

TABLE I
Kinetic data for the oxidation of substituted acetophenones with phenyl iodosoacetate

Substituent	$k_0 \times 10^5$ mol l ⁻¹ min ⁻¹	$k_1 \times 10^4$ min ⁻¹ (obs)	$k_1 \times 10^4$ min ⁻¹ (cal)	Relative rate	k_{obs} k_{cal}
None	2.34	4.42	—	1.00	
M-Methyl	1.62	3.15	—	0.71	
m-Chloro	1.48	2.80	—	0.63	
m-Bromo	1.82	3.25	—	0.74	
p-Methoxy	3.56	5.58	—	1.26	
4-Methoxy-3-methyl	3.56	6.06	3.98	1.37	1.52
3-Chloro-4-methoxy	2.05	4.20	3.54	0.95	1.19
3-Bromo-4-methoxy	1.59	5.32	4.10	1.20	1.30
3,5-Dimethyl-1-4-methoxy	2.65	4.90	—	1.11	
3,5-Dibromo-4-methoxy	4.21	2.81	—	0.64	

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SPECTROPHOTOMETRIC DETERMINATION OF Ni (II) AND Pd (II) BY EXTRACTION OF THEIR DIIMINE DIOXIME COMPLEXES WITH MOLTEN NAPHTHALENE.

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BISBIACETYLMONOXIME ethylene / o-phenylene diimine used for the gravimetric determination of nickel and palladium. Recently these compounds have been used as sensitive photometric reagents for iron in the presence of an anti-oxidant², and nickel in the presence of an oxidant³. The present paper describes a method of extractive photometric determination of Ni (II) and Pd (II) using the above mentioned diimine dioximes.

The extremely selective pH ranges¹ for the complexes of palladium (hydrochloric acid) and nickel (ammonia) has led us to investigate the extractibility of these complexes into water immiscible solvents to make the reagents more valuable at microgram level. Preliminary investigations showed that chloroform can partially extract these complexes and at high concentration of metals, the complexes accumulated at the water-chloroform interface. The conventional method of solvent extraction is not applicable when the solubility of the metal complex in the solvent is small and the complex is strongly hydrated. In such cases, a method involving 'solid-liquid separation after liquid-liquid extraction' has been applied to the spectrophotometric determination of metals by using molten organic compounds⁴⁻⁸. Hence, to overcome the difficulty of partial solubility of diimine dioxime complexes of nickel and palladium this technique has been adopted in the present work.

All absorbance measurements were made with Beckman Model-B spectrophotometer fitted with 10 mm borosilicate cells. Bisbi-acetylmonoxime-ethylene diimine (I) and bisbiacetylmonoxime-o-phenylene diimine (II) were synthesised as described earlier¹⁻².

An aliquot of nickel or palladium solution was taken in an Erlenmeyer flask and to this 1 ml of the reagent (0.1 M) was added followed by 5.0 ml of citric acid (0.5 M) solution. The pH of the solution was adjusted between 1-2 for palladium and 8.5-10 for nickel by adding either HCl-KCl or ammonia-ammonium chloride buffer⁸. The solution was diluted to about 30 ml and warmed to 60°C; 2 g of naphthalene were added and the temperature rised to 90°C to melt the naphthalene completely and shaken vigorously till naphthalene separated out. Again the contents were heated to melt the naphthalene and allowed to cool down to 30°C. Naphthalene was separated from the aqueous phase by filtration, dried in the folds of the filter papers and dissolved in chloroform and made up to 10 ml. The absorbance was measured at λ_{\max} (370-375 nm) against a reagent blank prepared similarly.

The diimine dioxime complexes of nickel and palladium in a naphthalene-chloroform mixture showed maximum absorption at 370/375 nm (table 1). The blanks showed negligible absorption at these wavelengths. The results indicated that extraction was quantitative at pH 1-6.5 and 6-11 for palladium and nickel respectively.

The validity of Beer's law, optimal concentration limit, molar absorptivity, sandell's sensitivity, standard deviation are given in table 1. The digestive time of 5-60 min did not affect the results. The method of continuous variation in two phase system^{10,11}, showed that nickel and palladium complexes have a metal-to-ligand ratio 1:1. The absorbance of the extract remained constant for several hours.

The amount of naphthalene was varied from 0.5 to 3g, the extraction being carried out by the recommended procedure; amounts exceeding 0.5 g did not improve the extraction. The volume of chloroform required to dissolve 1 g of naphthalene was 2 ml.

