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Spectrophotometric determination of palladium with 1, 5-diphenylcarbazone in aqueous and organic media

J. R. MUDAKAVI* AND T. V. RAMAKRISHNA
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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Abstract

Palladium (II) reacts with 1, 5-diphenylcarbazone to form a reddish violet complex, which can be retained in aqueous solution without precipitation by the addition of lauryl sulphate ($\lambda_{\max} = 560$ nm) or cetyltrimethylammonium bromide ($\lambda_{\max} = 460$ nm and 630 nm) or can be extracted into isobutyl methyl ketone ($\lambda_{\max} = 480$ nm and 620 nm). Based on this, methods have been described for the determination of palladium over the range 5–100 or 125 μg in aqueous solution and 1–15 μg in the organic medium. The molar absorptivities are $\varepsilon^{LS}_{560\text{ nm}} = 1\cdot6 \times 10^4$ 1 mole^{-1} cm^{-1} $\varepsilon^{CTAB}_{460\text{ nm}} = 2\cdot3 \times 10^4$ 1 mole cm^{-1} and $\varepsilon^{MIBK}_{620\text{ nm}} = 4\cdot8 \times 10^4$ 1 mole^{-1} cm^{-1}. Suggestions are made on the nature of the absorbing species present in the aqueous and organic media.

Key words: Palladium, diphenylcarbazone, spectrophotometry, surfactants, extraction.

1. Introduction

1, 5-diphenylcarbazone (DPCO) has received relatively little attention as an analytical reagent in spite of its close structural and chemical relationship to dithiazone which finds extensive use in the extractive separation and determination of many metals. Essentially, only the diphenylcarbazone complexes of copper(II), iron(III), lead(II), zinc(II), cadmium(II) and mercury(II) have been studied[1–5] in addition to that of rhodium (III) for which Ayres and Johnson[6] advocated the use of perchloric acid medium.

During a systematic study of the detection of mercury with DPCO in the presence of noble metals, Miller and Lowe[7] observed that palladium(II) reacted very similar to mercury(II) and that there was no interference from platinum(IV), rhodium(III) and iridium(IV). It therefore seemed worthwhile to explore the use of this reagent more

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[*] Present Address : Department of Chemical Engineering, Indian Institute of Science, Bangalore 560 012.

fully for the separation and determination of platinum group metals. During the investigation, it was found that in weakly acidic solutions, palladium(II) with DPCO produced a reddish violet product that precipitated out on standing. Surfactants like gelatin, lauryl sulphate, cetyltrimethylammonium bromide (CTAB) or cetylpyridinium bromide (CPB) stabilised the system to give a pink coloured solution. In the presence of CTAB or CPB, however, the coloured solution gradually turned green on standing. Similar colour change was noticed when the precipitate was extracted into various organic solvents. These observations prompted us to examine the reaction in detail to assess the analytical potentiality of the reagent for the spectrophotometric determination of palladium in both aqueous and organic media.

2. Experimental

2.1. *Apparatus*

A Carl-Zeiss PMQII spectrophotometer with 10 mm quartz cells and a Knick pH meter with an ingold combined glass-calomel electrode were employed.

2.2. *Reagents*

Palladium(II) solution, 10 ppm : Prepare a stock solution containing 1 mg/ml of palladium(II) by dissolving 1·662 g of palladous chloride in 1 litre of water containing 5 ml of concentrated hydrochloric acid. Standardise the solution volumetrically by titration with EDTA[8]. Dilute a suitable aliquot of this stock solution to provide a standard containing 10 ppm of palladium(II).

Diphenylcarbazone solution, $5 \times 10^{-3} M$: Purify the diphenylcarbazone sample by the method of Krumholz and Krumholz[9]. Dissolve 0·60 g of the purified sample in 250 ml of methanol and dilute to 500 ml wtih water.

Cetyltrimethylammonium bromide solution, 0·5% : Prepare an aqueous solution by dissolving 0·5 g of the reagent in 100 ml of water.

