Spectrophotometric Determination of Palladium, Tellurium and Iridium after Extraction with 2-Mercapto-4-methyl-5-phenylazopyrimidine

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A spectrophotometric method for the determination of palladium, tellurium and iridium from nitric acid media after extraction of their 2-mercapto-4-methyl-5-phenylazopyrimidine complexes into molten naphthalene has been developed and possible synergistic effects have been investigated. Dioxane, methanol, ethanol, 1-propanol, acetone and acetonitrile are used as the organic component of the mixed (polar) phase; the maximum enhancement is obtained with acetonitrile. Solid naphthalene containing the metal complex is separated by filtration and dissolved in chloroform; trace amounts of these metals are determined spectrophotometrically. Beer's law is obeyed in the following concentration ranges: Pd, 7.0 – 84.0 μg ; Te, 10.0 – 125.0 μg and Ir, 6.0 – 90.0 μg /10 ml of the final solution. The molar absorptivities ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and Sandell's sensitivities ($\mu\text{g cm}^{-2}$) were calculated: Pd(II)= 2.05×10^4 and 0.0052, Te(IV)= 1.84×10^4 and 0.0069 and Ir(III)= 0.95×10^4 and 0.020, respectively. Ten replicate analyses containing 12.5 μg of Pd(II), 21.0 μg of Te(IV) and 85.0 μg of Ir(III) gave mean absorbances of 0.241, 0.302 and 0.420 with relative standard deviations of 0.53, 0.36 and 0.85%, respectively. The interference of various ions was studied, and conditions were developed for the determination of these metals in certain alloys and synthetic mixtures.

Keywords Extraction-spectrophotometry, palladium, tellurium, iridium, 2-mercapto-4-methyl-5-phenylazopyrimidine

The pyrimidine ring is one of the most widely distributed systems of heterocyclic compounds as revealed by various reviews.¹⁻⁴ Pyrimidine derivatives play vital roles in several biological processes.⁵ 2-Mercaptouracil and its derivatives have also aroused some interest on account of their antithyroid activity.⁶ Recently, pyrimidines have also been reported as anti HIV⁷, antiamoebic⁸, antimalarial⁹ and antiviral¹⁰ agents. The chemistry of pyrimidine has received a feature filip, since many of these are found to possess anticancer¹¹ properties. An arylazo group is well known for its importance in promoting antineoplastic activity.¹² In view of the important biological activities display by pyrimidines and azo grouping, tremendous interest has been initiated.

Fujinaga *et al.*¹³ have developed a method involving the extraction of a complex with molten naphthalene, followed by solidification, separation and dissolution of the metal complex and naphthalene. This method is especially useful for the extraction of those metal ions that form complexes with complexing agents at high temperature, or that have low solubilities in non-aqueous organic solvents at room temperature.¹⁴ The sensitivity of the proposed method can be further enhanced by the introduction of polar organic additives¹⁵ to the aqueous phase. The developed conditions have been applied for the determination of these metals in certain alloys and synthetic mixtures.

Experimental

Reagents

All of chemicals used were of Analar R and GR grades of BDH or E. Merck, respectively. 2-Mercapto-4-methyl-5-phenylazopyrimidine (MMPAP) was synthesized and characterized based on IR, UV-visible spectra and elemental analyses. A 0.1% (w/v) solution of MMPAP in DMF was used for extraction. Stock solution (1000 ppm) of the metal salts were prepared from palladium chloride, potassium tellurite and iridium chloride and standardized by an established method.¹⁶

Apparatus

A Shimadzu 160A UV visible and Chemito 215 D visible spectrophotometer with 10 mm quartz cells was used for the absorption spectra of organic extractants. IR spectra in nujol mull between CsI discs were recorded using a Pye Unicam Model 1912 spectrophotometer over the 4000 – 200 cm^{-1} range.

General procedure

An appropriate volume of the sample solution (aqueous phase) and pre-equilibrated 2.0 ml of MMPAP (organic phase) were mechanically stirred in a 100 ml stoppered round-bottom flask. In all of the extractions, the polar phase was adjusted to the desired nitric acid

Fig. 1 Effect of the nitric acid concentration on the extraction of Pd(II), Te(IV) and Ir(III) with 0.2 M MMPAP from a pure nitric acid solution (Pd: ○, Te: ●, Ir: ○); a solution containing 30% (v/v) acetonitrile (Pd: □, Te: △, Ir: ⊗).

molarity (2 mol dm^{-3}) and contained 30% organic additive (acetonitrile). The solution was heated on a water bath at about 60°C for about 5 min, and 1.5 g of naphthalene was added. The temperature was increased to about $85-90^\circ\text{C}$ in order to melt the naphthalene. The mixture was then stirred and allowed to stand. The naphthalene containing the metal complex was then separated by filtration through filter paper, and dissolved in chloroform in a 10 ml calibrated flask. The solution was dried with about 2 g of anhydrous sodium sulfate, and the absorbance in 1 cm cell against a reagent blank was measured.

