

range 3-8 ml. The order of addition of reagents was not critical. The colour intensity remained practically unchanged up to 60°. The development of full colour takes place immediately after mixing the reagents and remained constant thereafter for about 75 min. It was found that a five-fold molar excess of the reagent over Pd(II) was required in order to obtain maximum absorbance.

Beer's law was valid over the Pd(II) concentration range 0.2-12 µg. The optimum concentration range evaluated by Ringbom's method^{4,5} was 0.8-11 µg. Errors were in general ±1%. A molar absorptivity of 4.63×10^3 litre mole⁻¹ cm⁻¹ was obtained at 480 nm.

The sensitivity of PPM is more than that of 8-mercaptoquinoline⁶, methylglyoxime^{6,7}, salicylaldehyde^{6,7} and diethazine hydrochloride⁸ which have been proposed as sensitive spectrophotometric reagents for Pd(II). The sensitivity of PPM is less than that of phenyl- α -pyridylketoxime^{6,7}, pyridine-RBE⁹, *p*-nitrosodimethylaniline⁹ and 1,10-phenanthroline-RBE⁹.

The method of Vosburgh and Cooper¹⁰ was used to find out the number of complexes formed under the experimental conditions of the study. Only one sharp maximum was obtained around 480 nm in each case indicating the presence of only one complex. The red complex exhibits absorption maximum at 480 nm. The reagent does not absorb at this wavelength. All subsequent studies were performed at 480 nm.

A stock solution of Pd(II) was prepared by dissolving 1 g of Pd(II) chloride (M/s Johnson Matthey) in 500 ml of 1.0M hydrochloric acid and standardized gravimetrically by the dimethylglyoxime method¹¹. Working solutions were made by suitable dilution of this solution.

A stock solution of PPM (M/s Sandoz Ltd, Switzerland) was prepared by dissolving 0.25 g of PPM in 250 ml of 0.1M hydrochloric acid and was standardized by the ceric sulphate method¹². This was stored in an amber coloured bottle in a refrigerator.

Beckman model DB spectrophotometer with matched 1 cm optical cells was used for absorbance measurements. The pH of the solutions was measured (vs SCE) with a pH meter model L1-10 (M/s Electronic & Industrial Instruments, Hyderabad).

Recommended procedure for colorimetric determination — The sample solution containing 5-300 µg of Pd(II) was transferred to a 25 ml volumetric flask. To this was added 5 ml of 1M hydrochloric acid-1M sodium acetate buffer of pH 1.4 and 5 ml 0.1% PPM solution and the solution diluted to the mark with doubly distilled water. The solution was mixed thoroughly and the absorbance measured at 480 nm against a corresponding reagent blank. The Pd(II) concentration of the sample solution was read directly from a calibration curve.

Effect of diverse ions — Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents. The following amounts (µg per ml) of foreign ions were found to give less than 2% error in the determination of 5 µg of Pd(II) per ml: osmium(VIII), 10; platinum(IV), 4; ruthenium(III), 1; rhodium(III), 5; iridium(III), 8; iron(III), 2; cobalt(II), 80; nickel(II), 550; copper(II), 850; fluoride, 450; chloride, 800; bromide, 230; iodide,

0.5; nitrate, 1640; sulphate, 560; phosphate, 700; acetate, 720; oxalate, 600; citrate, 1600; tartrate, 1150 and EDTA, 2. Ag(I), Au(III) and thiosulphate interfere at all concentrations and, therefore, no tolerance limits could be determined.

Composition of the Pd(II)-PPM complex — Job's method of continuous variation^{13,14} and mole ratio method¹⁵ were employed to establish the composition of the complex. The composition determinations were made in a medium of constant ionic strength (0.1M sodium nitrate) at a pH value of 1.4 ± 0.1 and a temperature of $27^\circ \pm 1^\circ$. The absorbance values were measured at 480 nm. The results indicated the formation of 1:2 complex between the metal and the reagent.

The apparent stability constant values of the complex calculated from the absorbance data by (a) method of Foley and Anderson¹⁶ modified by Mukherji and Dey¹⁷ and (b) mole ratio method¹⁵ were 11.2 ± 0.1 and 11.0 ± 0.1 respectively.

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Thiobenzoylacetone as an Extracting & Colorimetric Reagent for Ni(II)

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Thiobenzoylacetone can be used for the simultaneous extraction and direct spectrophotometric determination of Ni(II). Ni(II) can be extracted in the pH range 8.8-9.4 as a red coloured complex and measured spectrophotometrically at 500 nm. The Beer's law is valid in the concentration range 0.5-10 µg/ml of Ni(II). The complex is stable for 120 hr. 10 ml of 10⁻³M reagent is adequate for quantitative extraction. Ni(II) can be selectively separated from mixture containing a large number of cations and anions.

A NUMBER of β -diketones have been used as the extractants for Ni(II) in different pH ranges¹⁻⁵. The methods involving other chelating ligands for extraction of Ni(II) are summarized in a recent monograph⁶. We report here the results of our studies on solvent extraction and spectrophotometric determination of Ni(II) with thiobenzoylacetone (3-mercapto-1-phenylbut-2-en-1-one) (SBA). The method proposed is simple, rapid, selective and sensitive, and applicable at trace concentrations.