Lauryl sulphate solution 0·1% : Dissolve 0·1 g of lauryl sulphate in methanol and dilute to 100 ml with water.

Buffer solutions pH 4·0 *and* 3·5 : Prepare acetate and citrate buffers of pH 4·0 and 3·5 respectively.

Isobutyl methyl ketone.

3. Procedure

3.1. *Aqueous solution* (5–100 μg)

Transfer a suitable aliquot containing up to 100 μg of palladium(II) into a 25 ml volumetric flask. Add 5 ml of acetate buffer solution (pH 4·0), 1 ml of CTAB solution followed by 2 ml of diphenylcarbazone solution. Mix well and allow it to stand for 20 minutes before diluting to volume with water. Measure the absorbance at 460 nm against a reagent blank. Establish the concentration by reference to a calibration graph prepared for 5–100 μg of palladium.

3.2. *Aqueous solution* (5–125 μg)

Proceed as in 3·1 using 1 ml of Lauryl sulphate instead of CTAB. Mix well and let stand for 10 minutes. After diluting to mark with water, measure the absorbance against the reagent blank at 560 nm. Determine the palladium(II) by reference to a calibration graph prepared for 5–125 μg of palladium(II).

3.3. *Extraction method* (1–15 μg)

Place an aliquot of the sample containing not more than 15 μg of palladium(II) in a separating funnel. Add with mixing, 5 ml of citrate buffer (pH 3·5) and 2 ml of DPCO solution. Allow the solution to stand for 10 minutes and then extract for 1 minute with 10 ml of isobutyl methyl ketone. Separate the organic layer, remove the water droplets with anhydrous sodium sulphate and let stand for 20 minutes. Then measure the absorbance of the extract at 620 nm against a reagent blank carried through the procedure. Determine the palladium content with the aid of calibration graph prepared by the same procedure with 1–15 μg of standard palladium solution.

4. Results and discussion

4.1. *Studies in aqueous media*

The absorption spectrum of the reagent and its palladium complex in the presence of lauryl sulphate and CTAB, obtained after a standing time of 30 minutes, are shown in Figs. 1 and 2. The complex absorbs maximally at 560 nm in presence of lauryl sulphate and at both 460 nm and 630 nm in the presence of CTAB. With CTAB, since the absorption was more pronounced at 460 nm, it was decided to use this wavelength for all future measurements.

The influence of pH on the formation of the coloured species showed that the absorbance was constant over the pH range 1·5–4·4 with lauryl sulphate and over the range 2·3–5·5 with CTAB. The results are shown as curves *B* and *A* respectively in Fig. 3. Subsequent experiments with both the systems were carried out at pH 4·0 using acetate buffer.

The effect of variation of DPCO concentration in the range 1–10 ml of 10^{-4} M solution revealed that with both systems, the absorbance increases with increasing concentration up to 7 ml and further increase does not affect the absorbance. Similar studies on the variation of lauryl sulphate or CTAB concentration in presence of fair excess of DPCO (2 ml of 5×10^{-3} M) showed that the addition of 5 ml of a 0·1% solution

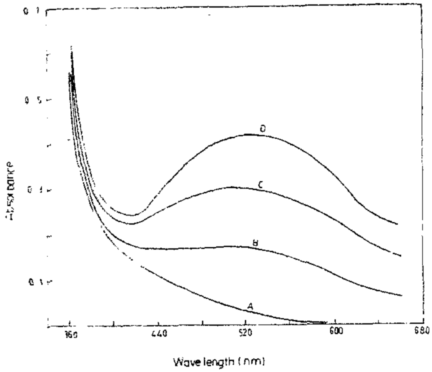


FIG. 1. *Absorption spectra* : (Total volume 25 ml, 1 cm cells) (A) 2 ml of 5×10^{-3} M DPCO and 5 ml of acetate buffer with lauryl sulphate. (B–D) as in (A) with the addition of 2 ml (B), 4 ml (C) and 6 ml (D) of 1×10^{-4} M palladium solution.

