

Spectrophotometric Determination of Pd(II) With P-Dimethylaminebenzylidenerhodanine

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ABSTRACT

p-Dimethylaminebenzylidenerhodanine in methyl isobutyl ketone was employed as selective and sensitive reagent for the extraction and determination of palladium(II) in metal alloys and rocks. Beer's Law is followed in the concentration range 0.2–2.4 $\mu\text{g}\cdot\text{mL}^{-1}$ of organic phase with a molar absorptivity of $3.0 \times 10^4 \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The detection limit observed for aqueous solution was 0.1 $\mu\text{g}\cdot\text{L}^{-1}$. The extractions were performed at pH 2.4 and no interference of foreign ions such as Cu^{2+} , Zn^{2+} , Fe^{3+} , Pb^{2+} , Hg^{2+} , etc., were observed in jewellery alloy and rock sample analyzed. The complex of reagent and palladium(II) was pH dependent and it should be carefully controlled during extraction. Continuous variation and mole ratio methods showed that the complex composition was 1:1.

Key words: p-dimethylaminebenzylidenerhodanine; palladium(II); extraction-spectrophotometry; rocks; metal alloy

INTRODUCTION

The compound 5-(4-dimethylamine benzylidene) rhodanine (DMABR) and its derivatives are reagents that form very strong and stable complexes with platinum group elements (Pd^{2+} , Au^{3+} , Ag^+ , Ir^{3+} e Rh^{3+}) in weak acidic media (Sandell, 1948), (Natelson and Zuckerman, 1951), (Sandell and Numayer, 1951), (Narang and Ayres, 1961), (Doycheva et al., 1971), (Borissova et al., 1975), (Borissova, 1975), (Pangarova, 1977), (El-Zawawy et al., 1995), (Borissova et al., 1975). The spectrophotometric method for the determination of Pd^{2+} with DMABR was first proposed to be performed in acidic media such as formic, hydrochloric, acetic and propionic acids (Narang and Ayres, 1961). It was observed that Au^{3+} , Ir^{3+} and Cr(VI) were serious interfering ions, (especially gold). On the other hand, the interfering action of silver was easily masked by hydrochloric acid, removing the silver chloride formed.

Hydrochloric acid medium, pH 1.0, was used to the determination of Pd^{2+} , without the interference of silver by Borissova et al. (1975). The determination of Pd^{2+} with DMABR was

performed using the toxic nitrobenzene as solvent (Doycheva et al., 1971). It was also observed that Au^{3+} was a serious interferer even in trace amounts, while ions such Fe^{3+} , Bi^{3+} , Pt^{4+} , Hg^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , CN^- , etc., showed interfering actions only at larger concentrations.

In this paper, we report the results on selective extraction of Pd^{2+} from aqueous solution, pH 2.4, with DMABR in methyl isobutyl ketone (MIBK). The spectrophotometric determination of Pd^{2+} was performed directly in organic phase. The separation of Pd^{2+} and Au^{3+} was also investigated to be employed for samples with higher gold concentration.

MATERIALS AND METHODS

Reagents

The solution of DMABR (Aldrich-USA) $1.0 \times 10^{-4} \text{mol}\cdot\text{L}^{-1}$ was prepared in MIBK. The solution of Pd^{2+} ($73.40 \mu\text{g}\cdot\text{mL}^{-1}$) was prepared from PdCl_2 (Aldrich-USA) and standardized by the $\text{Th(NO}_3)_4$ -EDTA method (The Merck Index, 1976). A solution of NaF ($1.0 \text{mol}\cdot\text{L}^{-1}$) was employed as

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masking reagent of Fe^{3+} , ethanolic solution of 0,25 mol.L⁻¹ dimethylglyoxime was used for Pd^{2+} and Au^{3+} separation, and a mixture of EDTA 0,100 mol.L⁻¹ with 1,2 mol.L⁻¹ sodium citrate as masking agent to the other ions such as Fe^{3+} , Cu^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} , Ni^{2+} , etc.