SBA forms a red-coloured complex which is quantitatively extracted by benzene in the pH range of 8.8-9.4. Below and above this pH the extraction is partial. Measured against the reagent blank, the absorption spectrum of Ni(II) complex showed maximum absorbance at 500 nm and a molar absorptivity of 5.804×10^3 . The sensitivity according to Sandell's definition is $0.0101 \mu\text{g cm}^{-2}$ per ml.

Different amounts of Ni(II) ranging from 4.98 to $98.6 \mu\text{g}/10$ ml of Ni(II) were extracted at pH 9.0 with $0.001M$ reagent in benzene (10 ml) and the absorbance of the complex measured at 480, 500 and 520 nm. The Beer's law was obeyed in the concentration range 0.5 - $10 \mu\text{g}$ of Ni/ml at 500 nm. Therefore, all the absorbance measurements were carried out at 500 nm. The complex was found to be stable for more than 120 hr as shown by constancy in absorbance values.

It has been observed that a single extraction with 10 ml of $10^{-3}M$ reagent is adequate for the quantitative extraction of Ni(II). The extraction was carried out in the reagent concentration range of 2.5×10^{-4} - $2.0 \times 10^{-3}M$. The extraction is partial with smaller volumes of the reagent and there is no significant enhancement in the extraction with larger volume of the reagent. The extraction was quantitative within a period of 8-10 min of equilibration.

The salting-out agents like nitrates of ammonium, sodium, potassium, calcium ($1.4M$) have no significant effect on the process of extraction of Ni(II) with $10^{-3}M$ SBA at pH 9.0.

Thiobenzoylacetone (SBA) was prepared by a modification of the procedure of Chaston *et al.*⁷ and Berg⁸. A solution of benzoylacetone (1 g) in methyl alcohol (100 ml) was cooled to -10° and H_2S gas passed for 3 hr followed by passage of dry HCl gas for 1 hr. The resulting orange coloured solution was poured on crushed ice and the mixture allowed to stand for 30 min. The orange solid obtained was filtered off, washed with water and placed in a refrigerator to yield bright orange-red crystals; yield, 0.6 g (60%), m.p. 28° (Found: C, 67.5; H, 5.8 reqd: C, 67.4; H, 4.65%). To get the best yield, temperature and reagent concentration should be very low. The substitution reaction is electrophilic in nature in the controlled highly acidic medium.

$0.001M$ SBA in benzene was used for the extraction of Ni(II). The reagent was preserved in a refrigerator.

A stock solution of Ni(II) nitrate was prepared by dissolving 2.47 g of Ni(II) nitrate hexahydrate (Riedel) in 100 ml of distilled water containing 1 ml of conc. nitric acid. The solution [4.93 mg of Ni(II)/ml] was standardized gravimetrically⁹. A buffer solution of pH 9.0 was prepared from $0.1M$ ammonium chloride and $0.1M$ ammonium hydroxide.

TABLE 1 — EFFECT OF DIVERSE IONS [Ni(II)] = $19.72 \mu\text{g}$, pH = 8.8-9.4 AND [REAGENT] = $10^{-3}M$

Tolerance limit ($1 \times 10^3 \mu\text{g}$)	Ion
20	Ca^{2+} , Mg^{2+} , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-}
10	Sr^{2+} , Ba^{2+} , NO_2^- , SO_3^{2-} , $\text{S}_2\text{O}_8^{2-}$, SCN^-
4	Cu^{2+} , malonate ²⁻ , ascorbate ⁻ , tart ³⁻
2	Al^{3+} , VO_5^- , SeO_3^{2-} , TeO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$
1	Tl^+ , Sb^{3+} , Bi^{3+} , Ir^{3+} , Tb^{4+} , Ce^{4+} , $\text{Mo}_7\text{O}_{24}^{6-}$, WO_4^{2-} , Cit^{3-}
0.5	Ag^+ , Cr^{3+} , Fe^{3+} , UO_2^{2+} , Be^{2+} , Ru^{2+}
0.1	Cd^{2+} , Os^{6+} , Mn^{2+}

General procedure — 10 ml of the buffer solution were added to an aliquot of Ni(II) nitrate solution containing $19.72 \mu\text{g}$ of Ni(II) and volume made up to 25 ml with the addition of distilled water. The solution was shaken with 10 ml of $10^{-3}M$ SBA solution in benzene for 10 min and the layers were allowed to separate and settle. The red-coloured organic phase was removed into a 10 ml volumetric flask and absorbance of the complex measured at 500 nm against a reagent blank prepared similarly.

Effect of diverse ions — Various ions were tested for possible interference (Table 1). The tolerance limit was calculated as the amount of foreign ion required to cause $\pm 2\%$ error in the recovery of Ni(II). Ions such as alkali and alkaline earth metals were tolerated even when present in 500-fold excess. Common complexing anions such as tartrate, ascorbate, oxalate, malonate, thiourea and thiocyanate were tolerated in 100-fold excess. Thallium, antimony, bismuth, manganese, iridium and some oxyanions were tolerated in 50-fold excess. However, copper, lead, zirconium, mercury, palladium and cobalt and cyanide and EDTA showed strong interferences. The interference of some of the cations were eliminated by masking with sequestering agents such as thiourea (for silver and bismuth) and tartaric acid (for iron and aluminium).

From ten determinations with $19.72 \mu\text{g}$ of Ni(II) the absorbance was found to be 0.195 ± 0.005 . The relative standard deviation was $\pm 1.00\%$. The time of operation is about 30 min.

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