm^{-3} Os(VIII)+1×10^{-4} mol dm^{-3} *p*-QAP[in 50% ethanol (v/v)], (D) 2×10^{-5}mol dm^{-3} Au(III)+1×10^{-4} mol dm^{-3} *p*-QAP(in ethanol: water : cyclohexanol=4 : 4 : 2).

Comparison of Sensitivities of the Methods. However many classes of organic spectrophotometric reagents, like oximes, nitroso compounds, hydrazones, reagents containing sulfur as ligand atom, are known for palladium, a number of heterocyclic azo dyes have also been suggested as sensitive reagents for this metal. Sensitivity index[8] 'ϕ' (defined as number of micrograms of an element, present as the absorbing species, in a column of solution of 1 cm^2 cross section giving an absorbance of 0.001 at a specified wavelength) of some important heterocyclic azo dyes are: 1-(2-pyridylazo)-2-naphthol[9] (0.0075 at 678 nm), 4-(2-pyridylazo)resorcinol[10] (0.0057 at 440 nm and 0.012 at 630 nm), 4-(2-thiazolylazo)resorcinol[11] (0.013 at 650 nm), 5-(ethylamino)-2-(2-pyridylazo)-*p*-cresol[12] (0.0039 at 520 nm), 3-(2-thiazolylazo)-2,6-diaminopyridine[13] (0.0077 at 665 nm) and 4-(2-thiazolylazo)-1,3-benzenediamine[14] (0.002 at 585 nm). The present method has the sensitivity index of 0.0027 µg Pd(II)/cm^2 at 580 nm.

A very few heterocyclic azo dyes are known as reagents for gold and osmium. 4-(2-Thiazolylazo)-resorcinol[19] forms a red colored complex with gold-

Table 2. Tolerance Limits of the Foreign Ions in the Determination of the Metal Ions

Foreign ion	For 2.13 µg ml^{-1} of Pd(II)		For 1.90 µg ml^{-1} of Os(VIII)		For 3.98 µg ml^{-1} of Au(III)	
	Toleranse limits /µg ml^{-1}	Masking agent	Tolerance limits /µg ml^{-1}	Masking agent	Tolerance limits /µg ml^{-1}	Masking agent
Fluoride	1000	—	1000	—	500	—
Chloride	1000	—	1000	—	1000	—
Bromide	1000	—	1000	—	1000	—
Iodide	80	—	15	—	Interfere	—
Nitrate	1000	—	1000	—	1000	—
Nitrite	200	—	Interfere	—	400	—
Phosphate	200	—	100	—	80	—
Sulfate	1000	—	80	—	1000	—
Sulfite	200	—	1000	—	Interfere	—
Sulfide	Interfere	—	Interfere	—	Interfere	—
Borate	1000	—	1000	—	1000	—
Cyanide	Interfere	—	—	—	Interfere	—
Thiocyanate	Interfere	—	Interfere	—	Interfere	—
Thiosulfate	Interfere	—	Interfere	—	Interfere	—
Thiourea	Interfere	—	Interfere	—	Interfere	—
Thiosemicarbazide	5	—	Interfere	—	Interfere	—
Oxalate	80	—	Interfere	—	60	—
Citrate	80	—	60	—	50	—
Tartrate	20	—	60	—	50	—
EDTA	150	—	150	—	300	—
Zinc(II)a)	20	—	20	—	20	—
Cadmium(II)a)	20	—	20	—	7	—
Mercury(II)	5	—	20	—	5	—
Copper(II)	12	Masked by EDTA	12	Masked by EDTA	50	Masked by EDTA
Silver(I)c)	10	Masked by Cl$^-$	6	Masked by Cl$^-$	20	Masked by Cl$^-$
Gold(III)	15b)	—	15	Masked by SO$_3^{2-}$	—	—
Tin(II)	5	—	5	—	Interfere	—
Lead(II)	20	—	20	—	50c)	—
Iron(II)	5	Masked by EDTA	5	Masked by EDTA	7	Masked by EDTA
Iron(III)c)	20	—	20	—	40	—
Cobalt(II)	10	Masked by EDTA	10	Masked by EDTA	10	Masked by EDTA
Nickel(II)	15	Masked by EDTA	15	Masked by EDTA	50	Masked by EDTA
Uranyl(II)	20	—	20	—	50	—
Palladium(II)	—	—	Interfere	—	Interfere	—
Osmium(VIII)	10	Masked by NO$_2^-$	—	—	20	Masked by NO$_2^-$

a) Metal-(*p*-QAP) complexes unstable. b) Gold-(*p*-QAP) complex in 50% ethanol medium decompose fastly on warming. c) Precipitate centrifuged.

