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Short communication

Extractive spectrophotometric determination of palladium with *N*,*N*,*N*′,*N*′-tetra(2-ethylhexyl)- thiodiglycolamide T(2EH)TDGA

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ABSTRACT

A precise, sensitive and selective method for the spectrophotometric determination of palladium (II) using *N*,*N*,*N*′,*N*′-tetra(2-ethylhexyl) thiodiglycolamide T(2EH)TDGA as an extractant is described. Palladium (II) forms yellow colored complex with T(2EH)TDGA which exhibits an absorption maximum at ∼300 nm. The colored complex obeys Beer's law in the concentration range 1.0–15.0 $\mu g\,ml^{-1}$ of palladium with a molar absorptivity of $1.29 \times 10^5\ M^{-1}\ cm^{-1}$. The effects of various experimental parameters have been studied to establish the optimum conditions for the extraction and determination of palladium. The precision of the method has been evaluated and the relative standard deviation has been found to be less than 0.5%. The method has been successfully applied to the determination of palladium in simulated high level liquid waste (SHLW) solution.

1. Introduction

Palladium has extensive applications in various fields like catalysis, pharmaceuticals, petroleum, electronics, jewellery etc. Therefore, its separation and estimation at trace level is of significant importance.

Various techniques including Atomic Absorption Spectrometry, Inductively Coupled Plasma Atomic Emission Spectrometry, Ion Chromatography etc., have been used for palladium determination. Many of these techniques are either time consuming or require sophisticated and expensive instruments.

Extractive spectrophotometric methods are simpler techniques and have been widely used for determination of palladium. Palladium forms intensely colored complexes with hydrazones, dyes, dithiocarbonates, oximes, and thio compounds. Using this property a number of extractive spectrophotometric methods of palladium determination with various reagents such as di-2-pyridyl-methanone-2-(5-nitro) pyridyl hydrazone [1], pyridine-2-acetaldehyde salicyloyl hydrazone [2], di-2-pyridyl ketonebenzoyl hydrazone [3], Isonitroso benzoylacetone [4], isonitroso thiocamphor [5], o-butyl dithio carbonate [6], diphenyl thiovioluric acid [7], 2-carboxy-2′-hydroxy-5-methylazobenzene [8], pyridoxal-4-phenyl-3-thiosemicarbazone [9], Benzyloxy benzaldehyde thiosemicarbazone (BBTSC) [10], *N*-ethyl-3-carbazolecarbaxaledehydethiosemicarbazone [11] and α-benzoin oxime (ABO) [12] have been developed (Table 4). However, the existing methods suffer from various limitations such as longer extraction periods [1–3,7], temperature control [6], narrow pH range [2,4–6,9–11], less stability [4], and interference from other metal ions [1,6,8,12]. Moreover, in some methods [3–5], the extraction is not quantitative. Therefore, there is a need of more effective reagent for extractive and spectrophotometric determination of palladium. Recently, we have reported that *N*,*N*,*N*′,*N*′-tetra(2-ethylhexyl) thiodiglycolamide (T(2EH)TDGA), a member of thiodiglycolamide class, can be used for extraction of palladium from high level liquid waste (HLLW) solutions [13]. This extractant is found to be very selective for palladium over other metal ions [13,14]. The extractant is itself colorless but forms a colored complex with palladium. Therefore, it was envisaged to use this extractant as a reagent for spectrophotometric determination of palladium. The use of this reagent is advantageous as it can be synthesized at low cost with high purity and yield.

In the present paper the extraction and spectrophotometric determination of palladium using T(2EH)TDGA have been reported. The extractant have been evaluated for its use in separation and estimation of palladium present in simulated HLW.

2. Experimental procedure

2.1. T(2EH)TDGA

T(2EH)TDGA (Fig. 1) was synthesized by the condensation reaction of sodium sulphide nonahydrate with corresponding *N*,*N*-

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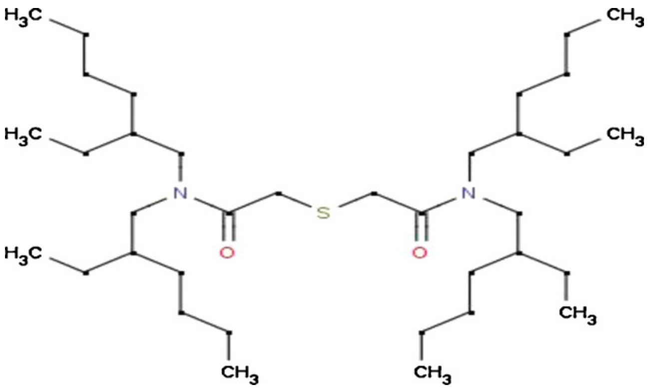

Fig. 1. *N,N,N′,N′*-tetra2-ethylhexylthiodiglycolamide T2EHTDGA.

di(2-ethylhexyl)-2-chloroacetamide according to the procedure described earlier [13]. The purity of product was 98.5% and yield of the reaction was 85.0%.