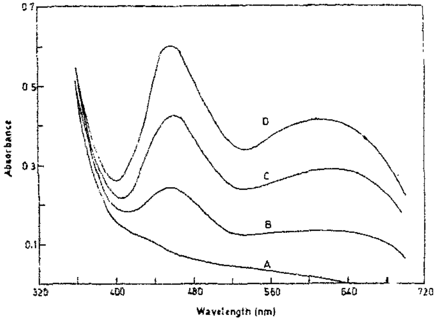


FIG. 2. *Absorption spectra* : (Total volume 25 ml, 1 cm cells) (A) 2 ml of 5×10^{-3} M DPCO and 5 ml of acetate buffer with CTAB. (B–D) as in (A) with the addition of 2 ml (B), 4 ml (C) and 6 ml (D) of 1×10^{-4} M palladium solution.

of CTAB or 1 ml of a 0·1% solution of lauryl sulphate was sufficient for maximum colour development. Under these conditions, the absorbance reached maximum value immediately with lauryl sulphate and then remained constant for at least two hours.

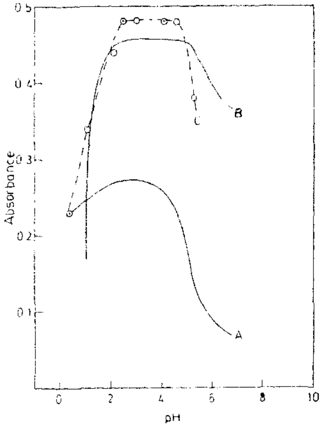


FIG. 3. *Effect of pH* : (Total volume 25 ml, 1 cm cells) (A and B) : 5 ml of 10^{-4} M palladium, 2 ml of 5 × 10^{-3} M DPCO at different pHs with CTAB at 460 nm (A) or lauryl sulphate at 560 nm (B) against reagent blanks. (C) 1 ml of 1 × 10^{-4} M palladium, 2 ml of 5 × 10^{-3} M DPCO adjusted to different pHs and extracted into 10 ml of isobutyl methyl ketone measured against reagent blanks at 620 nm.

With CTAB, on the other hand, maximum absorbance was obtained only after a standing time of 20 minutes, which then remained constant for at least 12 hours. On further standing, in both instances, the complexes were thrown out in the form of precipitates.

Both procedures were checked for Lambert-Beer law performance and straight line calibration graphs passing through the origin were obtained over the range 1 to 5 μg/ml of palladium(II) when lauryl sulphate was used for stabilisation purposes and over the range 1 to 4 μg/ml of palladium(II) in the presence of CTAB. The molar absorptivities were found to be:

$$\varepsilon^{\mathrm{L.S.}}_{560\,\mathrm{nm}} = 1\cdot7 \times 10^{4}\ \mathrm{l\ mol^{-1}\,cm^{-1}} \quad \text{and}$$

$$\varepsilon^{\mathrm{CTAB}}_{460\,\mathrm{nm}} = 2\cdot3 \times 10^{4}\ \mathrm{l\ mole^{-1}\,cm^{-1}}.$$

The precision of the methods developed were evaluated by analysing a series of solutions containing 25 μg of palladium. The standard deviations were found to be 0·023% for CTAB and 0·06% for the lauryl sulphate stabilised systems.

4.2. *Interferences*

The procedures developed were tested for the interfering effect of several extraneous ions in the determination of 50 μg of palladium(II). In these studies, the concentrations of the interfering ions were maintained at 1 mg excepting the noble metals which were supplied at 500 μg level.

