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2-Hydroxy-1-naphthaldoxime as an Analytical Reagent for the Determination of Molybdenum(VI)

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Received 24 October 1979; revised 3 December 1979; accepted 9 January 1980

Molybdenum(VI) forms a yellow coloured soluble complex with 2-hydroxy-1-naphthaldoxime at pH 3.0. The Beer's law is obeyed upto 53.7 ppm of Mo(VI) at 400 nm. The effects of pH, reagent concentration and diverse ions have been studied. The stability constant of the complex calculated from Job's method and Asmus method is found to be 4.35×10^3 . The molar absorptivity and Sandell sensitivity of the complex are 1.75×10^3 litre mol⁻¹ cm⁻¹ and 0.055 µg/cm² respectively. The proportional decrease in the colour of the complex with the addition of micro amounts of oxalate has been utilized for the determination of oxalate in microgram quantities.

2-HYDROXY-1-NAPHTHALDOXIME has been extensively used for the determination of various metal ions¹⁻⁴. We report here the use of this reagent in the determination of Mo(VI). The proposed method is simple, rapid and more selective than the methods reported in literature⁵⁻⁸, since most of them suffer from the interference of manganese, zinc, nitrate and iodide and involve extraction process. The reagent forms a yellow coloured soluble complex with molybdenum(VI) in the pH range 1-5. A study of pH effect showed that the complex has maximum absorption in the pH range 2.5-3.5. The complex showed maximum absorption at 400 nm in the visible range, where the reagent has no absorption. Hence the absorption measurements were made at 400 nm. 2-Hydroxy-1-naphthaldoxime (OHNAO), m.p. 157°, was prepared in the laboratory from 2-hydroxy-1-naphthaldehyde, and purified by recrystallisation. A 0.05 M solution in methanol was used for the studies.

Sodium molybdate (0.01 M) solution was prepared by dissolving requisite amount of a Riedel sample in distilled water and the molybdenum content was determined by the oxime method⁹. Sodium acetate-

hydrochloric acid buffer of pH 3.0 was used for the studies. Sodium oxalate (1.14×10^{-3} M) was prepared by dissolving the required amount of BDH, AR sample in distilled water.

ECIL spectrophotometer (model GS 865A) and ELICO pH meter (model LI-120) were used for the absorbance and pH measurements respectively.

Procedure — To 1 ml of the reagent in each of a set of 25 ml volumetric flasks, 8 ml of methanol and 10 ml of buffer solution (pH 3.0) were added. Varying amounts of molybdenum(VI) were added and the contents made upto the mark with the buffer solution. The absorbance of these solutions was measured at 400 nm against water as the blank. Absorbance values were plotted against molybdenum content. A straight line passing through the origin was obtained upto 53.7 ppm of molybdenum.

pH effect studies showed that the complex has maximum absorption in the pH range 2.5-3.5. A minimum of 50-fold excess of reagent was necessary for maximum colour formation. Beer's law was obeyed upto 53.7 ppm of Mo(VI) at 400 nm. Job's continuous variation method¹⁰ and Asmus method¹¹ indicated the composition of the complex as 1:1 and the values of the stability constant of the complex as 4.35×10^3 and 3.8×10^3 respectively.

Effect of diverse ions — Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Zn²⁺, Th⁴⁺, U⁶⁺, Cd²⁺, Cl⁻, Br⁻, I⁻, NO₃⁻, SO₄²⁻ and CH₃COO⁻ did not interfere. Ni²⁺, Al³⁺, Ti⁴⁺ and Pb²⁺ interfered even when present in traces. Cu²⁺, W⁶⁺, V⁵⁺, Ce⁴⁺, citrate and tartrate did not interfere when present in equal amounts with Mo⁶⁺(VI). Co²⁺, CO₃²⁻ and CrO₄²⁻ are tolerable upto 15, 38 and 200 ppm respectively. The interference of Fe³⁺ was eliminated by masking with potassium iodide and the liberated iodine was masked with hypo.

The molar absorptivity and Sandell¹² sensitivity of the complex are 1.75×10^3 litre mol⁻¹ cm⁻¹ and 0.055 µg/cm² respectively. The standard deviation of the method was found to be 0.006. The colour development of the complex was quite rapid and was stable for more than 48 hr.

Determination of oxalate — Addition of micro amounts of oxalate to the Mo(VI)-reagent complex resulted in the proportional decrease of the absorbance. This bleaching effect of oxalate has been utilized for its determination spectrophotometrically in the range 4-20 ppm using the following procedure :

To 1 ml of the reagent in each of a set of different 25 ml volumetric flasks, 8 ml of methanol, 10 ml of buffer solution (pH 3.0) and 3 ml of sodium molybdate (1×10^{-2} M) were added. Then varying amounts of oxalate (4-20 ppm) were added to these flasks and the contents made upto the mark with distilled water. The absorbance of the solutions was measured at 400 nm against water as blank. A calibration curve was constructed and the amount of oxalate in the unknown sample was determined from the calibration curve.