Solutions with desired concentration of T(2EH)TDGA were prepared by dissolving appropriate amount of T(2EH)TDGA in diluents namely *n*-dodecane, toluene and dichloromethane etc.

Palladium nitrate solution was prepared by dissolving appropriate amount of $Pd(NO_3)_2 \cdot xH_2O$ in nitric acid. The concentration of palladium and nitric acid in the inactive stock solution was 1.06 mg ml^{-1} (1×10^{-2} M) and 4.0 M, respectively. This stock solution was diluted appropriately to get desired concentrations of palladium and nitric acid. Aliquots from these solutions were used for different experiments. Palladium chloride solution was made by dissolving appropriate amount of $PdCl_2$ in hydrochloric acid. For sulphuric acid solution, $PdCl_2$ in 0.5 M HCl was evaporated to dryness and appropriate amount of sulphuric acid was added to obtain 1.0 M sulphuric acid solution.

2.2. SHLW feed solution

Simulated high level waste solution (SHLW), corresponding to the pressurized heavy water reactor (PHWR) with burn up of 6700 MWD ton^{-1}, was provided by Waste Management Divison, BARC. The concentrations of various metal ions present in SHLW solution are given in Table 1. As the uranium concentration in the HLW is usually high (~20 g L^{-1}), it was presumed that HLW will undergo three to four contacts with 30% TBP before extraction studies. Accordingly, SHLW was prepared without uranium. The acidity of the SHLW was ascertained by acid-base titration and the overall acidity was adjusted to 3.0 M. Quantitative determination of various metal ions present in SHLW was carried out using Inductively Coupled Plasma Atomic Emission Spectrometry technique (ICP-AES). Error in the measured concentrations was within ±5.0%.

Table 1
Composition of SHLW for PHWR, 6700 MWD/ton; Acidity: 3.0 M $HN0_3$.

Constituent element	Concentration (μg ml^{-1})	Constituent element	Concentration (μg ml^{-1})
Cr[a]	142.5	Sm	27.5
Ni[a]	127.5	Y	1.8
Ba	152.5	Ce	185
Mn[a]	347.5	La	127.5
Fe[a]	735.0	Nd	112.5
Mo	137.5	K[b]	355.0
Sr	40.0	Na[b]	4450
Zr	3.0	Pr	32.2
Pd	187.5	Cs	60.0

[a] Structural materials.
[b] Additives.

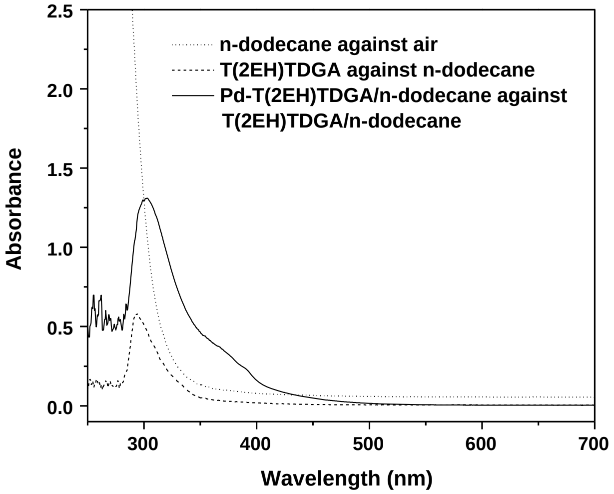

Fig. 2. Absorption spectrum of T(2EH)TDGA/*n*-dodecane and Pd–T(2EH)TDGA/*n*-dodecane complex. Concentration of Pd = 1.0×10^{-4} M in 1.0 M nitric acid. Concentration of T(2EH)TDGA = 2.0×10^{-3} M.

