

TABLE 1 — DEPENDENCE OF EXTRACTION COEFFICIENT OF Ni(II) BY CHLOROFORM IN THE PRESENCE OF ADDED SALTS

[[BHA]=0.005M; [L]=1.24M and pH=6.7]

[Salt] (M)	NaClO <sub>4</sub>		NaCl	
	Extraction (%)	q	Extraction (%)	q
0	53.7	1.16	53.6	1.11
1	88.4	7.66	74.9	2.92
2	95.9	24.5	86.7	6.57
3	97.9	48.0	92.6	12.25
4	98.1	51.0	95.7	22.5
5	98.1	51.0	—	—
6	—	—	97.9	48.0

Benzohydroxamic acid was prepared by the standard procedure<sup>3</sup> and recrystallized; m.p. 128°. Other chemicals and solvents used were of analytical grade. The alcohol-free chloroform was used. Nickel perchlorate was prepared and stock solution standardized by the literature method<sup>4</sup>.

**Procedure** — Nickel perchlorate solution (1 ml of  $1 \times 10^{-4}M$ ) was mixed with 8 ml of BHA and 1 ml of H<sub>2</sub>O. To this was added an equal volume of organic phase (i.e. 10 ml) containing pyridine or quinoline and shaken for 15 min at  $23^\circ \pm 1^\circ$ . The two phases were allowed to separate and from the aqueous phase an aliquot (2 ml) was taken each time and the nickel concentration estimated spectrophotometrically at 430 nm by furildioxime method, using a quartz spectrophotometer having silica cells of 1 cm path length. The equilibrium pH value of the aqueous phase was measured with pH meter, calibrated with standard buffer solution of pH 4.

The plot of log q against log [BHA] is linear with a slope of unity, suggesting a composition of [NiAL<sub>n</sub><sup>+</sup>] for the extracted adduct. Extraction of Ni(II) is enhanced in the presence of perchlorate, chloride ions (Table 1). The extraction coefficient of 94% Ni(II) in nitrobenzene, a solvent of high dielectric constant, ( $D = 36.1$  at  $20^\circ$ ) indicates that nickel is extracted probably as an ion pair. Depending upon the extraction coefficient, the solvents can be arranged in the following decreasing order: butanol > nitrobenzene > chloroform > benzene > cyclohexane > n-heptane > CCl<sub>4</sub>. This order indicates that the extraction order does not entirely depend on the dielectric constant of solvent employed. Thus, in chloroform ( $D = 4.80$ ) and butanol ( $D = 17.8$ ) extraction is 89 and 98% respectively.

The authors wish to thank Dr Rama Shanker, Department of Chemistry, University of Udaipur, for helpful discussions. One of the authors (B.L.H.) is grateful to the CSIR, New Delhi, for the award of a scholarship.

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## Polarographic Determination of Dimethylglyoximates after Extraction with Naphthalene: Trace Analysis of Ni(II) & Pd(II)

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Received 23 September 1974; accepted 8 April 1975

Ni(II) and Pd(II) have been extracted as their dimethylglyoximate into molten naphthalene, the naphthalene allowed to solidify, separated and dissolved in DMF and the metals determined polarographically with sodium perchlorate for nickel and sodium perchlorate-perchloric acid-profan extra-24 (maximum suppressor) for palladium as the supporting electrolytes. A large number of foreign ions which are expected to be reduced in the voltage range studied or to react with the reagent do not interfere in the estimations. The results show a mean deviation of 0.20 µg for Ni(II) and 0.16 µg for Pd(II). The extraction of nickel is not possible in the presence of EDTA. The method is fairly selective, rapid, sufficiently sensitive (the determination is possible down to 0.59 ppm for Ni and 0.66 ppm for Pd). However, the sensitivity can be further increased by taking larger volumes of the aqueous phase. The method can be applied for the determination of these metals in the complex materials.

