

The formal potential (E°_{redox}) was then calculated using Nernst equation.

$$E_{\text{redox}} = E^{\circ}_{\text{redox}} + \frac{2.303 RT}{2F} \log \frac{[\text{OX}]}{[\text{Red}]}$$

The values of E°_{redox} are presented in Table I. As seen from the value of the formal potential (1.24 volts), iodobenzene dichloride in acetic acid is a moderately strong oxidizing agent.

TABLE I
Measurement of the formal redox potential of the $\text{PhICl}_2/\text{PhI}$ couple in acetic acid
(Temperature = $35 \pm 0.02^\circ \text{C}$)

Expt. No.	Mole ratio $\text{PhICl}_2/\text{PhI}$	E (volts)	E° (volts)
1	0.5880	1.234	1.241
2	1.176	1.244	1.242
3	1.764	1.252	1.244
4	0.8822	1.240	1.242
5	1.176	1.250	1.248
6	1.471	1.252	1.247

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RAPID EXTRACTION AND DIRECT SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNT OF PALLADIUM WITH DIPHENYLCARBAZONE

DIPHENYLCARBAZONE forms chelate complexes with the ions of many heavy metals¹. Its salt forming character with a number of metals was reported by Skinner and Ruheman². Grosset³ used it for detection of chromium. The reagent has also been used for the extractive spectrophotometric determination of mercury^{4,5} and copper⁶. Its reaction with palladium is, however, not reported so far. It has been found that palladium in macro amounts forms a dark violet precipitate with diphenylcarbazone in acidic solution which is extractable with isobutyl methyl ketone. Extractive spectrophotometric determination of palladium in micro amounts using reagents, viz., dimethylglyoxime, dithiozone, *p*-nitrosodimethylaniline, etc., is known. In this paper, we

describe the extractive spectrophotometric determination of palladium in micro amounts using diphenylcarbazone reagent.

Experimental

Absorbance measurements were made with a Beckmann DK-2 spectrophotometer. A stock solution was prepared by dissolving 1.1660 g of palladium chloride (B.D.H. Analar) in 100 ml of distilled water containing a few ml of concentrated HCl. The solutions of lower concentrations were prepared by dilution from the stock solution and was made 0.1 N with respect to nitric acid.

A 1% solution of diphenylcarbazone (B.D.H. product) in absolute alcohol was employed as the reagent.

Analytical and Separation Procedure

An aliquot of the palladium solution containing 1 μg to 35 μg of palladium was made upto 5 ml with 0.1 N nitric acid. Diphenylcarbazone reagent (1 ml) was added followed by the addition of 10 ml of isobutyl methyl ketone. The resulting mixtures were shaken for 1 minute and the organic layer was separated and allowed to stand for 40 minutes. The absorbance was measured at 610 nm against the pure solvent. The amounts of palladium in unknown solutions were calculated from the standard calibration curve. The results, which are the average of three determinations, in each case showed that the error involved is less than 2%. In the concentration range, 5–30 μg of palladium, the error is less than 1%.

In a separate set of experiments, the standard palladium solution containing 21 μg of palladium was mixed with an aqueous solution of the metal ions Fe^{3+} , Co^{3+} , Ni^{2+} , Pt^{4+} , Cu^{2+} , Ag^+ , Au^{3+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , V^{5+} , Cr^{3+} , Cr^{6+} , Mo^{6+} ; W^{6+} and Mn^{7+} in amounts almost equal to that of palladium taken and the volume in each was made upto 5 ml with 0.1 N nitric acid solution. The estimation was completed as described above. These experiments were repeated in presence of 100 μg each of the above metal ions and also in presence of 100 μg each of the common anions, viz., F^- , Cl^- , Br^- , I^- , CN^- , SCN^- , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} and NO_3^- . It was found that Mo^{6+} , V^{5+} and Fe^{3+} and also CN^- , SCN^- and I^- interfered badly and Cr^{6+} only slightly. The other ions did not interfere.