2.3. Extraction and absorbance measurement

An aliquot of sample containing 1–20 μg ml^{-1} of palladium (II) solution in desired acidity was taken in a separatory funnel and was contacted with equal volume (4 ml each) of dodecane containing appropriate concentration of T(2EH)TDGA for 15 min. The two phases were allowed to separate and the organic phase was dried over anhydrous sodium sulphate. The absorbance of the solution was measured against neat T(2EH)TDGA/*n*-dodecane solution.

2.4. Instruments

The absorption spectra of Pd bearing solutions were recorded using a UV–vis spectrophotometer (JASCO V-550) in the wavelength range of 200–700 nm in steps of 2 nm. A special cell with path length 1 mm was used for absorbance measurement.

A JY-50P poly-scan instrument with axial ICP (Jobin Yvon, Longjumeau Cedex, France), operated at 40.68 MHz, was used in this study. The instrument known as "Panorama" model has the unique facility for simultaneous and sequential operation in the same spectrometer assembly. Thus, the spectrometer has a polychromator covering 35 elements and is also able to function as a sequential unit over a spectral range of ±2.2 nm around each channel.

3. Results and discussion

3.1. Absorption spectra

Fig. 2 shows the absorbance spectra of both the neat T(2EH)TDGA/*n*-dodecane and Pd–T(2EH)TDGA/*n*-dodecane complex. The yellow colored complex absorbed strongly at ~300 nm. Since neat T(2EH)TDGA/*n*-dodecane also shows absorption in this region, it has been used as reagent blank during the absorbance measurement of Pd–T(2EH)TDGA complex.

3.2. Effect of diluents

10^{-4} M Pd in 1.0 M nitric acid was contacted with 0.002 M T(2EH)TDGA dissolved in different diluents. Fig. 3 shows the absorption spectra of Pd loaded T(2EH)TDGA in different diluents. Almost comparable absorbance observed for the diluents could be due to the fact that uptake of palladium by T(2EH)TDGA is

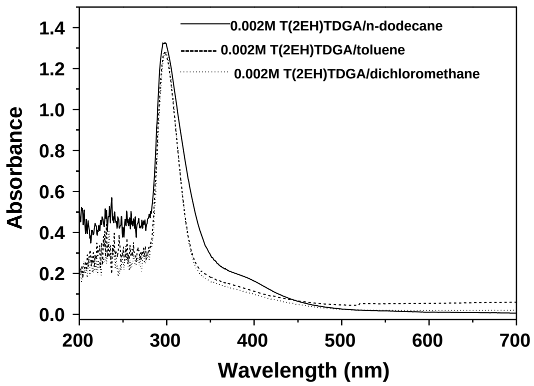

Fig. 3. Effect of diluents. Concentration of Pd = 1.0×10^{-4} M in 1.0 M nitric acid. Concentration of T(2EH)TDGA = 2.0×10^{-3} M.

quantitative irrespective of the nature of the diluents as reported earlier [13]. Furthermore, since palladium is extracted as neutral species [Pd$(NO_3)_2$·T(2EH)TDGA] its extraction and, therefore, the absorbance of extracted complex is maxiumum in neutral diluents like *n*-dodecane. Therefore, in subsequent experiments, *n*-dodecane was used as diluent.

3.3. *Effect of acids*

Fig. 4 shows the absorption spectra of 0.002 M T(2EH)TDGA/*n*-dodecane after contacting with palladium solutions in different acids, namely, nitric, sulfuric and hydrochloric acid. Smaller absorbance values observed in sulphuric acid medium could be attributed to low uptake of palladium by T(2EH)TDGA in sulphuric acid medium. The maximum absorbance was obtained in nitric acid medium and hence it was used in all subsequent experiments. To investigate the effect of nitric acid concentration on absorbance, 0.002 M T(2EH)TDGA/*n*-dodecane was contacted with palladium in nitric acid solution of 0.5–3.0 M. The absorbance was found to be almost same for the acid range studied. Thus the analysis of Pd can be done in the nitric acid concentration range of 0.5–3.0 M.

3.4. *Validity of Beer law*

Aqueous solutions containing varying amount of palladium in 0.5 M nitric acid were contacted with 0.002 M T(2EH)TDGA/*n*-dodecane. Fig. 5 shows that there is a linear increase in the absorbance within the concentration range of 1.0–15 μg ml^{-1} of palladium (II) at ~300 nm, indicating that Beer's law is applicable within this range. The molar absorptivity of the complex was found to be 1.29×10^5 M^{-1} cm^{-1} at ~300 nm which is higher than most of the earlier reported methods (Table 4).