Table I

Interference studies

Group	
I.	Li^+, Cu^{2+}, Ag^-, Au^{3+}
II.	Mg^{2+} Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}
III.	$B_4O_7^{2-}$, BO_3^{2-}, Al^{3+}, Ce^{+4}, Tl^{+4}, Tl^{+1}, La^{+3}, Th^{+4}
IV.	Sn^{4+}, Pb^{2+}
V.	NH_4^+, Sb^{3+}, Bi^{3+}, AsO_4^{3-}, AsO_3^-, VO_3^-, PO_4^{3-}, NO_3^-
VI.	Cr^{+3}, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, SeO_3^{2-}, TeO_3^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, WO_4^{2-}
VII.	Mn^{2+}, F^-, Cl^-, Br^-, IO_3^-, I^-
VIII.	Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ru^{3+}, Rh^{3+}, OS^{+8}, Pt^{+4}
Miscellaneous :	Citrate, tartrate, oxalate, EDTA, cyanide and thiocyanate.

Both procedures were found to be free from the interferences of many ions listed in Table I. Among the anions, serious interferences were encountered in the presence of sulphite, thiosulphate, iodide, thiocyanate and cyanide as they completely masked the reaction of palladium. EDTA caused a diminution in colour intensity by about 50%.

Bismuth(III), antimony(V), molybdenum(VI), tungsten(VI), Copper(II), tin(IV) and aluminium(III) interfered in both procedures. Apart from bismuth(III), which produced turbidity, all these ions produced red coloured solutions. The addition of citric acid eliminated the interference due to antimony(V), bismuth(III) and copper(II). Fluoride overcame the interfering effect of cerium(IV), aluminium(III), tin(IV) and tungsten(VI) and the effect of molybdenum(VI) was eliminated by the addition of oxalate.

Among the noble metals, though gold(III), mercury(II) and platinum(IV) did not interfere in the lauryl sulphate procedure, they were found to produce turbidity in the presence of CTAB. However, excess of CTAB caused the disappearance of turbidity due to mercury(II) and gold(III) and they no longer interfered. Platinum(IV) interference was no longer evident when absorbance measurement was made after centrifugation. Both methods were free from interference due to rhodium(III) but osmium (VIII) and ruthenium(III) interfered when their concentration exceeded twice that of palladium. Although the interfering effect of iridium was not examined, it may be expected to behave similar to platinum and rhodium as observed by Miller and Lowe[7].

