

**Procedure**—In the volumetric method, excess potassium dichromate was added to a known volume of  $N_2H_4$  (the ratio of dichromate varying from 1:2 to 1:25 depending upon the concentration of hydrazine) and acidity adjusted to 0.2-0.8N HCl. After 5 min, 10 ml of KI (10%) were added and solution titrated against standard sodium thio-sulphate at room temperature under proper conditions<sup>7</sup>. Blank titrations have shown that the reaction between  $N_2H_4$  and  $K_2Cr_2O_7$  is completed in 5 min before the addition of KI.

In the potentiometric procedure, the oxidation process involves the direct titration of  $N_2H_4$  with  $K_2Cr_2O_7$  or the reverse process at an acidity ranging between 3 and 5N HCl in the presence of 0.015M  $CuSO_4$ , where a sudden change in the potential indicates the end point. The titration apparatus was the same as previously described<sup>8</sup>.

The oxidation of  $N_2H_4$  with excess  $K_2Cr_2O_7$  was investigated at different acidities and time intervals. At lower acidities (<0.20N HCl), the reaction is slow and requires 15 to 30 min for completion. However, in 0.20 to 0.80N HCl, the reaction is completed in 5 min. Above 0.8N HCl, the volume of  $K_2Cr_2O_7$  consumed is less than the theoretical value which may be due to the lowering of the reaction rate.

Under the optimum conditions, good results are obtained when the initial amount of  $N_2H_4$  varies from 0.08 to 24 mg. Similarly amounts of chromium in the range 0.17-52.5 mg can be determined with good results.

The optimum ratio of  $K_2Cr_2O_7$  to  $N_2H_4$  depends on the amount of the latter. With higher amounts of  $N_2H_4$  (6-24 mg), the ratio should not be less than 1.5 : 1, whereas with lower amounts (4 to 0.60 mg) the ratio should be increased to 3 : 1. Higher ratios were used for determination of micro amounts.

In the potentiometric titration of hydrazine solutions with  $Cr_2O_7^{2-}$  at different acidities, the attainment of equilibrium at the Pt electrode seems to be very slow even on heating to 60°. The reaction was found to be catalysed by  $Cu^{2+}$  ions. The role played by  $Cu^{2+}$  is mainly restricted to enhance the attainment of equilibrium<sup>9</sup>.  $Cu^{2+}$  in the concentration range 0.01-0.025M is sufficient for successful quantitative determination of  $N_2H_4$  by the potentiometric method. Good end points are obtained at acidities ranging from 3 to 5N HCl in the presence of 0.015M  $CuSO_4$  at room temperature. At lower acidities, the equilibrium becomes more or less smooth at temperatures between 40 and 50°C and good results are obtained. The titration curves obtained are characterized by sharp inflections of the order of 280 mV per 0.1 ml  $K_2Cr_2O_7$  at the end points. The potentiometric titration can be carried out safely at temperatures up to 60°, provided the optimum conditions of acidity and  $Cu^{2+}$  concentration are maintained. Amounts of  $N_2H_4$  varying from 0.029 to 18 mg can be determined with errors not exceeding  $\pm 0.50\%$ . The inflection at the end point decreases with decreasing hydrazine concentration.

The reverse reaction, reduction of  $K_2Cr_2O_7$  by hydrazine, is very slow at different acidities even on heating to 60°. However, the reaction proceeds

smoothly at room temperature in the presence of 0.01-0.025M  $CuSO_4$  and 3-5N HCl. The titration curves are smooth and characterized by sharp inflections of the order of 225-235 mV/0.1 ml  $N_2H_4$  at the end point. 0.35-49 mg of Cr can be estimated accurately in the presence of appropriate amount of  $CuSO_4$  and 3N HCl.

The statistical analysis of the data can be considered in terms of the *t*-value and the coefficient of variation<sup>10</sup>. It was found that the *t*-value obtained from the *t*-table with 18 degrees of freedom is much larger than the *t*-calc. (0.004) at all levels of significance. Furthermore, the coefficient of variation corresponding to different amounts of  $N_2H_4$  are less than 1%. These facts indicate that the experimental and theoretical volumes of  $K_2Cr_2O_7$  consumed by  $N_2H_4$  are not significantly different. This supports the suitability of our method for the determination of  $N_2H_4$ .

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#### Synergistic Effect in Solvent Extraction of Ni(II) with Benzohydroxamic Acid

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The extraction of Ni(II) with benzohydroxamic acid (BHA) in the presence of pyridine or quinoline in chloroform has been investigated. Nickel is extracted as an ion pair ( $NiAL^+$ , where A=BHA and L=pyridine or quinoline).

**B**ENZOHYDROXAMIC acid (BHA) has been widely used in analytical chemistry<sup>1</sup>. It is a good extracting reagent and easy to obtain. It was, therefore, thought worthwhile to investigate the extraction of Ni (II) with BHA.

During the course of the present studies it was observed that the extraction of nickel with BHA is difficult, probably because the complex formed is either not soluble in organic solvent<sup>2</sup> or takes long time to attain equilibrium. However, in the presence of pyridine or quinoline it forms an extractable complex and extraction equilibrium is attained within 15 min.

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 (%)	<i>q</i>	Extraction (%)	<i>q</i>
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  $23 \pm 1^\circ$ . 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.

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

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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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