

Xanthates as Analytical Reagents: Extractive Photometric Determination of Nickel & Palladium

P K PARIJA* & S K MAJUMDAR

Department of Chemistry, North Bengal University, Darjeeling
734430

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The 1:2 (metal-ligand) complexes of nickel and palladium with various xanthates are extractable into chloroform and the resulting bright yellow extracts can be measured spectrophotometrically. The sensitivity is 0.018 to 0.03 and 0.5 to 0.65 $\mu\text{g}/\text{cm}^2$ for nickel and palladium respectively. The molar absorptivities range from 2.8×10^3 to 3.2×10^3 litre $\text{mol}^{-1} \text{cm}^{-1}$ and 1.76×10^2 to 1.9×10^2 litre $\text{mol}^{-1} \text{cm}^{-1}$ for nickel and palladium systems respectively. Major interfering ions are platinum metals, bismuth, copper, vanadate, molybdate and EDTA. The interferences of some of these can be eliminated by the use of masking agents.

Numerous complexing agents are known for the determination of nickel and palladium by liquid-liquid extraction¹. The authors in their previous communications² reported that these metals formed complexes with xanthates. The complexes were extractable into chloroform and the resulting bright yellow extracts could be measured spectrophotometrically. This provides the basis for the rapid extraction and photometric determination of these metals.

Beckman DU 2 model spectrophotometer fitted with optically matched cells of 10 mm path length was used for absorbance measurements. The standard Ni(II) and Pd(II) solutions were prepared by dissolving weighed quantities of palladium chloride (Johnson Matthey) and nickel sulphate (BDH) in doubly distilled water (with 1 ml conc HCl in case of PdCl₂). Standard solutions of diverse ions were prepared from their chlorides, sulphates or from sodium, potassium or ammonium salts.

Buffers of different pH values were prepared by standard procedures. Different xanthates were prepared and purified in the laboratory³ and their aqueous solutions (0.5%) were used for extraction purpose. Chloroform was distilled before use. All other chemicals used were either chemically pure or reagent grade materials unless mentioned otherwise.

General procedure

An aliquot of Ni(II)/Pd(II) test solution was mixed with a calculated volume of hydrochloric acid of known strength to give the desired acid concentration

and diluted with doubly distilled water. To this was added reagent solution (0.5%, 1 ml), total volume made up to 15 ml and extracted with chloroform. To study the effect of pH different buffer solutions were used. After equilibration the chloroform layer was separated and the volume made up to 25 ml by adding chloroform. The absorbance was measured at a suitable wavelength against a reagent blank prepared under identical conditions. The amount of metal ion extracted was directly read from the calibration curve. To study the interferences the respective foreign ions were added to the system before the dilution step. Different masking agents were also used to avoid some interferences.

Though extraction of Ni(II) starts around pH 2, it is found that Ni(II) is quantitatively extracted in the pH range 5-9. Other variables remaining the same, 1 ml (0.5%) aqueous solution of the respective xanthate is sufficient to extract 150-300 μg of nickel in a single operation with a shaking period of 2 min.

Nickel complexes show absorption maxima at 415 and 475 nm. Measurements at 415 nm were preferred due to high absorbance. The composition of the nickel complexes with various xanthates is found by mol ratio method to be 1:2 (metal: ligand). The colour of the organic extracts is stable for ~36 hr.

Iron(III) and lead (II) should be masked with fluoride and acetate respectively. Mercury(II) and cadmium(II) are tolerated at low concentrations. Cobalt(II) should be removed by extracting with thiocyanate into isoamyl alcohol. Bismuth(III) and Cu(II) interfere due to their characteristic colours. High results are obtained in presence of Mn(II), Pt(IV) and Rh(III). Osmium(VIII) forms a black precipitate. Attempts to mask these ions failed. When potassium ethyl and butyl xanthates were used as complexing agents interference due to palladium was avoided by its prior extraction in 2 M HCl medium. The aqueous phase was then adjusted to the required pH and nickel extracted as usual. EDTA prevents the extraction of nickel. Vanadate and molybdate interfere. The extraction data are presented in Table 1.

Palladium-xanthate complexes in chloroform show maximum absorption at 460 nm, except Pd(II)-ethyl xanthate complex which exhibits absorption maximum at 465 nm. Absorbance measurements were carried out at respective absorption maximum against reagent blanks. Xanthates show practically no absorbance from 410 nm onwards.

Potassium ethyl xanthate permits quantitative extraction of palladium from 10 M HCl to pH 8.0.