Preparation of standard Pd^{2+} solution

Titration of a 50 mg.L⁻¹ of Th^{4+} as $\text{Th}(\text{NO}_3)_4$ solution, adjusted to pH 1.0-2.0 with HNO_3 , was performed with 0.100 M EDTA to a xylenol orange end point, according to the reaction:

$$1.0 \text{ mL of } 0.100 \text{ M EDTA solution} = 23.204 \text{ mg of } \text{Th}^{4+}.$$

In the following step, 10.0 mL of 0.100 M EDTA(excess) were added to an acidic solution of ~50 mg of Pd, pH ~3.0, using xylenol orange as indicator. The back titration was performed with 0.100 M $\text{Th}(\text{NO}_3)_4$, and the concentration was calculated using the following relationship:

$$1.0 \text{ mL of } 0.100 \text{ M EDTA} = 10.64 \text{ mg of } \text{Pd}^{2+}$$

Sample preparation

The pegmatite rock was collected from Campo Largo County, Parana State, Brazil. A rock sample with mineral veins and an average of 6.0 (Mohs' scale of hardness), irregular masses and grains of many sizes, specific gravity of ~ 2.7, where the presence of other minerals such as fluorite, feldspar, and chalcopyrite gave a grey-brown colour. The sample containing Si, Pd, Au, Fe, As, S, etc., was crushed to 100 mesh, heated at 800⁰C for 3 h, and dissolved with aqua-regia. After filtration and separation of undissolved SiO_2 , the pH was adjusted to 2.4. The liquid-liquid extraction were performed five times with 2.0 mL of 1.0×10^{-4} mol.L⁻¹ solution of DMABR in MIBK.

Extraction and Pd^{2+} determination

The optimum conditions for the extractions of the complex Pd^{2+} :DMABR, such as pH of aqueous solution, reagent concentration, presence of interfering ions, etc., were investigated using a 125 mL separatory funnel. The Pd^{2+} from aqueous solution was extracted with 2.5 mL of DMABR and the organic phase was transferred to a 10.0 mL volumetric flask. The extractions were performed four more times using the same volume of

DMABR. The spectrophotometer Beckman-DU-70 was used for absorbance reading with 10 mm cell at 502 nm. The stability of Pd^{2+} -DMABR complex was investigated reading the absorbance in time intervals of 5 minutes during 90 minutes. The calibration curve was prepared changing the concentrations of Pd^{2+} in aqueous solution, using the same procedure for extraction and spectrophotometric determination.

Complex stoichiometry

The molar ratio and continuous variation methods (Skoog and Leary,1992) were employed for the determination of Pd^{2+} :DMABR stoichiometry in MIBK. Volumetric flasks of 10.0 mL were used adjusting the pH to 2.4, and reading the absorbance at 502 nm up to 60 minutes.

Interfering ions

The extraction efficiency of Pd^{2+} was investigated in the presence of several ions in aqueous solution, pH 2.4. To the standard solutions of Pd^{2+} (0.12 $\mu\text{g}.\text{mL}^{-1}$), several ions with known concentrations were added to investigate its interfering action on Pd^{2+} -DMABR complex.

Separation of Pd^{2+} and Au^{3+}

The separation of Pd^{2+} and Au^{3+} was investigated to be applied in samples with higher gold concentrations. To a 200 mL solution containing Au^{3+} , Pd^{2+} , Ni^{2+} , and Fe^{3+} , 0.5 mL of NaF, 1.5 mL of the mixture of EDTA-sodium citrate were added and the pH was adjusted to 5.5 with solutions of 0.1 M Na_2CO_3 and HCl. The solution was warmed at 60 – 70⁰C and an alcoholic solution of dimethylglyoxime (DMG) was added drop by drop until complete precipitation of Pd^{2+} . After digestion of the precipitate for 30 minutes at the same temperature, hot filtration was performed with 10-20 μm porosity Buchner funnel. The precipitate was washed three times with 0.1 M HCl and several times with distilled water. Aqua-regia (2 mL) was used to dissolve the precipitate, and the solution was heated to expel oxides of nitrogen. The residue was redissolved with 6 ml of 6 M HCl, diluted to ~90 ml with distilled water, the pH was adjusted to 2.4, and completed to the mark (100.0 ml) with distilled water. The selective extraction of Pd^{2+} was performed with DMABR and MIBK at this pH.