Table 3. Determination of Palladium in Synthetic Solutions Corresponding to Some of Its Alloys36)

Alloy	Amount of Pd(II) taken (ppm)	Amount of foreign ions taken (ppm)	Amount of Pd(II) found (ppm)	Percentage error
Palladium-copper alloy of vicker hardness 145 (composition-40% Cu, 60% Pd)	(i) 2.0	1.33 Cu(II)	2.01	+0.50
	(ii) 2.0	1.33 Cu(II)	2.01	+0.50
	(iii) 2.0	1.33 Cu(II)	2.02	+1.00
Palladium-silver alloy (composition-40% Ag, 60% Pd)	(i) 2.0	1.33 Ag(I)	2.00	0.00
	(ii) 2.0	1.33 Ag(I)	1.99	−0.50
	(iii) 2.0	1.33 Ag(I)	2.00	0.00
Palladium-gold alloy of vicker hardness 85 (composition-50% Au, 50% Pd)	(i) 2.0	2.0 Au(III)	2.00	0.00
	(ii) 2.0	2.0 Au(III)	2.01	+0.50
	(iii) 2.0	2.0 Au(III)	2.00	0.00

(III) in xylene and 1-butanol mixture (4 : 1) and has the sensitivity index 0.013 µg Au(III)/cm^2 at 520 nm. The sensitivity index of some other organic reagents known for gold could be enlisted as dithizone24) (0.007 at 420 nm), methylviolet25) (0.0017 at 600 nm), chromopyrazole I26) (0.003 at 580 nm), di-2-pyridyl ketone oxime27) (0.0098 at 459 nm), furil-α-dioxime28) (0.0062 at 550 nm), and rhodamine B29) (0.002 at 565 nm). For

Table 4. Determination of Gold in Synthetic Solutions Corresponding to Some of Its Alloys[36]

Alloy	Amount of Au(III) taken (ppm)	Amount of foreign ions taken (ppm)	Amount of Au(III) found (ppm)	Percentage error
Purple gold	(i) 4.0	1.0 Al(III)	3.98	−0.50
(composition-79% Au, 21% Al)	(ii) 4.0	1.0 Al(III)	3.95	−1.25
	(iii) 4.0	1.0 Al(III)	4.00	0.00
Gold 16 carat	(i) 4.0	0.5 Cu(II)+1.5 Ag(I)	4.05	+1.25
(compositon-67% Au, 8—27% Cu, 6.6—26% Ag)	(ii) 4.0	1.0 Cu(II)+1.0 Ag(I)	3.99	−0.25
	(iii) 4.0	1.5 Cu(II)+0.5 Ag(I)	4.07	+1.75
Gray gold	(i) 4.0	0.66 Fe(II)	4.01	+0.25
(composition-86% Au, 5.7—17% Fe, 0—8.6% Ag)	(ii) 4.0	0.4 Fe(II)+0.26 Ag(I)	4.03	+0.75
	(iii) 4.0	0.33 Fe(II)+0.33 Ag(I)	4.0	0.00
White gold	(i) 4.0	0.4 Ni(II)+0.4 Zn(II)	4.02	+0.50
(composition-75—85% Au, 8—10% Ni, 2—9% Zn)	(ii) 4.0	0.4 Ni(II)+0.3 Zn(II)	3.95	−1.25
	(iii) 4.0	0.5 Ni(II)+0.3 Zn(II)	3.96	−1.00

osmium, very less reagents are known. Diphenylcarbazide[30] forms a blue-green complex, absorbing maximum at 560 nm (ϕ, 0.00127). A simple thiourea method[5,6] is popular but is insensitive. Some other known methods have the following sensitivity indices: acenaphthoquinone monoxine[31] (0.0323 at 430 nm), 1-naphthylamine-4,6,8-trisulfonic acid[32] (0.0063 at 573 nm), *o*-aminophenol-*p*-sulfonic acid[33] (0.01 at 440 nm), 3-nitroso-2,6-pyridinediol[34] (0.0079 at 550 nm), and 2-amino-3-pyridinol[35] (0.038 at 600 nm and 0.024 at 540 nm). The sensitivity indices for the present methods are 0.0098 at 550 nm for gold(III) and 0.0039 at 550 nm for osmium(VIII).

Effect of Foreign Ions on the Determination of Palladium(II), Osmium(VIII), and Gold(III). In the determination of the three metal ions [Pd(II)=2.13 μg ml^{-1}, Os(VIII)=1.90 μg ml^{-1} and Au(III)=3.98 μg ml^{-1}] calcium, magnesium, barium, strontium, aluminium, gallium, indium, antimony(III), manganese(II), lanthanoids upto 100-fold excess and vanadium(V), molybdenum(VI), platinum(IV), rhodium(III), iridium(IV), ruthenium(III) upto 25-fold excess do not interfere. The tolerance limits of other ions which do not cause a deviation of more than ±2% in the absorbance in the determination of the metals are given in Table 2.

Determination of Palladium(II) and Gold(III) in Synthetic Solution of Their Alloys. To ascertain the suitability of the reagent for the determination of palladium(II) and gold(III) in alloys, estimation has been carried out, adopting the appropriate conditions, in synthetic solutions identical in composition to some of their alloys.[36] The results obtained are recorded in Tables 3 and 4 and the percentage recovery obtained suggest that the methods are fairly successful.

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