Discussion

Diphenylcarbazone forms a chelate with palladium in acidic solution which is extractable with isobutyl methyl ketone forming a blue violet solution. This complex has an absorption maximum at 610 nm and obeys Beer's law over the concentration range 0.1 to 3.5 μg per ml. Measurement of absorbance immediately after extraction gave a low

value for the absorbance which, however, increased gradually with time and reached a constant value after 40 minutes and remained stable for more than 12 hours.

Although extraction of palladium was possible from dilute nitric acid (0.05 N to 0.5 N), the absorbance values of the extract decrease with an increasing acidity beyond 0.15 N. Maximum absorbance was obtained for the extract when the acid strength was 0.05 N to 0.15 N. The acid concentration in the aqueous layer was, therefore, maintained at 0.1 N.

A 1% alcoholic solution of the reagent was found to be most suited for the determination. When the reagent concentration exceeds 1%, there is significant absorption at 610 nm. This is not the case when the reagent concentration is $\leq 1\%$. Thus the absorbance values measured against the reagent blank do not differ from those measured against the pure solvent. Further the solution of the reagent in the solvent itself requires more than 24 hours time for the attainment of stability of the colour of the complex.

An examination of the effect of other ions revealed that iron (III), cobalt (III), nickel (II), platinum (IV), copper (II), silver (I), gold (III), zinc (II), cadmium (II), mercury (II), chromium (III), chromium (VI), molybdenum (VI), tungsten (VI), vanadium (V) and manganese (VII) when present in almost equal amounts with palladium did not interfere and a good recovery of palladium (within 4% error at μg level) was achieved. However, molybdenum (VI), vanadium (V), iron (III) and chromium (VI) when present in higher amounts interfered. Amongst the anions iodide, cyanide and thiocyanate interfered seriously when present even in very small amounts, whereas the chloride, bromide, fluoride, oxalate, sulphate and nitrate did not interfere even when present in excess.

Thus the method is simple and rapid and yet provides a good recovery of palladium in trace concentrations in presence of most of the common metal ions.

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TRANSFORMATION OF PLAGIOCLASE

A THIN pinkish aplite vein, varying from 3" to 6" in thickness, has been found cutting across both granite and dolerite at Ramapuram temple in the Mid-Pennar Reservoir project area in Anantapur District, Andhra Pradesh (Survey of India, Topo-sheet No. 57 F/5). The aplite is a compact vein in the granite but, as it enters the dolerite, changes its pattern into shreds and veinlets. As the dolerite is jointed, thin veinlets branching off from the vein, project themselves along with the joint planes of the dolerite.

Granite often contains two types of plagioclase of which one is the most commonly occurring, more basic oligoclase-andesine variety while the other is albite which generally occurs as rims and granules. The origin of such albite in granitic rocks has been discussed by earlier investigators (Rogers, 1961; Ramberg, 1962). Microscopic examination of the aplite has revealed evidence of decalcification of plagioclase and soda metasomatism with attendant development of albite.

The aplite consists of micropegmatite (67.2%), quartz (6.8%), basic plagioclase (6.9%), albite (3.0%), epidote (5.4%), alteration materials (sericitic and clayey products) (8.0%), opaque ore (1.8%), and chlorite (0.9%). The most striking feature of the thin sections of this rock is the presence of a highly turbid, nearly opaque plagioclase surrounded by a mantle of fresh twinned albite [maximum extinction: $16.5^\circ \perp (010)$] which in turn is partially surrounded by a chain of epidote grains (Figs. 1–3). These grains are variegated with tints in light green or light yellow. Some grains are feebly pleochroic while some are non-pleochroic.

The writer believes that the formation of epidote and albite rims must have taken the following course:

Most of the compounds of $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ are unstable and exist without dissociation only through a small range of temperature (Morey and Bowen, 1925). Earlier workers (Lyons, 1955; Fyfe *et al.*, 1958; Waard, 1959) have observed a gap in composition between albite and oligoclase. The more Ca-rich phase of the plagioclase is unstable in the presence of water and excess CaO, and the reaction: Calcic plagioclase \rightleftharpoons albite + epidote, is favoured

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