Results and Discussion

Dependence of distribution on nitric acid concentration

The effect of water-miscible admixtures on the extraction was investigated at increasing nitric acid molarties (Fig. 1) in the polar phase. The distribution ratio (D), defined as the ratio of the metal in the organic phase per ml, and the concentration of the metal in polar phase per ml was calculated. From knowledge concerning D , the volume of the aqueous phase (V_a) and that of the organic phase (V_o), the percentage extraction ($E\%$) was calculated: $E\% = 100D/(D + V_a/V_o)$. The distribution ratio (D) was considerably enhanced by the replacement of water with organic solvents, such as acetonitrile or methanol. The maximum extractability was shifted towards lower acidity in the presence of an organic additive. This was probably caused by the replacement of water with organic additives. After this, the value of D decreased along with a further increase in polar phase activity. At a higher acid concentration ($>4 \text{ mol dm}^{-3}$), the extraction was less influenced by an organic component in the polar phase, where higher D

values were obtained by adding organic solvents, particularly at a low acid concentration ($2-3 \text{ mol dm}^{-3} \text{ HNO}_3$). This phenomenon had been observed earlier for extraction from mixed aqueous organic media.¹²

Dependence of distribution on the MMPAP concentration

The dependence of D on the MMPAP concentration was studied at $[\text{HNO}_3] = 2 \text{ mol dm}^{-3}$. The extraction process follows the reaction

where subscripts a and o refer to the species presents in aqueous and organic phase respectively, for which the equilibrium constants, (K_{ex}) is given by

$$K_{ex} = \frac{[\text{M}(\text{NO}_3)_m \cdot n\text{MMPAP}]_{(o)}}{[M^{m+}]_{(a)}[\text{NO}_3^-]_{(a)}^m[\text{MMPAP}]_{(o)}^n}$$

By introducing the distribution ratio (D) as

$$D = [\text{M}(\text{NO}_3)_m \cdot n\text{MMPAP}]_{(o)} / [M^{m+}]_{(a)}$$

we obtain $\log D = \log K_{ex} + m \log [\text{NO}_3^-]_{(a)} + n \log [\text{MMPAP}]_{(o)}$.

A plot of $\log D$ vs. $\log [\text{MMPAP}]_{(o)}$ in the organic phase yielded a slope of 2.2 for Pd(II), 4.02 for Te(IV) and 2.9 for Ir(III), indicating that the extracted species would be $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{MMPAP}$, $\text{Te}(\text{NO}_3)_4 \cdot 4\text{MMPAP}$ and $\text{Ir}(\text{NO}_3)_3 \cdot 3\text{MMPAP}$.

Influence of diluents

The extractability and selectivity for the extraction of metals by organic extractants are greatly affected by the nature of the solvent. To study the influence of several typical commonly available aliphatic and aromatic organic solvents on the efficiency of extraction by MMPAP, the extractability of the metals from $2 \text{ mol dm}^{-3} \text{ HNO}_3$ was investigated with $0.2 \text{ mol dm}^{-3} \text{ MMPAP}$ dissolved in various solvents (diluent). Although a non-polar diluent, such as xylene, yielded less extraction than did a polar diluent, polarizable solvents, such as benzene and toluene, gave high metal extraction. A significant enhancement was obtained in extraction by introducing of 30% polar organic additives having a high dielectric constant, such as methanol, ethanol, 1-propanol, acetone, dioxane and acetonitrile (Table 1), to the aqueous phase. The addition of these polar additives decreased the dielectric constants of the aqueous phase. The maximum enhancement in extraction was obtained in the presence of 30% acetonitrile. At a low additives concentration, a dihydrogen effect due to the presence of additives, which provides a better chance for interaction with the nitrate ions to form extractable nitrate complexes, should lead to an increase in the metal extraction.

Effect of naphthalene

Extraction was carried out by varying the amount

Table 1 Extraction of the metals into naphthalene-DMF by MMPAP from acidic solutions

Organic additive	Dielectric constant	Distribution ratio, <i>D</i> , %		
		Pd	Te	Ir
Acetone	20.07	7.06	8.70	4.38
Acetonitrile	37.50	8.00	9.05	4.85
Benzene	2.28	2.50	4.80	3.20
Chloroform	4.81	1.70	3.75	2.00
Ethanol	24.60	6.85	8.35	4.20
Methanol	32.70	6.20	8.00	4.00
Toluene	2.38	3.80	6.00	3.65
Xylene	2.27	1.80	4.00	2.50

Organic phase: 0.2 mol dm⁻³ MMPAP in DMF; aqueous phase: 2 mol dm⁻³ HNO₃+organic additives.

from 0.25 – 4.5 g under constant conditions. In all cases the absorbance remained constant for 1.0 – 3.5 g of naphthalene. Below 1.0 g extraction was incomplete, and above 3.5 g it was difficult to dissolve naphthalene in a limited amount of chloroform.

