EXTRACTION - SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH TETRABUTYL - AMMONIUM IODIDE

Dadfarnia, Sh.
Shamsipour, M.*
Department of Chemistry, Shiraz University, Shiraz, Iran.

(Received: May 9th 1991 , Accepted: May 18th 1992)

ABSTRACT : *A sensitive and selective extraction - spectrophotometric method for the determination of trace amounts of palladium is reported. The method is based on quantitative extraction of brownish tetrabutylammonium tetraiodopalladium (II)ion pair into a small volume of chloroform at pH 1.3 - 12.0, followed by spectrophoto- metric measurements. The Beer's law is obeyed over the range 0.02 - 1.09μgml^{-1} at 445 nm with the molar absorptivity of 5.3 × 10^{3}lmol^{-1}cm^{-1}. The Sandell's sensitivity is 0.80 mg cm^{-2} for 0.001 absorbance unit. The method has a wide range and is simple, rapid and free from interferences from many cations and anions. The procedure was applied to the determination of palladium in the activated carbon.*

KEY WORDS : *Palladium determination, Extraction, Spectrophotometric, t- But. Ammonium iodide.*

INTRODUCTION :

Prior to 1930, palladium was used only in moderate amounts, principally in dental alloys and jewelry [1]. With increased and reliable supplies available, it has found a widespread use in different areas of science and technology, including coating agents [2], brazing alloys [3], petroleum [4] and electrical [5,6] industries as well as a wide variety of catalytic chemical reactions [7]. Thus, because of its increasing use, the separation and determination of palladium

* Corresponding author

1011-3509/ 92/ 1/ 14 6/ $ 1.62

in trace levels are of special interest.

Most of the spectrophotometric methods reported for the determination of Pd(II) are based on the chelate formation with organic reagents [8-13] or ion pair formation with basic dyes [14-16]. However, these methods usually suffer from poor selectivity, due to interferences from several commonly associated ions, relatively low sensitivity and need for the rigid control of the pH. In additon, some of the ion- association compounds precipitate out at the phase boundary or on the walls of separatory funnels when the aqueous solution is shaken with an organic solvent [16].

It has already been reported that addition of an excess amount of potassium iodide to the aqueous solution of Pd(II) results in the formation of a brown colloidal solution of $K_2[PdI_4]$ complex [17]. In this work, we found out that the use of tetrabutylammonium iodide, instead of KI, not only provides the required iodide ion for the complex formation with Pd(II), but also its cation serves as a suitable counter ion for the formation of an ion- association compound with $[PdI_4]^{2-}$ ion which is quantitatively extractable in a small volume of chloroform. In this paper, we wish to report a sensitive and selective extraction- spectrophotometric method for the determination of palladium in ppb levels.

EXPERIMENTAL :

Reagents

All of chemicals used in this study were of highest purity available and were used as recieved.

Tetrabutylammonium iodide (TBAI, Merck Darmstadt; Germany) solution, 0.3% w/v. Prepared in triply distilled water.

Palladium (II) stock standard solution. An appropriate amount of $PdCl_2$ (Merck) was dissolved in 25 ml of 1 M hydrochloric acid in a 100 ml volumetric flask. The solution was diluted to the mark with triply distilled water and the concentration of palladium was determined gravimetrically using dimethylglyoxime [18]. The working solutions were prepared by suitable dilution of the stock solution

Potassium chloride (Merck) solution, 3 M. Prepared in triply distilled water.

Apparatus

The visible spectra were obtained with a Beckman DK-2A ratio recording spectrophotometer and the absorbance measurements were made with a *Perkin- Elmer* 35 spectrophotometer. The pH values were determined with a Corning 125 pH meter.

Procedure

In a 100 ml calibrated flask place an aliquot of the sample containing 2-109 μg of Pd(II). Add 2.5 ml of 0.3% TBAI and 5 ml of 3 M KCl solutions and dilute to the mark with triply distilled water and mix well. Transfer the solution into a 250 ml separatory funnel. Extract the mixture with 4 ml of chloroform (exactly measured) by shaking the funnel vigorously for 5 min. Allow the phases to separate and measure the absorbance of the organic phase at 445 nm against a reagent blank.

Determination of Palladium in the Activated Carbon. The dreid sample ($\sim$ 0.2 g) is treated with two 20 ml portions of aqua regia and heated nearly to dryness. After cooling, 10 ml of triply distilled water is added and the solution is filtered. After washing the precipitate with several portions of dilute nitric acid, the filterate is diluted to volume with water in a 250 ml calibrated flask. The palladium content is then determined according to the above procedure. In this case, because of the relatively high concentration of nitrate ion, it is necessary to add some extra amount of potassium iodide to ensure the complete complex formation of Pd^{2+} ion.