One of the authors (VKR) thanks the CSIR, New Delhi for the award of junior research fellowship. The authors are thankful to Prof. S. Brahmaji

Rao for his interest in the work and the authorities of SVU Autonomous Post-graduate Centre, Anantapur for providing facilities.

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Extraction of Zinc by Long Chain Amines

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Received 21 October 1978; revised 8 February 1979; rerevised and accepted 27 October 1979

Extraction of zinc by long chain amines from thiocyanate medium has been studied. Amberlite LA-2, triisooctyl amine (TIOA) and Aliquat 336 were used as representatives of secondary, tertiary and quaternary amines using chloroform and carbon tetrachloride as diluents. The extraction efficiency increases in the order: secondary < tertiary < quaternary amine. The effect of diluents on the extraction is found to be considerable.

LONG chain amines have found considerable use as extractants in industry and atomic energy programme because of their low cost, ease of availability and stability towards radiation. Another factor of interest is their selectivity for anionic metal complexes in the aqueous phase. Long chain amines have a great potential as extractants for the removal of toxic metal ions from industrial wastes¹. Numerous amine compounds with low aqueous solubility have been screened and evaluated as extractants²⁻⁵. Solvent extraction by long chain amines has been utilised for the separation⁶ and estimation^{7,8} of zinc and also for the study of complexes⁹⁻¹². In

this note the extraction of zinc from thiocyanate medium has been studied with a view to evaluating the effects of amine and diluent.

Amberlite LA-2 (BDH) and triisooctyl amine, TIOA (K & K Labs) diluted suitably with carbon tetrachloride or chloroform (BDH, AR) were converted to the chloride form by equilibrating with hydrochloric acid and then to thiocyanate form by shaking repeatedly with ammonium thiocyanate (BDH, AR). Aliquat 336 (trioctyl monomethyl ammonium chloride, K & K Labs) was also converted to the thiocyanate form. The amines were estimated by stripping the thiocyanate with sodium hydroxide and then titrating the acidified aqueous phase with silver nitrate using ferric ion as the indicator.

Zn⁶⁵ obtained from the Isotope Group, BARC, was assayed by γ -spectrometry. The concentration of the metal was of the order of $10^{-6}M$. Extraction experiments were carried out by equilibrating for 5 hr at $23 \pm 1^\circ$ 10 ml of the aqueous phase with an equal volume of the organic phase containing the extractants. All the activity measurements were corrected for background activity. The pH of the solution after equilibration was around 4.

Extraction of zinc by Amberlite LA-2 — Extraction of zinc by Amberlite LA-2 was studied at different concentrations of ammonium thiocyanate, keeping the concentration of the amine constant. Log distribution ratio, log D, was plotted (Fig. 1) as a function of log [CNS] and the slopes of the rising portion of the curves were about 1-1.5 in both the solvents indicating the formation of $Zn(CNS)_3^-$ and $Zn(CNS)_2^{2-}$ in the aqueous phase. The extraction reached a maximum at thiocyanate concentration of about 0.5 M and then decreased with increasing concentration of thiocyanate. The slopes of the plot in this region were about 1.6-1.9 indicating the predominance of $Zn(CNS)_2^{2-}$ in the aqueous phase.

The results were also confirmed by measuring the distribution ratio of zinc at different concentrations of the amine and at two different concentrations of thiocyanate. The slopes of the log plots (Fig. 2) representing the amine-metal ratio in the organic phase were 1.2 and 1.6 in chloroform and carbon tetrachloride respectively indicating the extracted

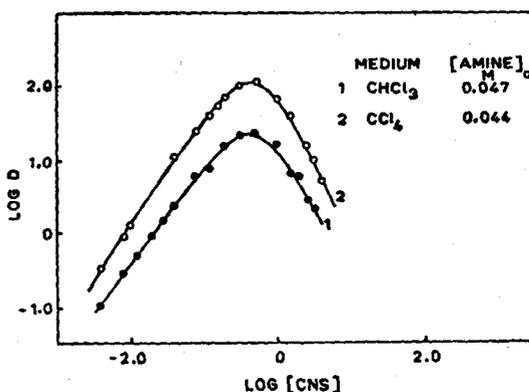


Fig. 1 — Plot of log D against log [CNS] at constant [amine].

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