RESULTS AND DISCUSSION

Figure 1 shows the extraction efficiency of Pd²⁺ with DMABR as function of pH of aqueous phase. The concentrations used were: DMABR 1,0x10⁻⁴ mol.L⁻¹ and Pd²⁺ 0,12 µg.mL⁻¹ in aqueous phase.

Optimum pH range was 2.0 – 2.5 with maximum efficiency at pH 2.4. Figure 2 shows the stability for the complex Pd²⁺:DMABR in organic phase as function of time with absorbance reading at 502 nm. The complex was very stable for at least 60 minutes as shown in Figure 2.

Table 1. Effects of interfering ions (*).

Ion	tolerance limit	tolerance limit	observed error %
Investigated	(µg.mL ⁻¹)	(µg.mL ⁻¹) (**)	
UO ₂ ²⁺	300		0
Cu ²⁺	100	300	+5
Fe ³⁺	30	300	+3
Pb ²⁺	30	300	+5
Ti ³⁺	30	300	0
In ³⁺	50		0
Al ³⁺	50		0
Ni ²⁺	30	300	0
Th(IV)	300		0
Si(IV)	300		0
Au ³⁺	0,30		+2
Au ³⁺	0,60		+ 39
Au ³⁺		300 (#)	0
Ag ⁺	0,30		0
Ag ⁺	0,60		+6
Ag ⁺		300	0
Hg ²⁺	0,30		0
Hg ²⁺	0,60		+38
Hg ²⁺		300	0

(*) In the presence of 0,12 µg.mL⁻¹ of Pd²⁺ in aqueous phase, pH 2.4.

(**) In the presence of masking substances in aqueous phase.

(#) Separation of Pd²⁺ and Au³⁺ after precipitation of Pd²⁺ with dimethylglyoxime.

Table 2. Pd²⁺ determination in quartz vein(*) and metal alloy used in (**).

(*) Pd ²⁺ determination in quartz vein		
Samples n ^o .	[Pd ²⁺] (mg/g) spectrophotometry	[Pd ²⁺] (mg/g) ICP-MS(#)
1	0,20	0,24
2	0,18	0,21
3	0,22	0,18
4	0,20	0,20
5	0,20	0,22
Average	0,20 ± 0,01	0,21 ± 0,02
(**) Pd ²⁺ determination in metal alloy		
Samples	[Pd ²⁺] (mg/g) Spectrophotometry	[Pd ²⁺](mg/g) ICP-MS(#)
1	0,27	0,27
2	0,20	0,23
3	0,24	0,28
4	0,26	0,22
5	0,28	0,30
Average	0,25 ± 0,03	0,26 ± 0,03

(*) Quartz vein = pegmatite sample from Campo Largo County, Parana State, Brazil.

(**) Metal alloy used in jewelry containing Pd, Cu e Ag.

(#) Performed by ICP-MS (Instituto de Tecnologia do Paraná-TECPAR-Brazil).

