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LIGNOCAINE HYDROCHLORIDE AS A HIGHLY SELECTIVE EXTRACTANT FOR SPECTRO-PHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH THIOCYANATE

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A NUMBER of reagents reported for extraction photometric determination of molybdenum have been reviewed[1-3]. During our investigation it was found that the sensitivity and stability of the molybdenum-thiocyanate complex could be enhanced by adding lignocaine hydrochloride (LH) to form a new ion-association complex which could be extracted into an organic solvent. The proposed method offers the advantages of rapidity, reproducibility, stability and high sensitivity without the need for heating and dependence of colour intensity upon a number of factors such as volume of aqueous phase, coefficient of expansion of isopentyl alcohol, concentration of iron and tin (II) chloride.

A stock solution of molybdenum (VI) was prepared from AR grade ammonium molybdate tetrahydrate in doubly-distilled water containing a few drops of ammonia, and standardised gravimetrically using 8 hydroxy quinoline[4]. The stock solution was further diluted to give a standard solution containing 20 μg Mo (VI)/ml.

A 10% aqueous solution of potassium thiocyanate (AR) was prepared. A 5% aqueous solution of ascorbic acid was prepared.

A 2% aqueous solution of LH (ASTRA-IDL) in water was used. Beckman model DB spectrophotometer with 1 cm matched silica cells was used for absorbance measurements.

Recommended procedure: An aliquot of the stock solution containing 1–30 μg of molybdenum(VI), 10 M hydrochloric acid (3 ml), 5% ascorbic acid (2 ml) and 10% potassium thiocyanate (5 ml) solutions were taken in a 150 ml separatory funnel and diluted to 15 ml with doubly-distilled water. The contents in the separatory funnel were mixed and left at room temperature for 15 min. To this was added LH solution (2%, 3 ml) followed by 5 ml of chloroform and the mixture equilibrated for 3 min. The deep orange red chloroform layer was separated and the aqueous solution extracted twice with chloroform (2 × 5 ml). The chloroform extracts were combined and made upto 10 ml with chloroform, dried (anhyd. Na_2SO_4) and its absorbance measured at 465 nm against a corresponding reagent blank prepared under similar conditions.

Molybdenum (V) formed by the reduction of molybdenum (VI) with ascrobic acid combines with potassium thiocyanate to form a red molybdenum (V) thiocyanate complex in 0.9–3 M hydrochloric acid solution. On adding LH solution an orange-red ion-association complex is formed at the same range of hydrochloric acid concentration. The mixed complex can be extracted into chloroform while binary molybdenum (V)-thiocyanate complex is not extracted.

Molybdenum (V)-thiocyanate complex in 1.5 M hydrochloric acid concentration has an absorption maximum at 465 nm showing a bathochromic shift of 20 nm. The reagent blank in chloroform does not show any absorption either at 445 nm or at 465 nm. All subsequent measurements were made at 465 nm.

Effect of experimental variables: Various water immiscible organic solvents such as benzene, toluene, carbon tetrachloride and chloroform were examined for extracting the ion-association complex. The ε values for molybdenum complex in various solvents are, chloroform; 2.12×10^4; carbon tetrachloride 4.40×10^2; toluene, 1×10^3; benzene, 1×10^3 dm^3 mol^{-1} cm^{-1}. Hence chloroform was selected for further studies. A double extraction was

necessary to remove molybdenum completely.

The effect of acid concentration on the formation and extraction of the ion-association complex into an organic phase was investigated with hydrochloric, sulphuric, phosphoric and nitric acids. The ε values of the complex in 0.3 to 3 M hydrochloric, 1.3 M sulphuric and 1.3 M phosphoric acid solutions are: 2.12×10^4; 1.88×10^4 and 4.17×10^3 $dm^3\ mol^{-1}\ cm^{-1}$, respectively. The complex is not quantitatively extracted in nitric acid medium. Hence hydrochloric acid was selected for further work. Addition of large excess of ascorbic acid, LH and thiocyanate had no adverse effect on the absorption and maximum wavelength of the coloured complex. The chloroform extract of the complex obeys Beer's law in the range 0.2–3 ppm of molybdenum.

The following amounts (ppm) of foreign ions are found to give +2% error in the determination of 2 ppm of Mo: Na (I), 1000; K (I), 1000; Mg (II), 100; Ca (II), 300; Ba (II), 250; Pb (II), 50; Zn (II), 100; Cd (II), 3000; Mn (II), 1000; Ti (IV), 750; V (V), 250; Cr (VI), 750; Cr (III), 2000; W (VI), 250; Al (III), 2000; Bi (III), 15; Fe (III), 1000; Ni (II), 100; Ru (III), 100; Rh (III), 200; Pd (II), 50; Ag (I), 20; Os (VIII), 100; Pt (IV), 50; Au (III), 750; Co (II), 200; U (VI), 1000; Zr (IV), 100; La (III), 250; As (III), 50; fluoride, 1000; bromide, 1000; iodide, 2000; phosphate, 10000; nitrate, 1000; sulphate, 3000; acetate, 5000; citrate, 5000; tartrate, 2000; and carbonate, 15,000. However, thiosulphate interferes.

Composition of Mo-SCN-LH Complex: The ratio of molybdenum to the thiocyanate and LH was determined by Job's method of continuous variations. The results indicate that the molar ratio of Mo (V) to SCN^- is 1:4 and of Mo (V) to LH is 1:1. The mole ratio method confirms the ratio of Mo (V) to LH as 1:1. Hence the composition of the extracted thiocyanate-molybdenum (V) complex with LH is: (LH) [$MoO(SCN)_4$]. Analysis of steel sample by the proposed method gave a result of 0.94% Mo (certified value is 0.95%).

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ALLANITE-BEARING MIGMATITES OF THE ARCHAEAN SCHIST BELT OF KHAMMAM, ANDHRA PRADESH

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THE Archaean schist belt of Khammam, Andhra Pradesh occurs in the area included in the toposheets of 65 C/3, 4, 7 and 8. The schist belt has been equated with the 'Sargur belt' of Karnataka on the basis of lithology, amphibolite to granulite facies metamorphism and geologic setting[1–4]. The migmatites of pelitic derivation of Khammam schist belt are represented principally by feldspathised schists and to a lesser extent by quartz-biotite-oligoclase (with or without K-feldspar) gneiss. In the feldspathised schist, the neosome defined by feldspar and recrystallised biotite is parallel to palaeosome of mica schist which on a regional scale is parallel to the foliation. The quartz-biotite-oligoclase gneiss shows neocrystallisation with the melanosome and leucosome separated by 1–2 cm. In the migmatites of Khammam, both metamict and non-metamict allanites occur. The metamict allanite is coloured light greenish yellow or reddish yellow and is non-pleochroic and is isotropic. The non-metamict allanite is pleochroic with α = light greenish brown, β = light brown and γ = reddish brown. The $2V(-)$ = 36°, $n_\gamma - n_\alpha = 0.023$. It gives an extinction angle ($Z \wedge c$) of 10° to 12°. Allanite is described as an epidote group mineral containing Ce, La, Y and Th which occur replacing calcium in the structure[5]. It is generally held that the alpha particles which generate in the process of disintegration of the radioactive components bombard the structure of allanite causing metamictization[6].

Allanite grains show different growth pattern in the migmatites of Khammam which are described below from photomicrographs. It occurs in rectangular plate or semi-oval shape with a grain size varying from 0.4 mm to 1.5 mm. It lies in the plane of foliation