RESULTS AND DISCUSSION :

Absorption spectra

The absorption spectra of the ion- association compound and of the corresponding reagent blank in chloroform are shown in Fig. 1. As it is seen, the brownish complex shows two maxima at 550 and 445 nm. Since the intensity of the 445 nm band was higher, in one hand, and the spectral

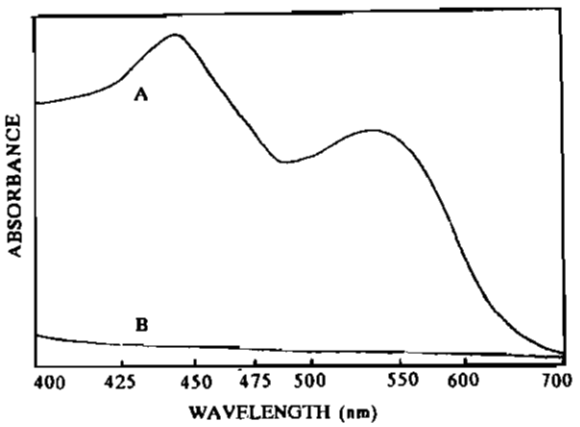

Fig. 1 : Absorption spectra of the ion- association complex of Pd(II) with TBAI, (A) the reagent blank , (B) in chloroform

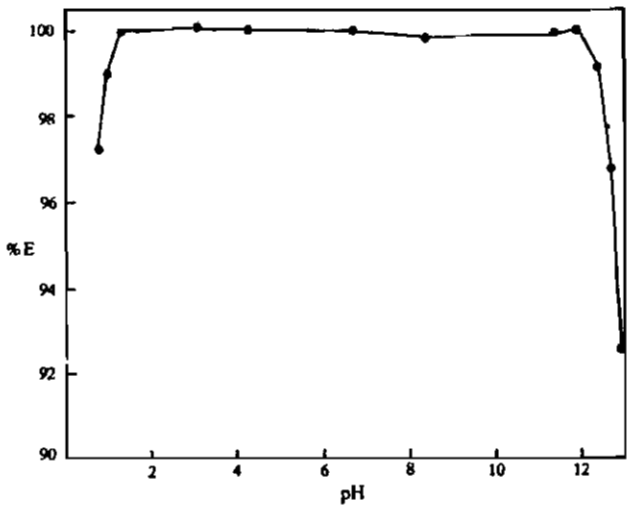

Fig. 2 : Effect of pH on the extraction of Pd(II).

Conditions:

Pd(II): 1.012 μg ml⁻¹ *TBAI: 1m of 1.5% in H_2O*

KCl : 5 ml of 3.5 M *λ_{max}: 445 nm*

Color: brown

contamination from the interferences was much lower, on the other, this wavelength was used for the further studies. The molar absorptivity at 445 nm was found to be 5.3×10^3 $lmol^{-1}cm^{-1}$, where the blank shows a negligible absorbance.

Effect of pH

The optimum pH for the complete extraction of palladium with TBAI in chloroform was studied over the range of 0.9- 12.9, using proper amounts of HCl or NaOH for the pH adjustment. The results are given in Fig. 2. It is observed that the extraction is quantitative in the pH range 1.3- 11.9. Beyond this range the percent of extraction (%E) decreases drastically. The decrease in %E at pH values greater than 11.9 is probably due the formation of palladium hydroxide, whereas the decrease in extraction at high concentrations of H_3O^+ can be explained on the basis of competition between tetrabutylammonium and hydronium ions for PdI_4^{-2}.

Effect of TBAI concentration

The influence of TBAI concentration on the extraction process was studeid in Fig. 3. The extraction is quantitative when the TBAI to Pd(II) mole ratio of about 9 is reached. A further excess of TBAI has no effect on %E.

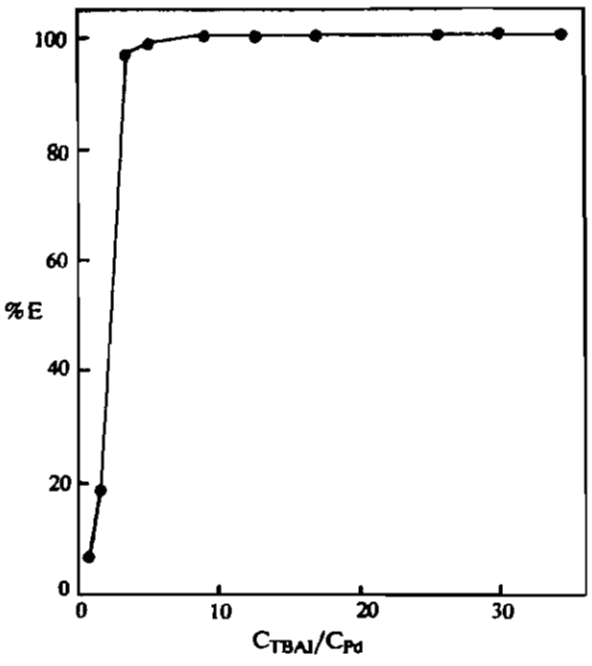

Fig. 3: Effect of TBAI concentration of the extraction of Pd(II).

