

TABLE 1 — OPTIMUM CONDITIONS FOR THE EXTRACTION OF V(IV)-SCN⁻ COMPLEX IN THE PRESENCE OF VARIOUS BASES AND THE STABILITY CONSTANTS OF THE MIXED COMPLEXES

Base	Solvent	pH	[SCN ⁻] _{aq,total} (M)	[Base] _{org,total} (M)	log $\beta_{2,3}$ (at 28°C)
Pyridine	Benzene	4.5-5.5	0.0492	0.5000	6.63
3-Picoline	do	4.5-5.5	0.0274	0.2500	8.12
4-Picoline	do	4.5-5.5	0.0219	0.2000	8.82
Quinoline	do	4.0-5.0	0.2670	1.4678	7.96
Isoquinoline	do	4.0-5.0	0.0366	0.3786	10.39
2,2'-Bipyridyl	<i>n</i> -Butanol in benzene (30% v/v)	1.0-3.0	0.3377	0.0075†	4.25
<i>o</i> -Phenanthroline*	<i>n</i> -Butanol in benzene (25% v/v)	1.0-3.3	0.0625	0.0050†	6.00

*P. V. R. Bhaskara Sarma, Ph.D. thesis, Andhra University, 1970.

†The bases are taken in the aqueous phase.

coefficients for quinoline and isoquinoline are taken as 110 and 114 respectively⁴. The amount of base in aqueous phase is calculated as suggested by Irving and Al-Niami⁴ and Akaiwa and Kawamoto⁵. The equilibrium constants obtained by substituting the equilibrium concentrations of the ligands are given in Table 1.

It is clear from the constants given in Table 1 that the effectiveness of these bases as synergists in the extraction of V(IV)-thiocyanate complex into benzene follows the order: 4-picoline > 3-picoline > pyridine and isoquinoline > quinoline. 2-Picoline is found ineffective in forming a mixed complex due to probable steric hindrance caused by the methyl group in the *ortho*-position.

Similar studies were also made into *n*-butanol, a coordinating solvent, where the extent of synergism is much less than in benzene and the extracting species is found to be VO(NCS)₂B.2ROH where ROH is *n*-butanol. The same order of the bases as synergists is observed in this solvent also.

2,2'-Bipyridyl, a bidentate ligand, was also studied and the results obtained are similar to those obtained by Rao and Sarma¹ in the case of *o*-phenanthroline. Of these two bases *o*-phenanthroline is found to be more effective as synergist, the stability constants (log *K*) being 6.0 and 4.25 for *o*-phenanthroline and 2,2'-bipyridyl complexes respectively.

It is very interesting to observe that the equilibrium constants for the *o*-phenanthroline and 2,2'-bipyridyl bases, which are bidentate ligands, are lower than those for pyridine and quinoline bases which are unidentate ligands. This may be attributed to the fact that the extracting species of bipyridyl and *o*-phenanthroline complexes do contain a molecule of *n*-butanol, an oxygen donor VOLL(NCS)₂ROH (LL = bipyridyl or *o*-phenanthroline) whereas the pyridine and quinoline complexes are formed from only pure nitrogen donors VO(NCS)₂B₃. The introduction of an oxygen donor might have reduced the stability of the mixed complex by changing the environment of the central metal ion.

Procedure — Aqueous phase (20 ml) containing V(IV) (overall conc. $5 \times 10^{-4}M$) and the ligand was equilibrated with organic phase (20 ml) for 2 min maintaining the ionic strength constant at 1M with potassium chloride. The amount of vanadium in the aqueous phase was determined by the methods described by Rao and Sastry².

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2-Hydroxy-1-naphthaldoxime as an Analytical Reagent for Pd(II)

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2-Hydroxy-1-naphthaldoxime is proposed as a new selective and sensitive reagent for the gravimetric determination of Pd(II). The complex having the composition 1:2 (metal-ligand) can be dried to a constant weight at 105-10° and the conversion factor is 0.2223. It is stable up to 280° and the weight loss from 285° to 470° corresponds to the complete loss of ligand molecules. IR studies reveal that the complex is formed by the replacement of the hydrogen of phenolic OH by Pd(II) which coordinates through oxime nitrogen. A square planar structure is suggested for the diamagnetic (ESR) complex.

AMONGST the gravimetric reagents for Pd(II), oximes occupy an important place. However, even amongst the oximes the claims for superiority over the long established dimethylglyoxime method¹ have not been confirmed.

In the course of our work on the use of several organic compounds as possible gravimetric reagents for Pd(II), it was noted that 2-hydroxy-1-naphthaldoxime gave a bright yellow precipitate with Pd(II) in the cold at pH 0.5-3.0 and no precipitate with Ni(II), Co(II), Zn(II), Mn(II), U(VI), Rh(III) and Pt(IV). The limits of identification and dilution determined by Feigl's method² were 2.0 µg and

TABLE 1 — DETERMINATION OF Pd(II) AS OXIME COMPLEX

Wt of complex (mg)	Palladium, mg		Error (mg)
	Taken	Found	
13.7	3.0	3.0	0.0
27.0	6.0	6.0	0.0
40.6	9.0	9.0	0.0
54.2	12.0	12.1	+0.1
67.8	15.1	15.1	0.0
81.0	18.1	18.0	-0.1
95.0	21.1	21.1	0.0
108.7	24.1	24.1	0.0
122.0	27.1	27.1	0.0
135.0	30.1	30.0	-0.1

1:25000 respectively. Thus, it can be employed as a spot test reagent for Pd(II). The Pd(II)-oxime complex is insoluble in methanol, ethanol, *n*-butanol, isobutanol, cyclohexanol, acetone, ethyl methyl ketone, cyclohexanone, isobutyl methyl ketone, ether, CHCl_3 , CCl_4 , EtOAc, benzene, dioxan, tributyl phosphate and DMF.