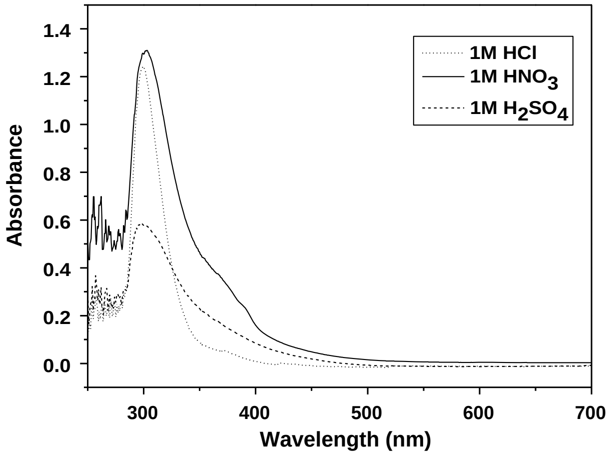

Fig. 4. Effect of aqueous phase acid. Absorption spectra of Pd [1.0×10^{-4} M] extracted into T(2EH)TDGA (2.0×10^{-3} M) in *n*-dodecane.

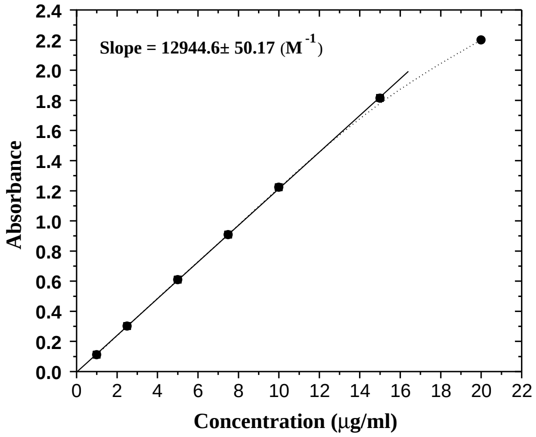

Fig. 5. Calibration plot. Concentration of Pd = 1.0–20.0 μg ml^{-1}, concentration of T(2EH)TDGA = 2.0×10^{-3} M.

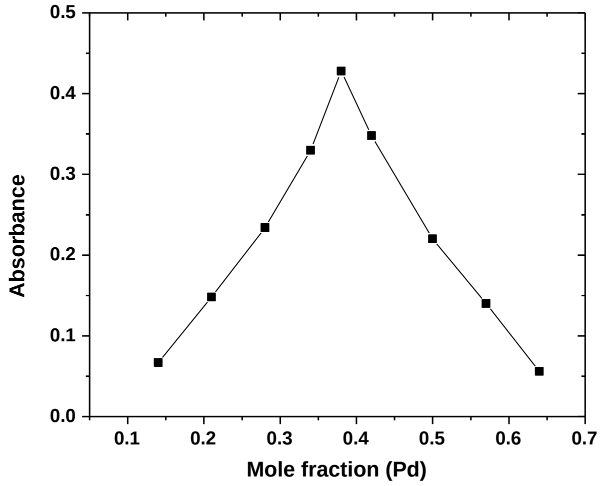

Fig. 6. Job's plot. Concentration of Pd = 1.0×10^{-4} M in 0.5 M HNO_3, concentration of T(2EH)TDGA = 1.0×10^{-4} M.

Table 2
Determination of concentration of palladium using Spectrophotometric method. Organic phase: 2.0×10^{-3} M in *n*-dodecane. Aqueous phase acidity: 1.0 M HNO_3.

Pd taken (μg ml^{-1}) in each sample	10
Pd found (μg ml^{-1}) in samples	9.89 ± 0.04 (1σ)
Relative standard deviation	0.45%
Standard error	0.02

3.5. *Nature of the extracted species*

The composition of Pd-ligand complex was determined by Job's continuous variation method [15] (Fig. 6). Equimolar solu-

Table 3
Determination of concentration of palladium using ICP-AES and Spectrophotometric method. Organic phase: 2.0×10^{-3} M in *n*-dodecane, Aqueous phase: SHLW diluted 20 times (final acidity 1.0 M HNO_3).

Pd estimated using ICP-AES	9.37 μg ml^{-1}
Pd estimated using Spectrophotometric method	9.22 ± 0.04 μg ml^{-1}

Table 4
Comparison of the present method with the other spectrophotometric methods for the determination of palladium(II).

