Extractive spectrophotometric determination of nickel (II) using 4-methyl 2,3-pentanedione dioxime (H₂MPDDO)

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A new analytical reagent, 4-methyl 2,3-pentanedione dioxime (H₂MPDDO), is proposed for the extraction and spectrophotometric determination of nickel. H₂MPDDO reacts with nickel (II) to give yellow coloured complex, which can be quantitatively extracted into chloroform at pH 9.0. The organic extract shows maximum absorption at 370 nm where absorption due to a similarly prepared reagent blank is negligible. The Beer's law is followed in the concentration range 0.5-10 μg/ml of nickel (II). The molar absorptivity and Sandell's sensitivity of Ni (II)-(H₂MPDDO)₂ complex are 3.039x10³ l/mol/cm and 0.0192 μg/ml/cm², respectively. The stoichiometry of extracted species was found to be 1:2 (M:L). The proposed method is rapid, sensitive, reproducible and accurate, and has been satisfactorily applied for the determination and separation of nickel in synthetic mixtures and spent catalyst samples.

Keywords: Nickel determination, 4-Methyl 2,3-pentanedione dioxime, Extractive spectrophotometry, Separation

IPC Code: C22B23/00; G01J3/00

Introduction

Earlier methods used for spectrophotometric determination of nickel¹-¹² suffer from less stability⁷, interference from some ions⁸ and critical pH⁹-¹¹. In the present method, a new analytical reagent, 4-methyl 2,3-pentanedione dioxime (H₂MPDDO), was used for the extractive spectrophotometric determination of nickel (II). New method can be employed for efficient determination of nickel at μg level. The results of analysis obtained were compared with those obtained by known method (Dimethyl Glyoxime) with certified value of nickel. The proposed method is sensitive, rapid and free from many limitations.

Materials and Methods

Instruments

An Elico pH-meter was employed for the pH measurements while absorbance measurements were carried out on Bausch and Lomb Spectrophotometer (Spectronic-20).

Chemicals

Isonitroso 4-methyl 2-pentanone (HIMP)¹³, taken in three-necked flask, was added with amylnitrate by constant stirring and cooling. An alcoholic solution of 1M 4-methyl 2-pentanone (3 g) was mixed with aqueous solution of 1M hydroxylamine hydrochloride (5 g) and, on reflux for 1 h on water bath, shiny crystals of H₂MPDDO were separated and filtered off, washed with hot water and dried. A stock solution of nickel (II) (5000 μg/ml) was prepared by dissolving calculated amount of NiSO₄.5H₂O in double distilled water containing conc. H₂SO₄ (2 ml). The solution was then diluted to 250 ml with distilled water and standardized¹⁴. For all extraction studies, 0.2 percent reagent solution was used.

Development of Method

To an aliquot of 1 ml of 100 μg Ni (II) solution was added 1ml of 0.2 % H₂MPDDO in alcohol, followed by 1ml of NH₃ solution with 4N HCl buffer solution (1:1) to adjust pH at 9.0. The volume was made up to 10 ml with distilled water and equilibrated with 10ml of chloroform for 60 sec. The yellow coloured organic phase was separated and anhydrous sodium sulphate was added to remove traces of water. The absorbance of the organic phase was measured at 370 nm against similarly prepared reagent blank. The amount of nickel present was computed from the standard calibration curve.

Effect of Diverse Ions

Nickel (II) could be extracted in the presence of large number of foreign ions. Under optimum
conditions, the effect of diverse ions on the extraction of 100 μg nickel (II) was investigated. The solution of diverse ions, required for interference studies, were prepared by dissolving their commonly available chemically pure salts in distilled water to give the cations (10 mg/cm³) and anions (20 mg/cm³).

**Determination of Nickel in Synthetic Mixtures, Spent Catalysts and Alloy Samples**

The usefulness of the developed method was demonstrated by determination of nickel in various synthetic mixtures of associated elements, alloys and catalytic samples (Table 1). Spent catalyst sample was treated with (5+5) ml aqua-regia and heated to near dryness, followed by treatment with HClO₄ (1 ml) to decompose organic matter. The residue obtained was extracted with 2N HNO₃ (20 ml), filtered and diluted to known volume. Suitable aliquots of this solution were used for nickel determination.

Different alloy samples were analyzed for nickel content. Stainless steel samples were dissoluted in (5+5) ml aqua-regia and evaporated to dryness. The residue of each sample obtained was extracted with 2N HNO₃ (20 ml) and diluted to known volume with distilled water. Suitable aliquots of these solutions were taken for the estimation of nickel.

Ni-Al powder samples were dissolved in HNO₃ (10 ml). The solution was evaporated to dryness. The residue was extracted in distilled water (20 ml) and diluted to known volume. A suitable aliquot of this solution was employed for nickel determination.