**DIMETHYLGLYOXIME** has been widely utilized in the gravimetric, volumetric, amperometric, colorimetric and extractive spectrophotometric determination of Ni(II) and Pd(II)<sup>1-8</sup>. In spite of its wide use in the analysis of these metals, none of these methods seems to be selective. Though selectivity has been achieved to some extent in extractive spectrophotometric method by using masking agents, the method is less accurate and more time-consuming. The selectivity may also be achieved in extractive polarographic method, but due to the low dielectric constant of the organic solvents and the large volume required for the complete extraction it is difficult to get well-defined waves. In certain cases well-defined waves have been obtained using mixed solvents<sup>9</sup>, but the sensitivity is very much decreased in such cases. We have developed a new extractive polarographic method in which metal chelate is extracted with molten naphthalene at high temperature, dissolved in dimethylformamide (DMF), mixed with the supporting electrolyte and analysed polarographically. This method of extraction is quite rapid, equilibrium is achieved in a few seconds due to high temperature, and a very small amount of the organic phase is required for the complete extraction. The interferences due to various ions have been studied in detail.

**Reagents** — The reagents used were of GR quality. Nickel chloride solution in distilled water was standardized gravimetrically<sup>1</sup>. Palladium chloride solution (0.4433 g in 10 ml of conc. HCl) was diluted

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to 500 ml with distilled water and standardized with oxine gravimetrically<sup>2</sup>. Dimethylglyoxime (oxine) was dissolved in ethanol to give a 0.1M solution. Solution of sodium perchlorate and perchloric acid were prepared in water and DMF respectively. Profan-Extra-24 solution (5%) prepared fresh for each run in DMF was used as a maximum suppressor.

Polarograms were recorded at  $28^{\circ} \pm 0.5^{\circ}$  with a Yanagimoto P-8 three-electrode polarograph. An H-type cell with fine porosity sintered glass disc between the compartments was used. The saturated calomel electrode was connected to the polarographic cell via a potassium chloride-agar bridge. The parameters for the mercury drop in open circuit were:  $m = 1.3$  mg/sec,  $t = 4.2$  sec,  $h = 50$  cm. All the solutions were deaerated by passing nitrogen through them for 5 min.

*General procedure* — An aliquot of nickel chloride or palladium chloride solutions was taken and to this was added 1 ml of the reagent solution. Citrate solution (5 ml) was added to nickel solution and acetic acid-sodium acetate buffer (2 ml) to palladium chloride solution. The pH was adjusted between 7.5 and 11.8 for nickel and 1.0 and 8.8 for palladium with ammonia or perchloric acid. The solutions were warmed on the water-bath at  $60^{\circ}$  and naphthalene (2 g) was added and the temperature raised to  $90^{\circ}$  to melt naphthalene layer completely and stirred vigorously till naphthalene separated out as a solid mass. Once more the contents were heated to remelt naphthalene, shaken vigorously and allowed to stand. Naphthalene was separated from the aqueous phase by filtration, dried in the folds of the filter paper and dissolved in warm DMF. Then aq. sodium perchlorate (1 ml) was added in the case of nickel and 1 ml each of sodium perchlorate, perchloric acid and maximum suppressor in the case of palladium. The volume was made 20 ml with DMF in both the cases. Ten ml of this solution were taken individually in the polarographic cells, deaerated with nitrogen for 5 min and the polarogram recorded. In each case  $i_d$  was referred to the calibration curve prepared under similar conditions.

Due to the limited solubility of sodium perchlorate in DMF its aqueous solution was preferred in the case of Ni(II). In the case of Pd(II) well-defined wave was only possible in the presence of 0.1M perchloric acid = 0.1M sodium perchlorate and 5% profan extra-24 as the maximum suppressor; 0.3-0.8% of profan extra-24 was suitable for the purpose.

*Effect of water pH, reagent concentration and other variables on the polarograms of metal-oxides* — It was observed that 0.5 and 0.6 ml of water can be tolerated in the case of nickel and palladium respectively. Above this amount  $i_d$  starts decreasing in both the cases though  $E_{1/2}$  remains almost constant.

Extractions were carried out by the general procedure by taking aliquots of metal solutions at different pH values.  $i_d$  remained constant in the pH range 7.5-11.8 for nickel and 1.0-8.8 for palladium. In the case of nickel the pH range was 5.5-9.5 in the absence of citrate ions.

Extractions were also carried out by the general procedure with Ni(II) = 234.8  $\mu\text{g}$  and Pd(II) = 266.0  $\mu\text{g}$  by varying the amount of the reagent from 1 to 50 mg in the form of its 1% solution. It was observed that in both the cases  $i_d$  remained constant if the amount of reagent taken was in the range of 2-50. Higher amounts of the reagent had no effect on  $i_d$  and shape of the polarogram, but  $E_{1/2}$  was slightly shifted towards the negative potential in both the cases.