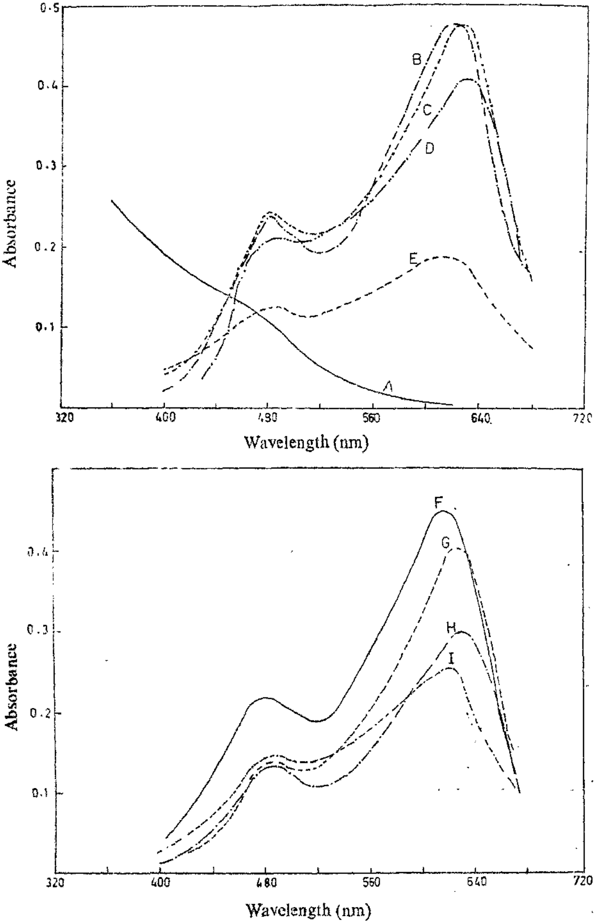
4.3. *Extraction studies*

The complex formed between palladium(II) and DPCO in weakly acidic medium readily gets extracted into both polar and nonpolar solvents. However, the spectral characteristics of the species in the organic layer was found to change with time, as the initially pink coloured extract turned green on standing. The spectra of the reagent and its palladium complex, extracted into various solvents after a standing time of 30 minutes, are shown in Figs. 4 and 5. In all the solvents tested, the complex showed two maxima, one at 480 nm, and the other around 620 nm. The spectrum of the reagent blank was very similar in all these solvents and showed negligible absorbance beyond 600 nm, where the complex was found to absorb maximally. Among the solvents tested, maximum absorbance was provided by isobutyl methyl ketone, ethyl acetate, and cyclohexane. However, in view of the rapid and clear phase separations with isobutyl methyl ketone, further studies were carried out with this solvent by measuring the absorbance at 620 nm to establish the optimum experimental conditions.

Curve C in Fig. 3 shows the absorbance of the complex extracted from solutions maintained at different pH values into isobutyl methyl ketone. The absorbance was found to be constant in the pH range 2–4·4. Since the reaction remained unaffected in the presence of citric acid and in view of the latter's ability to form stable complexes with many metal ions, it was decided to use a citrate buffer of pH 3·5 in all the subsequent investigations.

The time required for complete transformation from pink to green coloured species was examined by measuring the absorbance at 620 nm of the extracted species at intervals of five minutes. The results indicated that the extract should be allowed to stand at least for 20 minutes for the absorbance to reach a maximum after which no change occurred even after a standing time of 12 hours.

A study of the reagent concentration revealed that the use of 5 ml of 2×10^{-4} M DPCO was sufficient to provide maximum sensitivity. It was also established that the use of DPCO solution in isobutyl methyl ketone was not effective and that palladium should be allowed to react with DPCO in aqueous medium for at least 10 minutes prior to extraction. Under these conditions a single extraction for 1 minute was found to be



FIGS. 4 AND 5. *Absorption spectra* : (A) 1 ml of 5 × 10^{-3} M DPCO at pH 3·5 (Citrate buffer) extracted into 10 ml of isobutyl methylketone. (B-D) 1 ml of 10^{-4} M palladium, 5 ml of 5 × 10^{-3} M DPCO at pH 3·5 (citrate buffer) and extracted into 10 ml of isobutyl methyl ketone (B), cyclohexanone (C), benzene (D), butanol (E), ethyl acetate (F) carbontetrachloride (G), chloroform(H) and amyl alcohol (I).

sufficient for the quantitative recovery of palladium(II). An aqueous to organic phase volume ratio of 7·5 : 1 did not affect the absorbance.

With the established optimum conditions Beer's law was obeyed over the range 1–15 μg of palladium in 10 ml of the organic extract and an apparent molar absorptivity of $4 \cdot 8 \times 10^4$ l mol^{-1} cm^{-1} at 620 nm was obtained.

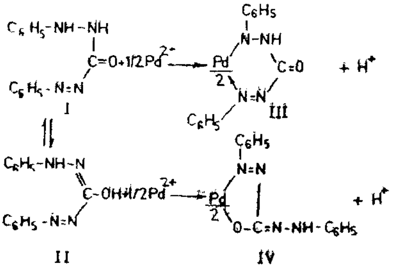
4.4. *Interference studies*

The ions studied included that of noble metals (Pt, Rh, Ru, Os, Au and Hg), associated base metals (Fe, Co, Ni, Cu, Zn and Mo) and the few anions, that were found to interfere in the aqueous procedures. In these studies 10 μg of palladium was used and in each instance, 500 μg of the interfering ion was added and the effect was noted. The anions were found to interfere seriously, causing low recovery of palladium(II). Among the cations molybdenum(VI), ruthenium(III) and osmium(VIII) interfered by giving high results. The addition of oxalate, however, effectively masked the reaction of molybdenum. As in aqueous procedures ruthenium(III) and osmium(VIII) were found to interfere only when their concentration exceeded twice that of palladium(II).