S. no.	Reagent [ref.]	Conditions	λ_{max} (nm)	ε_{max} ($L\,mol^{-1}\,cm^{-1}$)
1	Di-2-pyridyl-methanone-2-(5-nitro) pyridyl- hydrazone [1]	Dichloroethane, 0.1–2.5 M HCl	560	37,800
2	Pyridine-2-acetaldehyde salicyloyl hydrazone [2]	Chloroform, pH 2.0–4.25	425	13,087
3	Di-2-pyridylketonebenzoylhydrazone [3]	Benzene, 0.1 M H_2SO_4	455	9.3×10^3
4	Isonitrosobenzoylacetone [4]	Benzene, 0.5 M acetic acid solution	405	1.0×10^4
5	Diphenylthiovioluric acid [7]	Acetone, $CHCl_3$, pH 1.0–3.5	425	–
6	2-carboxy-2′-hydroxy-5-methylazobenzene [8]	pH 1.5–3.8	560	7109
7	Pyridoxal-4-phenyl-3-thiosemicarbazone [9]	Benzene, pH 3.0	460	2.2×10^4
8	Benzyloxybenzaldehydethiosemicarbazone [10]	Cyclohexanol, pH 5.	365	0.4×10^4
9	*N*-ethyl-3-carbazolecarbaxaledehyde-thiosemicarbazone [11]	*n*-butanol, pH-4.0.	410	1.6×10^4
10	α-Benzoin oxime [12]	Hexone, 1 M HNO_3.	332	4.0×10^3
11	T(2EH)TDGA (present work)	Dodecane, 0.5–4.0 M HNO_3.	300	1.3×10^5

tion of T(2EH)TDGA and Pd (1.0×10^{-4} M) having different volumes (1-7 ml) were contacted to obtain the different ratio of T(2EH)TDGA and Pd(II). Absobance of the organic phase was plotted against the mole fraction of palladium. The ratio of metal to ligand was found to be 1:2. This stoichiometry corroborates well with the previously determined values using slope analysis method [13].

3.6. Precision and accuracy

Table 2 shows the average palladium concentration of four samples, each containing 10 $\mu g\,ml^{-1}$ of palladium (II). Very small values of the standard deviation, relative standard deviation and standard error for this method clearly indicate good precision and accuracy of this method.

3.7. Extraction and spectrophotometric determination of Pd in SHLW

High level liquid waste (HLW) solution originating from PUREX process [13] contains significant amount of palladium along with other radioactive (long-lived and short lived) and stable (fission and decay) products like Zr, Mo, Ru, Cs, Ba, Lanthanides etc., which are produced in comparable quantities. In addition, the solution is also likely to contain corrosion products like Fe, Ni, etc. Determination of palladium in HLW solution is of interest because the concentration of palladium affects its solubility in glass matrix form during vitrification process. Accordingly, a SHLW was made representing the actual concentrations of various metal ions present in HLW. This SHLW was analyzed, in triplicate, for palladium by the procedure developed above and the same solution was also analyzed for palladium using ICP-AES. The results are shown in Table 3. The palladium concentration in simulated HLW obtained by extractive spectrophotometry is close to that obtained by ICP-AES within 2.0–5.0%. Corrosion products and most of the fission products present in simulated high level liquid waste do not interfere in the determination of palladium. The method has shown adequate tolerance for all the major metal ions expected to be present along with palladium in HLW.

This method can also be extended for the analysis of environmental samples where the palladium content is usually in the range of ng g^{-1}. However, such type of analysis will require preconcentration step prior to spectrophotometric determination, which can be achieved by extracting the metal ion in organic phase (T(2EH)TDGA/*n*-dodecane) by contacting it with aqueous phase with phase ratio ($\nu_{aq.}/\nu_{org.}$) greater than ten or more.

4. Conclusions

A simple and highly selective method has been developed for the extractive spectrophotometric determination of Pd (II) with T(2EH)TDGA. The complex is stable and obeys Beer's law over the range of 1–15 $\mu g\,ml^{-1}$ palladium at ~300 nm with molar absorptivity of $1.29 \times 10^5\ M^{-1}\,cm^{-1}$. The method was found to be precise with relative standard deviation less than 0.5%. The proposed method was satisfactorily applied to the determination of palladium in simulated high level liquid waste samples.

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