**Results and Discussion**

The absorption spectrum of nickel (II)-(H₂MPDDO)₂ complex, extracted into chloroform recorded against a similarly prepared reagent blank, showed an absorption maximum at 370 nm where absorption due to reagent blank was negligible. Hence all absorption measurements were carried out at 370 nm against similarly prepared reagent blank.

The complex could be quantitatively extracted at pH 7.2-10.5, where yield was maximum (> 99.94 %). A pH of 9.00 was therefore employed in the subsequent studies.

The effect of H₂MPDDO concentration was studied by carrying out extraction at fixed pH (9.00) but at varying concentration of reagent, 1ml of the 0.2 % reagent in alcohol was found to be sufficient for the quantitative extraction of 100 μg of nickel (II) into chloroform. Excess of reagent does not have any significant effect on the recovery of nickel. 0.2 % reagent (1 ml) was therefore used for further studies.

Nickel (II) was extracted with H₂MPDDO into various solvents (Table 2), of which chloroform (99.94 %) was selected as a solvent for further studies.

To a sample solution containing 100 μg of nickel (II), 1 ml of 0.2 % H₂MPDDO solution in alcohol and various amounts of ammonium buffer solution (pH 9.0) were added and the extraction was carried out in chloroform by the developed method. The absorbance remained constant when 0.7-1.0 ml of the buffer solution was used and hence 1.0 ml of buffer solution was used for all the experiments.

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<th>Ni found by present method*</th>
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<th>Standard deviation</th>
<th>Student test-t</th>
<th>Variance ratio F-values</th>
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#Value in μg, *Mean of three determinations, ®Value in percent
The colour development was instant, however, shaking period was varied (5-120 sec). The optimum period of shaking required to complete transfer of coloured complex into organic phase was found to be 60 sec. The studies on the absorbance of the organic extract at different time intervals revealed that the extracted Ni (II)-(H₂MPDDO)₂ complex was stable for 7 days.

The absorbance of the extracted species was a linear function of Ni (II) concentration in the range of 0.5-10.0 μg/ml at 370 nm. The optimum working range, obtained from Ringbom’s plot was found to be 0.31-1.0 μg/ml that confirmed the Beer’s range (Fig. 1). The Sandell’s sensitivity of the method was found to be 0.0192 μg/ml/cm², while the molar absorptivity was 3.039 x 10³ l/mol/cm.

The tolerance level for the diverse ions investigated were as follows: Cl⁻, Br⁻, I⁻, F⁻, CIO₃⁻, BrO₃⁻, IO₃⁻, NO₃⁻, SCN⁻, HPO₄²⁻, H₂PO₄⁻, SO₄²⁻, S₂O₃²⁻, S₂O₅²⁻, acetate, tartarate, oxalate, ura, thiourea, S₂O₅²⁻, S₂O₇²⁻, acetate, tartarate, oxalate, ura, thiourea, S₂O₅²⁻, S₂O₇²⁻ (20 mg each); CO₃²⁻, S₂⁻, Hg²⁺, Pb²⁺ (10 mg each); Cr₆⁺, (5 mg.); Cd²⁺, Zn²⁺ (3 mg each); Ag⁺, Li⁺, Ba²⁺, Se⁴⁺, V⁵⁺, Sn²⁺, Sr²⁺ (2.5 mg each); Cr³⁺, Ca²⁺, Mg²⁺, Mo⁶⁺, W⁶⁺ (2 mg each); Mn²⁺, As³⁺ (1.5 mg each); Pt²⁺, Au³⁺, Bi³⁺, Al³⁺, Sb³⁺ (1 mg each); V⁶⁺ (0.5 mg.); and Cu²⁺, Co²⁺, Pd²⁺, Fe³⁺ interference seriously. The tolerance limit was set as the amount of foreign ion that causes an error of not more than ± 2 percent in the recovery of metal ion. The precision and accuracy of the method were determined. The average of ten determinations with 100 μg Ni (II) was found to be 99.94 μg with a standard deviation of 0.169 and the deviation from mean at 95 percent confidence limit was ± 0.121. The nature of the extracted complex was as determined by the Job’s continuous variation method and was found to be 1:2 (M:L) i.e. Ni-(H₂MPDDO)₂ was confirmed by mole ratio method, which show sharp break corresponding to mole ratio 1:2. The reaction of Ni (II) with reagent may therefore represent as follows:

\[ \text{Ni(II)} + 2 \text{H}_2\text{MPDDO} \rightarrow \text{Ni(II)} + 2 \text{H}_2\text{MPDDO} \rightarrow \text{Ni(MPDDO)}_2 + 4\text{H}^+ \]

**Conclusions**

The proposed method can be used for determination of nickel at trace levels. Method has advantages of reliability, reproducibility, and good sensitivity, simple, instant colour development, and minimum interference. The method has been successfully applied for the separation of nickel at trace levels in synthetic mixture and spent catalysts. The results obtained are in good agreement with the certified values and are comparable to those obtained by known method.

**References**


