

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

TABLE 1 — RESULTS OF ESTIMATION OF Mn(II) WITH SODIUM BENZILATE

Amount of Mn(II) (mg)		Error (%)
Volumetric method using bismuthate	Present method	
10.00	10.10	+1.00
13.55	13.49	-0.44
21.95	21.95	0.00
32.53	32.43	-0.30
48.33	48.59	+0.53
55.83	55.42	-0.73
66.08	66.24	+0.24
74.52	74.36	-0.21
79.10	79.45	+0.44

gravimetric method for the estimation of Mn(II) using sodium benzilate as precipitating reagent is being reported in this note.

Manganous sulphate (GR, E. Merck) and benzoic acid, $(C_6H_5)_2C(OH)COOH$ (E. Merck) were used. Thermogravimetric analysis was carried out on a derivatograph (MOM).

Sodium benzilate when mixed with Mn(II) gave an instantaneous pale-pink precipitate of Mn(II)-benzilate. It was washed and dried at 120° and analysed [Found: C, 61.45; H, 4.78; Mn, 9.92. Required for $MnBz_2 \cdot 2H_2O$ [where $Bz = (C_6H_5)_2C(OH)COO^-$]: C, 61.65; H, 4.88 and Mn 10.10%]. On heating the sample (100 mg) in the derivatograph at a rate of $5^\circ/\text{min}$ decomposition started at 156° , the maximum decomposition occurring around 280° . The calculated and observed metal oxide (MnO) were 13.0 and 13.9 respectively for the composition $MnBz_2 \cdot 2H_2O$. The magnetic moment (Gouy method, $\sim 30^\circ$) of the solid complex has been found to be 5.88 BM which is only slightly lower than the value expected theoretically² for a d^5 system (5.92 BM) on the basis of spin-only formula. The infrared spectrum (Perkin-Elmer model 337) of the solid complex in nujol shows a peak around 815 cm^{-1} which is absent in free benzoic acid. This band may be due to the presence of coordinated water in the solid complex. This finds support from the earlier studies³⁻⁵ on aquo coordinated complexes which show bands between 795 and 910 cm^{-1} for the coordinated water. It is possible that $MnBz_2 \cdot 2H_2O$ has octahedral symmetry.

The insolubility of $MnBz_2 \cdot 2H_2O$ in water and the constant composition when dried at $110-20^\circ$ are the main advantages of sodium benzilate as the precipitating agent.

Procedure for the determination of Mn(II)—Aqueous sodium benzilate (0.2M) was added gradually with stirring to a solution of Mn(II) (10-80 mg) till the precipitation was complete. The optimum pH range was 3.2-5.4. The precipitate was filtered, washed thoroughly with water, 50% ethanol, dried at $110-20^\circ$ and weighed. The manganese content was calculated on the basis of formula $Mn[(C_6H_5)_2C(OH)CO_2]_2O$. The results are given in Table 1 which show an accuracy of about 1% as compared to the value obtained using volumetric method.

Effect of foreign ions—Interference due to Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , UO_2^{2+} , Cr^{3+} , Ti^{4+} , Ce^{4+} , Cl^- , NO_2^- , NO_3^- ,

SO_4^{2-} and CrO_4^{2-} was studied. Ti^{4+} , Cr^{2+} , Cl^- and SO_4^{2-} do not interfere. The estimations which were carried out in the presence of varying amounts of foreign ions indicate that for each 100 mg of manganese solution, the tolerance limit is 10 mg for all the divalent cations (except UO_2^{2+}) whereas only 5 mg of Ce^{4+} and UO_2^{2+} are tolerated. The anions NO_2^- , NO_3^- and CrO_4^{2-} interfere seriously since these anions oxidize benzilate and should be avoided under the condition of the experiment.

Estimation of Mn(II) in pyrolusite—The mineral was first dissolved in hydrochloric acid and contaminated Fe(III) removed by complexing the latter with ammonium bifluoride. After adjusting the pH, between 3.2 and 5.4 sodium benzilate solution was added. The precipitate was then washed, filtered, dried and weighed to constant weight. The accuracy of the method was found to be $\pm 1\%$ as compared to the value obtained by volumetric method using bismuthate (Table 1).

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Determination of V(V) & Cr(VI) in Presence of Chloride

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Two methods are described for the titrimetric estimation of V(V) and Cr(VI) in the presence of chloride. They differ only in the manner in which preferential oxidation of V(IV) by potassium permanganate is carried out. In the first method two titrations are recommended at room temperature in order to provide requisite time for V(IV) oxidation. The second method is useful when simultaneous estimation is to be done in the same aliquot. Here the solution is cooled to 5° and then V(IV) is oxidized selectively with excess potassium permanganate. Oxidation of Cr(III) which becomes prominent in the presence of chloride is made negligible in these methods.

AMONGST the titrimetric methods for the estimation of vanadium(V) and chromium(VI), the one generally employed involves titration with standard iron(II) sulphate in sulphuric acid medium in the presence of phosphoric acid, using diphenylamine sulphonate as the indicator^{1,2}. This gives the total titre value for both V(V) and Cr(VI). The vanadium is then selectively oxidized with excess potassium permanganate and after destroying the latter, V(V) is retitrated with iron(II); Cr(III) remains unaffected and its value is obtained by difference³. During our work on the recovery of