The tolerance limit of an ion was fixed as the maximum amount causing an error of 3% in the absorbance of the extract solution. Various ions were added individually to the solution containing 21.3 ppm of Pd (II) and 6.0 ppm of Ni (II) and extraction was carried out by the recommended procedure, Cl^- , Br^- , F^- , NO_4^- , SO_4^{2-} , PO_4^{3-} , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_3^{2-}$, EDTA, citrate, tartrate 100 mg; Pb(II), Mo(VI), Co(II), Cu(II), Cr(III), W(IV), Fe(III), Mn(II), Mg(II), Al(III), Cd(II), Zn(II) 5 mg; Pt(IV), Au(III), Rh(III), Os(VIII), Ir(III), Ag(I, HNO₃/KNO₃ buffer), 500 ppm did not interfere, EDTA interfered seriously in the estimation of nickel.

The technique described above is suitable for the photometric determination of nickel in ferrous and non-ferrous alloys, and palladium in hydrogenation catalysts, dental and ornamental alloys. Nickel was estimated in nichrome wire and monel metal, and palladium in catalysts. Accurately weighed amounts of palladium in calcium carbonate (Merck) was taken in a 100 ml beaker, and 10 ml of water was added followed by 10 ml of aquaregia. The solution was

TABLE I
Characteristics of diimine dioxime complexes

Metal Complex	λ_{\max} (nm)	ϵ (l/mol/cm)	Sandell's sensitivity $\mu\text{g}/\text{cm}^2$	Extraction pH	Validity of Beer's law (ppm)	Optimal Concn. (ppm)	S.D.
Ni-Reagent I	370	3300	0.0178	6.0-11.0	0-32.0	3.5-14.2	0.007
Pd-Reagent I	370	1800	0.059	1.0-6.5	0-100	12.0-47.0	0.009
Ni-Reagent II	375	3800	0.0155	6.0-11.0	0-28.0	3.0-12.0	0.005
Pd-Reagent II	375	2000	0.0532	1.0-6.5	0-95	10.6-42.0	0.006

S. D. = Standard deviation; 6.00 ppm of Ni (II)/21.3 ppm of Pd (II), for a series of 10 determinations

TABLE 2
Analysis of alloys and catalysts

Samples	Nickel content of the alloys		Values obtained by	
			Reagent I	Reagent II
Monel metal [Cu 31.60%, Fe 6.80%, Mn 0.70%]	Ni	60.55%	61.76%	61.50%
Nichrome wire [Fe 12.20%, Cr 10.50%, Mn 2.30%]	Ni	74.50%	73.40%	75.40%
CaCO ₃ + Pd (Merck)	Pd	5.0%	4.90%	4.88%
Active Carbon + Pd (Merck)	Pd	10.0%	9.72%	9.71%

evaporated to almost dryness and diluted to 100 ml with water. Samples of Pd(II) in active carbon was treated in a similar manner but 35 ml of 60% perchloric acid and 10 ml of con. nitric acid were added. The analytical results are given in table 2.

The diimine dioxime complexes of nickel and palladium are readily extracted into molten naphthalene. A characteristic of this method is that equilibrium distribution in two phases is attained rapidly due to the high temperature; and the complexes are extracted, merely by contact with molten naphthalene.

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A NOTE ON THE OCCURRENCE AND HABITAT FEATURES OF *ICHTHYOPHIS BEDDOMI* (PETERS) AND *URAEOTYPHLUS NARAYANI* (SESHACHAR)

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THE Apoda is a group of terrestrial amphibians, whose restricted distribution, both as species and as individuals, seems to be governed by a highly specialised environment. We have found that acidic soils, associated with certain other features, are favourable for the existence and survival of a species of this order¹. We have subsequently been able to determine the ecological conditions conducive to the life of two more species, *Ichthyophis beddomi* and *Uraeotyphlus narayani*.

In June 1981, adults and larvae of *I. beddomi* and *U. narayani* were collected around Sringeri, Karnataka. The chemical composition of the soils from the two localities (Hechagunda and Balemane), was analysed by procedures described earlier¹, and the data are presented in table 1. Both soils are acidic, rich in organic matter and organic carbon. Both had a temperature of 25°C, which varied insignificantly with depth (up to 25 cm).

That more than one species of the Apoda prefers acidic soils associated with certain other physical and chemical characters, is interesting and leads to the conclusion that this combination of ecological factors could be universal to the group. No data are available in regard to any other Apoda and it would be of immense interest to know the ecological conditions under which the African and the new world Gymnophiona live.

It has been the common belief that larval habitat of terrestrial Apoda differs from that of adults. The observations^{2,3} made many years ago that the larvae