Beer's law sensitivity

Under the optimum conditions described above, a calibration graph for these metals was constituted at 345, 415 and 280 nm against a reagent blank, respectively. Beer's law holds in the following concentration ranges: Pd, 7.0 – 84.0 µg; Te, 10.0 – 125.0 µg and Ir, 6.0 – 90.0 µg/10 ml of the final solution. The molar absorptivities (dm³ mol⁻¹ cm⁻¹) and Sandell's sensitivities (µg cm⁻²) were calculated: Pd(II)=2.05×10⁴ and 0.0052, Te(IV)=1.84×10⁴ and 0.0069 and Ir(III)=0.95×10⁴ and 0.020, respectively. Ten replicate analyses containing 12.5 µg Pd(II), 24.0 µg Te(III) and 85.0 µg Ir(III) gave mean absorbances of 0.241, 0.302 and 0.420 (Fig. 2) with relative standard deviations of 0.53, 0.36 and 0.85%, respectively.

Effect of foreign ions

The interference from foreign ions was studied under the optimum conditions. In general, a 1000 µg amount of salt of the studied anions and amounts equivalent to 500 µg of metal ions were added individually to an aliquot containing 12.5 µg Pd(II), 24.0 µg Te(III) and 85.0 µg Ir(III). Among the anions examined, EDTA interfered in the determination of all the metals and thiocyanate interfered in the determination of only palladium. The non-interference may be attributed to their low stability constants, compared to the metal complexes. Among the metal ions studied (Table 2), Cu(II), Ni(II), Fe(III), Co(II) and Hg(II) interfered in the determination of palladium. Iron(III) and copper(II) interfered in the determination of tellurium and iridium. Since EDTA has no influence, such metal ions as Ni(II), Co(II) and Hg(II) were masked by the addition of 5 ml of a 5% EDTA solution during extraction. The interference of Fe(III) was eliminated by adding 5 ml of a 1%

Fig. 2 Absorption spectra of Pd(II), 12.5 µg; Te(IV), 24.0 µg and Ir(III), 85.0 µg extracted with 0.2 M MMPAP from a 3 M HNO₃ solution containing 30% (v/v) acetonitrile.

Table 2 Effect of diverse salts and metal ions

Salt or ion	Tolerance limit/µg
KH ₂ PO ₄	2
CH ₃ COONa·3H ₂ O	700
NaCl, NH ₄ Cl	600
Ammonium citrate	300
Potassium sodiumtartrate	150
KNO ₃ , L-Ascorbic acid, Na ₂ C ₂ O ₄	100
KI	50
NH ₄ F, KCN, NaClO ₄ ·H ₂ O	2
Ca(II), Mg(II)	100
Mo(VI), Fe(III) ^a , Mn(II), Bi(III), Hg(II) ^b , Zn(II)	1
V(V), W(VI), Pt(III)	200
Cu(II) ^c	300
Pd(II)	500
Al(III)	200
Cr(III), Co(II) ^b , Ni(II) ^b	100

a. Masked by 5 ml of 5% EDTA solution.

b. Masked by 5 ml of 1% hydroxylamine solution.

c. Masked by 5 ml of 10% sodium cyanide solution.

hydroxylamine solution during extraction in all cases. The interference of Cu(II) was eliminating by adding 5 ml of a 10% sodium cyanide at pH 1.5. The interference due to various ions were studied and conditions were developed for the determination of these metals in certain alloys and synthetic mixture.

Sequential determination of palladium and iridium in synthetic solution

Various synthetic mixtures were prepared containing palladium and iridium together with other metals. These metals were determined by a general procedure after masking the interference of the metal ion by using a suitable masking agent. The results are presented in

Table 3 Simultaneous determination of palladium and iridium in synthetic sample

Composition of the mixture, %	AAS, ppm				Present method, ppm		RSD, %	
	Taken		Found		Found			
	Pd	Ir	Pd	Ir	Pd	Ir	Pd	Ir
Pd(II) 8.5, Pt(IV) 25.5, Ir(III) 17.0, Rh(III) 20.0, Mn(II) 24.0, Cu(II) 5.0	8.5	17.0	8.45	17.0	8.4	17.1	1.02	0.85
Pd(II) 6.0, Ag(I) 53.0, Ir(III) 21.0, Ni(II) 5.0, V(V) 15.0	6.0	21.0	6.10	20.64	6.06	21.05	0.65	0.75
Pd(II) 10.0, Pt(IV) 15.0, Ir(III) 24.5, Rh(III) 25.5, Co(II) 15.0, Cu(II) 10.0	10.0	24.5	9.68	25.0	10.04	24.1	0.99	1.04

Table 4 Determination of tellurium in synthetic sample

Te taken/ μg	Foreign ions added/ μg	Te found ^a / μg
25.0	Se: 10 Fe: 500 Ni: 400 SiO ₃ ²⁻ : 500	24.8 – 25.4 (25.14)
30.0	Se: 500 VO ₃ ²⁻ : 300 Co: 800 SiO ₃ ²⁻ : 300	29.7 – 30.35 (29.80)
12.5	Se: 20 W(VI): 250 Mn: 200 SiO ₃ ²⁻ : 500	12.0 – 13.10 (12.00)

a. Range of five replicate determinations and mean given in brackets.

Table 3.

Determination of tellurium in synthetic mixture

The method was also applied to the determination of tellurium in synthetic samples. The results are given in Table 4.

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