4.5. *Nature of the complex*

The stoichiometry of the species produced were established by continuous variation and mole ratio methods. The results obtained in the presence of CTAB and lauryl sulphate (Fig. 6), as well as after extraction into isobutyl methyl ketone showed a definite 1 : 2 ratio of palladium to DPCO in the complex. The ease of extraction into both polar and nonpolar solvents indicated that the coloured species produced are uncharged.

Both amido(I) and imidolic(II) forms of DPCO existing in tautomeric equilibrium n solution, may be expected to participate in the reaction as shown below :



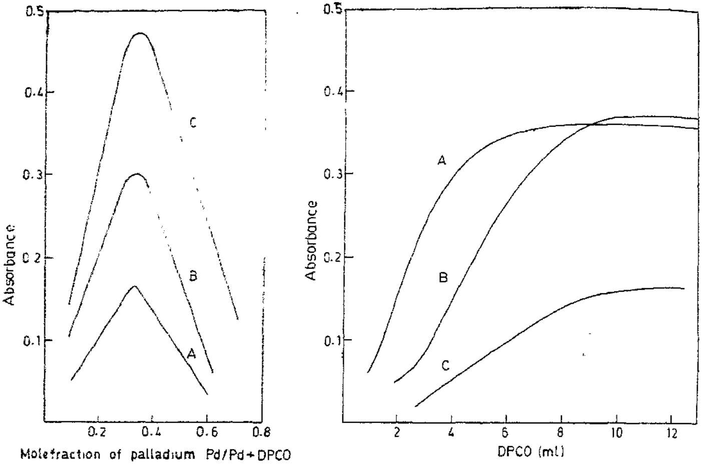
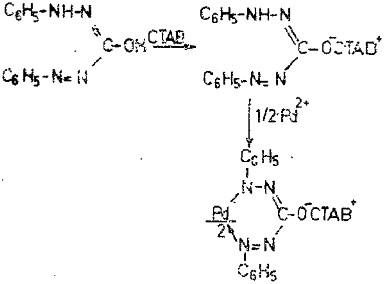


FIG. 6. *Composition studies*: (Total volume 25 ml): (ABC) continuous variation plots: Total concentration of palladium and DPCO = 10 ml of 10^{-4} M, acetate buffer added, (C) with CTAB at 630 nm, (B) with CTAB at 460 nm and (A) with lauryl sulphate at 560 nm, using 4 cm cells.
Mole ratio plots: 4 ml of 10^{-4} M palladium + x ml of 10^{-4} M DPCO + acetate buffer + CTAB, measured in 1 cm cells at 620 nm (C), and at 460 nm (B). (A) 2 ml of 10^{-4} M palladium + x ml of 10^{-4} M DPCO + acetate buffer + lauryl sulphate. Measured in 4 cm cells at 560 nm.

The resulting species can be expected to exhibit different spectral characteristics in view of the difference in the type of ligation involved. DPCO being a monobasic acid, under the experimental conditions it appeared reasonable to expect that palladium reacts preferentially with the imidolic form(II), rather than with the amido form(II), to give rise to a stable five-membered chelate(IV). The appearance of a single absorption maximum at 560 nm in the presence of lauryl sulphate may therefore be attributed to the imidolic complex(IV). The concentration of amido complex(III) if formed any, is perhaps too small to be detected spectrally, particularly in the presence of imidolic complex which absorbs over a broad range of the spectrum.

The existence of the amido complex(III) in the solution, however, became evident when the species were extracted into an organic medium. As indicated earlier, in the organic phase, the initially red coloured species gradually turned green which eventually absorbed maximally both at 480 nm and 620 nm. That the absorption at 620 nm was due to the imidolic complex was established by allowing the palladium to react with an alkaline solution of DPCO, to ensure that the ligand exists only as imidolic form (II), and obtaining the spectra of the species after extraction into isobutyl methyl ketone. The spectra, in fact, showed a single absorption maximum at 570 nm which gradually shifted to longer wavelengths on standing. On the basis of this, it was concluded that the imidolic complex, which absorbs maximally at 570 nm in aqueous solution, shows a gradual shift to 620 nm upon extraction into an organic phase. As a result, the other spectral maximum at 480 nm which was not evident in aqueous solution, became apparent and was attributed to be due to the six-membered amido complex (III).