The amount of naphthalene was varied from 0.5 to 4.5 g and the extractions were carried out by the general procedure. It was found that  $i_d$  was constant in this range. Below this range extraction was not quantitative in both the cases while above this range it was not possible to dissolve the naphthalene in the limited amount of DMF. The shape as well as  $E_{1/2}$  remained unaltered at this concentration range of naphthalene.

Extractions were also carried out by varying the amount of citrate (for pickel) from 0 to 20 ml in the form of its 20% solution.  $i_d$  was constant between 1 and 10 ml of the citrate and above this range  $i_d$  started decreasing slightly. Therefore 5 ml of 20% citrate was preferred. In the case of Pd(II) the amount of buffer was varied from 0 to 10 ml in the form of 1M solution;  $i_d$  was constant between 1 and 5 ml of the buffer. Above this amount  $i_d$  started decreasing slightly; so 2 ml of the buffer were preferred.

TABLE 1 — EFFECT OF DIVERSE IONS ON THE DETERMINATION OF Ni(II) AND Pd(II)

Salt added	Amount of foreign ion added mg	Ni found ( $\mu\text{g}$ )	Pd found ( $\mu\text{g}$ )
Sodium citrate	62.90	234.80	265.35
Sodium phosphate	25.00	235.27	266.32
Sodium borate	40.50	234.80	266.65
Sodium fluoride	45.20	233.86	265.35
Sodium azide	64.60	234.80	264.70
Sodium oxalate	66.60	233.86	265.65
Sodium thiosulphate	42.20	235.74	264.70
Sod-pot-tartrate	66.80	234.33	265.65
Disod-EDTA	79.90	—	265.65
Potassium thiocyanate	59.70	235.74	264.34
Potassium chloride	47.60	234.33	264.70
Potassium bromide	67.20	235.74	265.35
Potassium iodide	76.50	234.33	264.70
Lead nitrate	00.66	233.49	264.70
Sodium vanadate	00.43	234.33	264.34
Bismuth nitrate	00.43	234.80	265.35
Sodium molybdate	00.39	234.33	266.65
Cobalt nitrate	00.20	233.86	264.70
Uranyl acetate	00.65	234.80	266.65
Sodium tungstate	00.56	234.33	266.00
Copper nitrate	00.25	233.86	267.30
Ferric chloride	00.20	233.49	267.30
Mohar's salt	00.14	234.33	265.35
Manganese chloride	00.27	234.33	266.00
Cadmium chloride	00.60	234.80	266.65
Zinc nitrate	00.22	233.86	266.00
Palladium chloride	00.60	235.27	—
Nickel chloride	00.25	—	266.35

It was observed that when Ni(II)=234.8 µg and Pd(II)=266.0 µg were taken, the percentage extraction was above 99% in both the cases for a volume of 200 ml for the aqueous phase. Beyond this volume of the aqueous phase the extraction was not quantitative.

The linear dependence of the limiting current on the square root of the height of the mercury column indicates that the rate of reduction of these metal-oxinates is a diffusion controlled process. The plot of  $\log i/i_a - i$  versus  $E$  is linear in both the cases. The values of the slopes and  $E_{1/2}$  were calculated from these plots. The values of slopes (77 and 31 mV for Ni and Pd respectively) indicate that nickel is reduced irreversibly while palladium is reduced reversibly involving a two-electron change. With the optimum conditions described above the calibration curves for nickel and palladium were constructed. It was linear over the range 0.0-234.8 µg for nickel and 0.0-212.8 µg for palladium in 10 ml of the final solution. The sample solution containing 234.8 µg of nickel and 266.0 µg of palladium determined by the recommended procedures gave a mean deviation of 0.20 µg for nickel and 0.16 µg for palladium. The diffusion current constants calculated in both the cases using the Ilkovic equation are 2.393 and 2.874 for Ni(II) and Pd(II) respectively in the above concentration ranges.

Various ions (100 mg salt of the anions or 1 mg salt of the cations) were added individually to the solution containing 234.8 µg of nickel and 266.0 µg of palladium and the extractions were carried out by the general procedure. In the case of nickel the added ions had no effect, except EDTA in the presence of which the extraction was not possible. In case of palladium all the added ions had no effect on its estimation (Table 1).

The authors wish to thank the Japanese Society for the Promotion of Science for the award of a fellowship to one of them (B.K.P.).

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