Table 1—Salient Features of Extraction of Ni(II) and Pd(II) by Various Xanthates into Chloroform

Reagent	Metal ion	Absorption maxima(nm)	Accuracy (average) %	Relative mean dev. %	pH range	Molar absorp. litre mol ⁻¹ cm ⁻¹	Validity of Beer's law (ppm)	Sensitivity (µg/cm ²)
Pot. ethyl xanthate	Ni	415,475	±1.3	±1.1	4-9	2.9 × 10 ³	3-16	0.02
	Pd	465	±2.1	±1.8	10 M HCl pH 8	1.9 × 10 ²	90-500	0.58
Pot. propyl xanthate	Ni	415,475	±1.4	±1.3	5-9	2.8 × 10 ³	5-15	0.03
	Pd	460	±2.4	±1.7	1-7	1.9 × 10 ²	80-500	0.6
Pot. butyl xanthate	Ni	415,475	±2.0	±1.6	5-8	3.2 × 10 ³	4-15	0.18
	Pd	460	±1.7	±1.6	2 M HCl-pH 7	1.76 × 10 ²	80-500	0.65
Pot. benzyl xanthate	Ni	415,475	±1.5	±1.5	5-8	3.1 × 10 ³	5-15	0.02
	Pd	460	±2.5	±1.4	1-7	1.82 × 10 ²	10-50	0.5
Pot. isoamyl xanthate	Ni	415,475	±1.5	±1.4	5-8	3 × 10 ³	5-15	0.02
	Pd	460	±1.9	±1.6	1-7	1.8 × 10 ²	80-500	0.5

Above this range the extraction procedure is hindered due to the formation of some brown suspension at the interface of the aqueous and organic phases. To ensure complete extraction the shaking period is varied depending upon the acidity of the aqueous solution used. In strong acid medium, the shaking period is 2 min while in 1 M HCl and pH 8 shaking periods are 5 min and 10 min respectively.

In the case of potassium propyl, benzyl and isoamyl xanthates, palladium is quantitatively extracted in the pH range 1-7. Deviation from this range renders the procedure incomplete. However, with potassium butyl xanthate the range is from 2 M HCl to pH 7. In all the cases it is difficult to keep palladium in solution above pH 7 owing to the formation of brown coloured suspension at the interface of the two layers. Shaking period is normally 2-5 min in all the cases. Above pH 7 it takes 10 min for complete extraction.

Mol ratio method indicates 1:2 stoichiometries (metal-ligand) for the complexes. Colour is stable at least for 24 hr.

Palladium(II) to the extent of 2-5 mg can be determined in the presence of 20-fold excess of different cations. With potassium ethyl xanthate, the extraction is carried out in 1 M HCl medium. Interferences due to iron and lead may be overcome by performing the extraction in the presence of ammonium hydrogen fluoride and sodium acetate respectively. However, at higher acidities (> 2 M) sodium acetate fails to mask lead, as its chloride is precipitated. In the presence of Cu(II) extraction requires 10 M HCl medium, since at lower acidities it is coextracted. Bismuth(III) interferes because of its intense colour. Gold is precipitated during this process and hinders the procedure.

Among the Pt metals Rh(III) and Ru(III) do not interfere even if present in five-fold excess. The presence of Pt(IV) always produces high results. Osmium(VIII) produces a deep brown solution and hence it must be removed, prior to the determination

of Pd(II), by extraction with hexamethylenetetramine into chloroform in the presence of EDTA. After removing the organic layer containing Os(VIII), Pd(II) may then be extracted from the aqueous phase as usual. The presence of 30-fold excess of anions does not hamper the procedure. High concentration of thiosulphate results in incomplete extraction of palladium. In the presence of vanadate and molybdate the extraction should be carried out at pH 8.

In the case of potassium propyl xanthate, vanadate and molybdate interfere seriously. Ni(II) and Co(II) are tolerated upto 25-fold excess in the presence of EDTA as masking agent. Potassium butyl xanthate shows almost similar behaviour. Attempts to avoid interferences due to Bi(III) and Cu(II) failed. Hg(II) and Cd(II) are tolerated at a low concentration. Rhodium(III) and Ru(III) are tolerated upto two-fold excess.

Behaviour of potassium benzyl xanthate and isoamyl xanthate is almost similar to that of propyl or butyl xanthate. Copper, bismuth, vanadate and molybdate interfere. The system tolerated Pt(IV), Rh(III) and Ru(III) at low concentrations.

There is no major variation in the extraction property of the various xanthates except Pd-potassium ethyl xanthate system which differs slightly with respect to the acidity and pH range of quantitative extraction and interferences.

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