The appearance of the well defined absorption maximum at 460 nm in addition to that at 630 nm in aqueous solution containing CTAB may again be explained on the basis of the existence of five- and six-membered chelates in the solution. The experimental condition, though favourable for the formation of imidolic complex(IV) as before, also perhaps favours the ion-association of CTAB cation with imidolic DPCO through C-O⁻, thus weakening the bonding of the only azine proton adjacent to the phenyl ring to facilitate the reaction with palladium as shown below ;



The resulting six-membered complex being similar to the amido complex (III), is perhaps responsible for the appearance of the peak at 460 nm. The appearance of the broad band with maximum between 620 and 630 nm is then due to the shift of the absorption maximum of the imidolic complex (IV) owing to the adsorption on the micellar aggregates. This perhaps explains the high ratio of palladium to CTAB (1 : 10) that was obtained when mole ratio method was applied to estabish the molecular ratio. Since the intensity of the colour remained unaffected in the presence of large excess of CTAB and increased only with increasing concentration of palladium, it was concluded that, under the experimental conditions, both species are produced in definite ratio and absorption measurements at 460 nm or 630 nm can be used with equal success for the determination of palladium.

5. Conclusion

Most of the methods available for the determination of palladium are beset with difficulties such as lack of adequate sensitivity and interferences arising from many noble metals and associated base metals. The present investigation has disclosed that methods based on the use of diphenylcarbazone are an useful addition to those relatively few that are currently available for the selective determination of palladium at low concentrations. The extraction procedure is very sensitive and versatile while the direct procedures based on the use of lauryl sulphate or CTAB for stabilisation purposes offer manipulative simplicity and rapidity.

Although in this study a purified sample of DPCO was used, it was found that commercial samples can be used directly for accurate quantitative results. The reagent solution is stable for several days and the calibration graphs are highly reproducible. As ruthenium and osmium react very similar to palladium, these ions, if present, should be removed by suitable preliminary treatment, *viz.*, distillation as tetroxides, so that the reagent can be employed to good advantage for the analysis of palladium in many synthetic and natural samples.

Das and Kaimal[10] reported the use of DPCO for the spectrophotometric determination of palladium (5–30 μg) at 610 nm after extraction into isobutyl methyl ketone from 0·05 N to 0·15 N nitric acid. Their method, however, is slow and less sensitive, and appears to work satisfactorily only when high concentration of reagent solution is employed for the determination. Furthermore, the interfering effect of many ions at concentrations greater than that of palladium is not known. The present work, however, has clearly demonstrated that using a moderate excess of DPCO solution, the determination can be made more rapidly with increased sensitivity and selectivity, when carried out over the pH range 3 to 6.

References

1.	Balt, S. and Van Dalen, E.	*Anal. Chim. Acta*, 1961, **25**, 507.
2.	Balt, S. and Van Dalen, E.	*Anal. Chim. Acta*, 1962, **27**, 188.
3.	Balt, S. and Van Dalen, E.	*Anal. Chim. Acta*, 1963, **29**, 466.
4.	Balt, S. and Van Dalen, E.	*Anal. Chim. Acta*, 1964, **30**, 434.
5.	Einega, H. and Ishii, H.	*Analyst*, 1973, **98**, 802.
6.	Ayres, G. H. and Johnson, Jr. F. L.	*Anal. Chim. Acta*, 1960, **23**, 448.
7.	Miller, C. C. and Lowe, A. J.	*J. Chem. Soc.*, 1948, **143**, 1258.
8.	MacNevin, W. M. and Kriege, O. H.	*Anal. Chem.*, 1955, **27**, 535.
9.	Krumholz, P. and Krumholz, E.	*Montash*, 1937, **70**, 431.
10.	Das, H. K. and Kaimal, K. G.	*Curr. Sci.*, 1975, **44**, 663.