Figure 1. Extraction efficiency of Pd(II) as function of pH

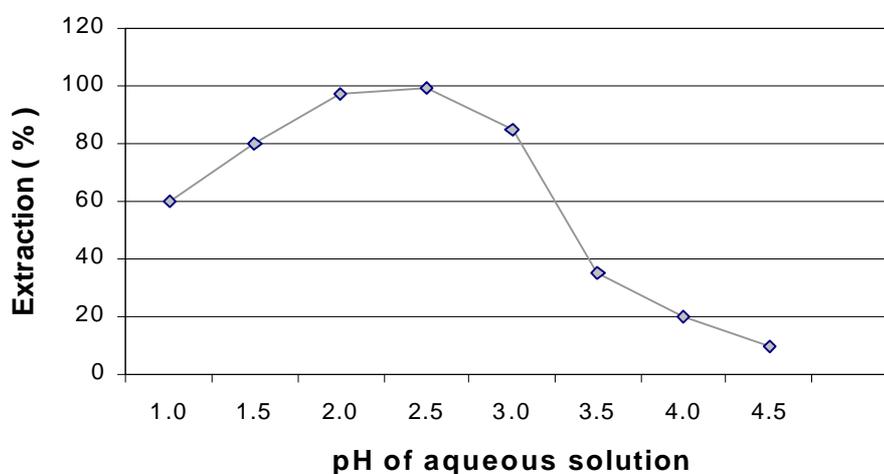


Figure 2. Stability of Pd:DMABR complex in organic phase as function of time

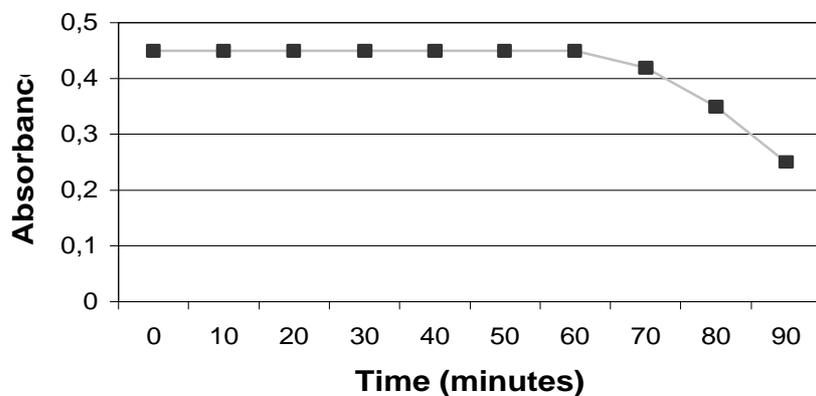


Figure 3. Continuous variations method for Pd:DMABR complex

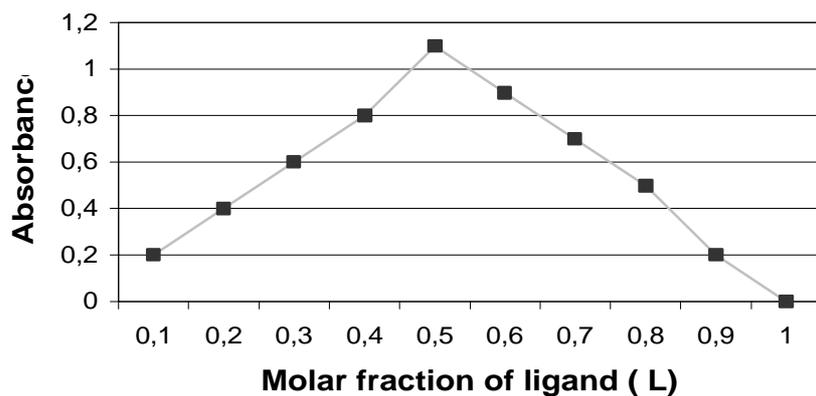


Figure 4. Molar ratio method of Pd:DMABR complex

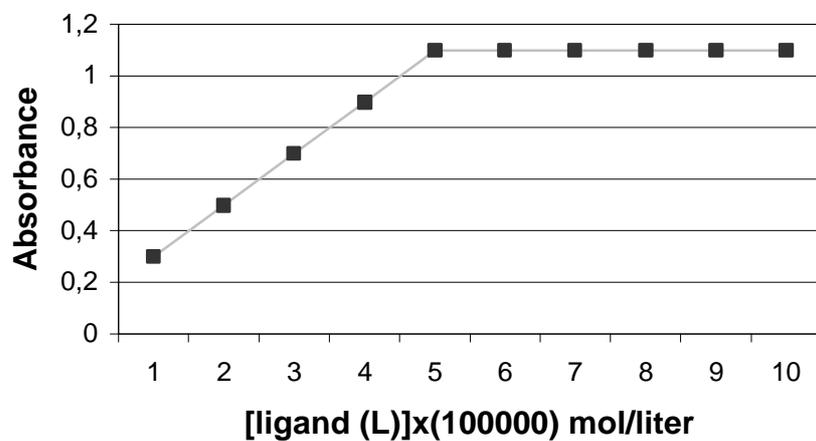


Table 1 shows the influence of several ions during the extraction of Pd²⁺:DMABR complex. Gold, silver and mercury were the main interfering ions in concentrations higher than 0.3 µg.mL⁻¹.

The analytical calibration curve showed that Beer's Law was followed from 0.2 to 2.4 µg.mL⁻¹ of palladium in organic phase. The detection limit observed for aqueous phase was 0.1 µg.L⁻¹. Table 2 shows the spectrophotometric determination of Pd²⁺ in metal alloy and pegmatite sample of quartz vein, and also the determination by ICP-MS (Inductively coupled plasma atomic emission spectroscopy).

Using the selective extraction of Pd-DMABR complex in MIBK at pH 2.4, no interference was observed by Ni²⁺, Fe³⁺, Au³⁺, etc. The following conditions were used for ICP analysis: Spectrometer Baird PSX; 1.0 kwatts; integration time of 5 deciseconds; argon flux 7.5 L.min⁻¹; auxiliary argon flux 1.2 L.min⁻¹; sample introduction rate 1.2 mL.min⁻¹; nebulizer pressure 26 psi; and wavelength 340.458 nm. The 1:1 stoichiometry of Pd²⁺-DMABR complex were investigated by continuous variation and molar ratio methods as shown in Figures 3 and 4. The calculated formation constant K_f was 2.4 x 10⁵ according to Skoog and Leary (1992).

CONCLUSIONS