Condition:

Pd(II): 1.012 μg ml⁻¹ *KCl: 5 ml of 3.5 M*

λ_{max}: 445 nm *Color: brown*

Effect of ionic strength

The ionic strength of the aqueous solution of Pd(II) was found to influence the extraction process (Fig. 4.). There is an increase in %E with ionic strength, maintained by the addition of KCl solution. Quantitative extraction results at ionic strength 0.11 M. When the ionic strength was adjusted with potassium perchlorate, instead of KCl, the same results was observed.

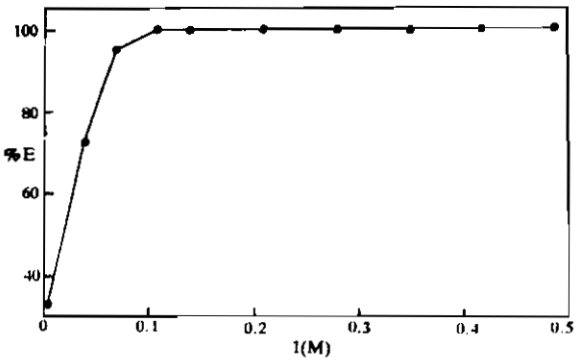

Fig. 4: Effect of ionic strength on the extraction of Pd(II)

Conditions:

Pd(II): 1.012 μg ml^{-1} *TBAI: 2 ml of 0.3% in H_2O*

λ_{max}: 445 nm *Color: brown*

Effect of shaking time

The extraction of Pd(II)with TBAI into chloroform is very rapid. A shaking time of 3-6 min was found sufficient for quantitative extraction.

Effect of organic solvents

The extraction of tetrabutylammonium tetraiodopalladium (II)ion pair was examined in carbon tetrachloride, benzene, isobutanol, diethyl ether, diethyl ketone, methyl isobutyl ketone and chloroform. It was found that the extent of extraction in the first four solvents is very low, while quantitative extraction is easily achieved in the rest. However, the reagent blank in diethyl ketone and methyl isobutyl ketone was found to absorb light considerably in the wavelength region of interest. Thus, chloroform with negligible reagent blank's absorption (Fig. 1) was chosen for the extraction process.

Beer's law study

A calibration graph for palladium was obtained over the concentration range 0.02- 1.09 μg ml^{-1}(r=0.99960) of Pd(II)at 445 nm. The Sandell's sensitivity [19] for 0.001 absorbance unit was found to be 0.80 mg cm^{-2}. The relative error (95% confidence level)for 0.402 μg ml^{-1} of palladium was ±1.6% (12 replicates). The complex is stable for at least 48 hr in organic phase. It should be noted that, by the used of a 50:1 aqueous to organic phase volume ratio, instead of the recommended value of 25:1 in the procedure, the palladium concentrations lower than 0.02 μg ml^{-1} could also be easily determined.

Effect of diverse ions

In order to determine the sensitivity and utility of the method, palladium (II) was extracted in the presence of several other ions. The results are given in Table 1. An error of ±2% was considered tolerable in the experiments. As it is seen, none of the cations and anions used interfere in the extraction of palladium, and most of them can be tolerated at a very high level.

APPLICATION :

The proposed method was applied successfully to the determination of palladium in the activated carbon (Aldrich, Chemicals, Inc Milwukee WI,USA) using the standard additon method. Three different sample solutions were prepared by the sampling procedure described in the experimental section and the amount of Pd(II) was determined according to the recommended procedure. The precent of palladium in the activated carbon used was found to be 10.21 ± 0.17 which is in a satisfactory agreement with the reported value of 10% by the company.

Acknowledgment :

The suport of this work by the Shiraz University Research Council is gratefully acknowledged.

Table 1: Tolerance of Pd(II) - TBAI System to Diverse Ions. Conditions: Pd(II), 0.40 $\mu g ml^{-1}$; TBAI , 2 ml of 0.3% in H_2O ; KCl , 5 ml of 3.5 M ; λ_{max} , 445 nm.

Foreign ion	Molar ratio	Foreign ion	Molar raion
Os(VIII)	884*	Ag(I)	609+
Cu(II)	4136*	Pb(II)	1269*
Ni(II)	4477*	Al(III)	9742*
Co(II)	4460*	Cr(III)	5055*
Zn(II)	4021*	Pt(IV)	50
Cd(II)	2338*	Fe(III)	38
Mo(VII)	2740*	As(III)	351
W(VII)	857*	Sn(II)	221
Hf(III)	1325*	Hg(II)	52†
Mn(II)	4784*	Tl(I)	64†
Th(IV)	283*	ClO_4^-	2646*
Te(IV)	515*	NO_3^-	4385*
La(III)	473*	CH_3COO^-	4460*
Bi(III)	314*	BrO_3^-	2057*
V(III)	1290*	$H_2PO_4^{2-}$	2712*
Ca(II)	1640*	IO_3^-	1504*
Rh(III)	638	OCN^-	63
In(III)	572*	SO_3^{2-}	3280*
Zr(IV)	720*	F^-	13850*
Sb(III)	540*	SO_4^{2-}	2741*
Se(IV)	832*	NO_2^-	115

* *Above of which was not tested.*

\+ *After separation of precipitate by decantation.*

† *After addition of some extra TBAI.*

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