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Spectrophotometric Determination of Nickel and Palladium after Separation by Adsorption of its Cyclohexylthioglycolate Complex on Microcrystalline Naphthalene

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A new spectrophotometric method for the trace determination of nickel and palladium after adsorption of its cyclohexylthioglycolate (CyHTG) complex on to microcrystalline naphthalene has been developed. The interference of various ions have been studied and the method has been applied to the determination of nickel and palladium in certain standard alloys and synthetic mixtures respectively.

INTRODUCTION

Several sulphur containing compounds are widely used as analytical reagents.[1-10] Among these compounds, cyclohexylthioglycolate (CyHTG) is one of the sensitive organic reagents which react with many elements. In this paper, the use of this reagent in the analysis of nickel and palladium by the adsorption spectrophotometric method has been reported. The complexes are extracted merely by contact with naphthalene in acetone and the main advantage is that a very small amount of the organic phase (0.4 gm) is required for the extraction which enhances the sensitivity. There is no need of adjusting the pH of the organic phase.

The reagent CyHTG reacts with these metal ions to form coloured complexes which can be adsorbed on microcrystalline naphthalene by shaking for a few minutes at room temperature. The adsorbed complex is separated by filtration and then naphthalene is dissolved in chloroform. In the present communication, conditions have been developed for the spectrophotometric determination of nickel and palladium using CyHTG as a complexing reagent. The method has been applied to the determination of nickel and palladium in certain standard reference materials and synthetic mixtures.

EXPERIMENTAL

Standard nickel(II) and palladium(II) solution of 5 ppm was prepared by diluting an aliquot of 1,000 ppm standard nickel(II) and palladium(II) solution with distilled water. CyHTG solution of 0.2% was prepared in ethanol. Buffer solutions were prepared by mixing 1 M acetic acid and 1 M sodium acetate solution for pH 3–5, and 1 M aqueous ammonia and 1 M ammonium chloride solution for pH 8-11. Chloroform, naphthalene and all the other reagents were of analytical reagent grade. All absorbance measurements were made with spectronic-20 spectrophotometer. Measurements of pH were carried out with a digital pH meter.

To an aliquot of sample solution containing 7.88 ppm of nickel or 10 ppm of palladium in a 100 ml stoppered Erlenmeyer flask and 1.0 ml of 0.2% CyHTG for Ni and 2.0 ml in case of palladium add 2.0 ml of buffer solution (pH 8.4 for nickel and pH 3.44 for palladium), 1.0 ml of 1 M potassium chloride for nickel making the total volume of 15 ml. Mix the solution well and allow to stand for 2 minutes at room temperature. Then add to it 2 ml of (20%) naphthalene-acetone solution and shake the mixture vigorously for a period of 2–10 minutes. Separate the solid by filtration using a fine filter paper, placed flat on a filter plate in a Buchner funnel or through a sintered glass filter (No. 2). Wash with water, dissolve in chloroform and make up to 10 ml exact in a standard flask. Record the absorption spectra of the solution in a 1 cm cell in each case. Maximum absorption occurs at 410 nm and 380 nm in the case of nickel and palladium respectively.

RESULTS AND DISCUSSION

Effect of pH

The adsorption of the metal complexes was carried out at different pH values keeping other conditions constant. The maximum adsorption occurred at pH 8.4 in case of nickel and at pH 3.44 in the case of palladium. The adsorption and hence the absorbance was less at pH lower or higher than mentioned above.

Effect of reagent concentration

Adsorption of nickel and palladium was carried out at optimum pH value by the general procedure but with the amount of reagent changed. It was observed that the adsorption was maximum with 0.5–2.0 ml of (0.2%) reagent in the case of nickel and 3.5–4.5 ml of reagent in the case of palladium.

Effect of time of shaking

Adsorptions were carried out under optimum conditions, while the time of shaking was varied from 1–10 minutes. It was observed that the absorbance was constant when the time of shaking was varied from 2–10 minutes for nickel and palladium.

Effect of standing time

Adsorptions were carried out for nickel and palladium under the optimum conditions described and the absorbance was measured. After intervals of 10 minutes, it was observed that the absorbance remained constant and hence the complexes were stable for more than 10 hrs.

Effect of naphthalene

The amount of naphthalene (20% in acetone) was varied from 0.5–4.0 ml and the adsorptions were carried out by the general procedure, both for nickel and palladium. Adsorption was constant irrespective of the amount of naphthalene. However, in all the experiments, 2.0 ml of 20% naphthalene-acetone solution was used for both the metals.

Composition of the complexes adsorbed

The nature of the nickel and palladium-cyclohexylthioglycolate complexes adsorbed on microcrystalline naphthalene was studied by the Job's method of continuous variation and also by the mole-ratio method. A peak at 0.33 mole fraction in Job's curve and a break at 1 : 2 (metal: CyHTG) in the mole-ratio plot suggested the adsorption of 1 : 2 (metal: CyHTG) complex on microcrystalline naphthalene.

Sensitivity and calibration curve

Under the optimum conditions described above, calibration curves were constructed for nickel and palladium at 410 nm and 380 nm respectively. It is observed that the Beer's law is obeyed from 1.97–9.85 ppm and 2.0–12.0 ppm for nickel and palladium respectively. The molar absorptivities and sensitivities in terms of Sandell's definition were calculated to be 0.56×10^4 l mol^{-1} cm^{-1}, 0.0103 μg cm^2 and 0.74×10^4 l mol^{-1} cm^{-1} and 0.014 μg/cm^2 for nickel and palladium respectively. Solutions containing 7.88 ppm of nickel and 10 ppm of palladium gave mean absorbances of 0.760 and 0.695 respectively with standard deviation of 0.003 and 0.0025 and relative standard deviations of 0.39% and 0.35% respectively.