The interfering action of gold and several ions were investigated and solved by the selective extraction of Pd-DMABR complex in MIBK at pH 2.4. Small amounts of gold in aqueous phase did not interfere during the extraction of Pd-DMABR complex in MIBK at pH 2.4. Samples with larger amounts of gold were separated after precipitation of Pd-DMG. The method investigated is very sensitive for palladium determination.

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FIGURE CAPTIONS

Figure 1. Extraction efficiency of Pd(II) as function of pH.

The extractions were performed using a 125mL separatory funnel. The volume used of DMABR in MIBK were 2.5 mL and after four extractions the total volume were 10.0mL. The absorbances reading were at 502nm using 10mm cell. The following concentrations were used: DMABR = 1.0×10^{-4} mol.L⁻¹ and Pd²⁺ = 0.12 µg.mL⁻¹.

Figure 2. Stability of Pd-DMABR complex in organic phase as function of time.

The organic extract of Pd-DMABR complex were investigated for stability, reading the absorbances at 502nm in time intervals of 5 minutes during 90 minutes.

Figure 3. Continuous variations method of Pd-DMABR complex.

Tem volumetric flasks of 10.0mL were used to investigate the continuous variations method. The initial concentrations of Pd²⁺ and DMABR were 7.34×10^{-5} mol.L⁻¹. The first flask shows that the volume proportion were 9.0mL of Pd(II) and 1.0mL of DMABR. In the stoichiometry ratio (1:1) the volumes proportions were 5.0mL of Pd²⁺ and 5.0mL of DMABR solutions, as shown in Figure 3.

Figure 4. Molar ratio method of Pd-DMABR complex.

The concentration of Pd²⁺ was 5.0×10^{-5} mol.L⁻¹ keeping constant over the total experiment. The concentrations of ligand (DMABR) were variable and changed from 1.0×10^{-5} mol.L⁻¹ to 9.0×10^{-5} mol.L⁻¹.

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