The reagent has the most favourable gravimetric factor (0.2223) compared to resacetophenone oxime (0.2430), nioxime (0.2737), salicylaldoxime (0.2811) and dimethylglyoxime (0.3161). The excess reagent has no tendency for coprecipitation with Pd(II) complex, and the precipitate is crystalline and easy to filter.

The standard deviation of a single measurement is 0.0463 mg and the standard deviation of the mean is ± 0.0164 mg.

The complex is stable up to 280° indicating it to be anhydrous. The first decomposition step ($\sim 285^\circ$) was associated with a rapid loss in weight up to 470° in which the ligand was almost completely lost. The increase in weight above 470° may probably be due to oxidation of the metal. The higher thermal stability of the chelate than the salicylaldoxime complex³ can be ascribed to the increased availability of electron density at the reactive centre due to the presence of a fused benzene ring system in the ligand.

In its IR spectrum the ligand did not exhibit any peak for free OH. The intramolecular hydrogen bonding in 2-hydroxy-1-naphthaldoxime was weaker than in salicylaldoxime⁴ as revealed by the IR-peaks due to O-H...N at 3340 and 3230 cm^{-1} respectively in these two compounds. The phenolic O-H peak in the ligand at 3340 cm^{-1} was shifted to a lower frequency region and appeared at 3245 cm^{-1} in the complex. The νCN band observed at 1590 cm^{-1} in the ligand appeared at 1543 cm^{-1} in the chelate, indicating that Pd(II) formed a stronger complex with 2-hydroxy-1-naphthaldoxime than with salicylaldoxime⁴, in agreement with the thermogravimetric results. The $\nu\text{C-O}$ and $\nu\text{N-O}$ of the ligand observed at 1265 and 1235 cm^{-1} respectively appeared at 1290 and 1178 cm^{-1} respectively in the complex. The metal-nitrogen and metal-oxygen stretching vibrations appeared at 525 and 563 cm^{-1} respectively.

Thus, it is clear that on chelation the hydrogen of phenolic O-H has been replaced by Pd(II) with the nitrogen of oxime group coordinating to the metal. The results of gravimetric method showed

that two moles of ligand react with one gram atom of Pd(II) [Found: C, 55.24; H, 3.39; N, 5.80; Pd, 22.21. $\text{Pd}(\text{C}_{11}\text{H}_8\text{O}_2\text{N})_2$ requires C, 55.18; H, 3.37; N, 5.85; Pd, 22.23%].

The coordination number of Pd(II) in the chelate is four. The ESR spectra showed that the chelate is diamagnetic. Hence a square planar structure can be assigned for the Pd(II) complex.

Determination of Pd(II) — A measured volume of standardized Pd(II) chloride solution (0.1N with respect to HCl) was diluted to about 150 ml with distilled water. The solution was heated to about 60°, pH adjusted to 0.5-3.0 with HCl (1N) and treated with a little excess of an ethanolic solution of 2-hydroxy-1-naphthaldoxime (1%). The precipitate was digested on a hot water-bath for 30 min with occasional stirring, filtered hot through a weighed sintered glass crucible (porosity 4), and the precipitate washed with hot water, dried to a constant weight at 105-10°, cooled and weighed. The results are given in Table 1.

Effect of added ions — The interference of various ions which are usually associated with palladium in the minerals and are precipitated with it in the analysis was investigated. Alkali metal salts were used for the solutions of anions and nitrates, chlorides and sulphates for the solution of cations. Co(II), Ni(II), Zn(II), Mn(II), Fe(II), U(VI), Rh(III), Pt(IV), tartrate, citrate, oxalate, EDTA, phosphate and fluoride did not interfere even if present in large amounts. Fe(III) gave a deep green colour and the reaction was prevented by adding EDTA. Rh(III) up to 2 mg did not interfere. Cu(II) even in the presence of EDTA interfered. Au(III) was reduced to metallic gold and interfered.

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Gravimetric Estimation of Mn(II) with Sodium Benzilate

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Mn(II) has been successfully determined gravimetrically (accuracy $\pm 1\%$) using sodium benzilate. The pale-pink complex obtained has the composition $\text{Mn}[(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{COO}]_2 \cdot 2\text{H}_2\text{O}$ and has an octahedral structure as revealed by magnetic moment and IR data. Water molecules are coordinated to the central metal ion.

THE pyrophosphate method for the determination of Mn(II) is of limited applicability because of interference of numerous other ions¹. An easy