Effect of diverse ions

The interference of various ions was studied in detail. Generally, 10 mg of the alkali salts and 2 mg of the metal salts were added individually to aliquots containing 7.88 ppm of nickel and 10 ppm of palladium and the adsorptions were carried out by the general procedure. Among the anions examined, results were low with EDTA, both in the case of nickel and palladium, due to the high stability constant of these metal-EDTA complexes. Among the cations examined, Pb(II), Mn(II), Mg(II), Zn(II), U(IV), Cr(III), Ba(II), Sr(II), Bi(III), Hg(II) and W(VI) did not interfere in the determinaton of nickel and palladium. However, Co(II) interfered seriously in the determination. Interference due to iron was eliminated by adding 5% NaF. Interference due to palladium in the determination of nickel was eliminated with 5% sodium thiosulphate solution. Results are given in Table 1.

TABLE 1
EFFECT OF DIVERSE IONS AND SALTS

Ni (II) = 78.8μg Pd = 100.0 μg
pH = 8.4 pH = 3.44

Ion/Salt	Tolerance limit for nickel	Tolerance limit for palladium
Mn(II)	2.0 mg	2.0 mg
Pb(II)	0.5 mg	0.5 mg
Cd(II)	2.0 mg	2.0 mg
Zn(II)	0.5 mg	0.5 mg
Ba(II)	2.0 mg	2.0 mg
Sr(II)	2.0 mg	2.0 mg
Ca(II)	2.0 mg	2.0 mg
Mo(VI)	2.0 mg	2.0 mg
Bi(III)	1.0 mg	1.0 mg
Cr(III)	1.0 mg	1.0 mg
Cu(II)	0.5 mg	0.5 mg
Pt(IV)	2.0 mg	2.0 mg
Co(II)*	5.0 μg	5.0 μg
Ni(II)†	–	5.0 μg
Pd(II)‡	10.0 μg	–
Fe(II)**	50.0 μg	50.0 μg
KBr	10.0 mg	10.0 mg
KI	10.0 mg	10.0 mg
NaF	10.0 mg	10.0 mg
KSCN	10.0 mg	10.0 mg
CH_3COONa	8.0 mg	10.0 mg
Na_2SO_4	10.0 mg	8.0 mg
$Na_2S_2O_3$	2.0 mg	0.1 mg
Sodium citrate	10.0 mg	10.0 mg
Sodium metabisulfate	10.0 mg	10.0 mg
Disodium EDTA	Interfers strongly	

*Interfered.
†Interference eliminated with sodium cyanide.
‡Masked with 5% sodium thiosulfate.
**Masked with 5% Sodium fluoride.

Determination of nickel in standard reference materials

A 0.1 g sample of alloy was completely dissolved in 10–15 ml of hydrochloric acid on a water bath. Added few drops of nitric acid to it. The volume was reduced to 5 ml. The mixture was cooled, added 10 ml of HCl and made with distilled water, up to the mark in a measuring flask. An appropriate volume of this solution was taken and nickel was determined by the general procedure. The results are given in Table 2.

TABLE 2
DETERMINATION OF NICKEL IN SOME ALLOYS

Name of the alloy	Certified % composition	Amount of nickel taken (ppm)	Amount of nickel found (ppm)	Average (ppm)
Monel 400	Ni: 63	2.00	2.02	
	C: 0.15	5.05		
	S: 0.0024		2.05	
	Mn: 0.01		2.00	2.02
	Si: 0.50		2.00	
	*Fe: 2.5		2.05	
	Cu: 32.0			
Stainless Steel	Cr: 16.5		5.05	5.07
No. 306	Mo: 2–3.0		5.05	
	Ni: 12.0		5.10	
	*Fe: 70–71.0		5.10	
			5.05	

Determination of palladium in some synthetic samples

Different amounts of metal salts including that of palladium were mixed together in such a way that the resultant mixtures corresponded to some standard reference alloys. The mixture (0.2–0.3g) was completely dissolved in 20–25 ml of aqua regia and the solution was evaporated to about 5 ml. Concentrated hydrochloric acid (10 ml) was added to it, and the solution was warmed. After cooling to room temperature, it was diluted to 500 ml in a standard flask. To an aliquot of the sample solution was added 2 ml of 5% sodium fluoride in order to remove the interference due to iron. The determination of palladium was then carried out by the general procedure. The results are given in Table 3.

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TABLE 3

DETERMINATION OF PALLADIUM IN SYNTHETIC SAMPLES

Sample	Certified % Composition	Amount of palladium taken (ppm)	Amount of palladium found (ppm)	Average (ppm)
Platinum-Iridium alloy	Pd: 3.5	4.00	4.03	4.02
	Pt: 55.0		4.02	
	Ir: 28.0		4.02	
	Rh: 7.0		4.02	
	Cu: 3.0		4.05	
	*Fe: 3.5			
Oakay alloy	Pd: 10.5	2.5	2.52	2.51
	Ni: 60.0		2.50	
	Pt: 20.0		2.51	
	V: 9.5		2.53	
			2.50	

*Masked with 5% NaF.

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