

## RAPID SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II) WITH HYDRAZINE CARBOTHIOAMIDE-2-(2-FURANYL METHYLENE): ANALYSIS OF ALLOYS AND MINERALS

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HYDRAZINE carbothioamide-2-(2-furanyl methylene), HCFM, was proposed as a spectrophotometric reagent for the determination of palladium<sup>1</sup>. Most of the spectrophotometric methods proposed for nickel involve extraction. HCFM forms a light yellow complex with nickel(II) which has not previously been studied. In the present investigation we report the rapid spectrophotometric determination of nickel using HCFM. The proposed method offers the advantages of simplicity, rapidity, sensitivity and determination at room temperature without the need for extraction.

A stock solution of nickel(II), prepared from AR grade ammonium nickel sulphate was standardised gravimetrically by the dimethylglyoxime method<sup>2</sup>. The solution was further diluted to get a standard solution containing 10 ppm of nickel(II). HCFM was prepared from hydrazine carbothioamide and furfural and purified<sup>3</sup>. A solution of HCFM [0.3% (m/v)] was prepared in 85% ethanol (v/v). Potassium dihydrogenphosphate—sodium hydroxide buffers of pH 5.8–10.6 were used. Beckman Model DB spectrophotometer with matched 1 cm silica cells was used for absorbance measurements.

An aliquot of the stock solution containing 0.50–55 µg of nickel(II), 5 ml of buffer of pH 7.1, 5 ml of ethanol and 5 ml of 0.3% HCFM solution were made up to 25 ml with distilled water. The solution was mixed well and the absorbance was measured at 366 nm against a reagent blank. The nickel in the sample solution was then determined from the standard calibration curve.

HCFM forms a light yellow coloured complex with nickel(II) in potassium dihydrogen phosphate-sodium hydroxide buffer instantaneously at room temperature. The study of nickel(II)—HCFM complex in hydrochloric acid, sulphuric acid, acetic acid or phosphoric acid medium is not recommended because the complex is unstable and less sensitive. Therefore, potassium dihydrogen phosphate-sodium hydroxide buffer medium has been selected for these studies. Maximum coloration takes place in the effective pH

range 6.4–8.7. The nickel(II)-HCFM complex is stable for 2.5 hr. All studies were confined to an effective pH of 7.8. The effective ethanolic concentration is found to be 28–52% (v/v). Below 28% turbidity is obtained and above 52%, maximum coloration is not obtained. A 40% ethanolic medium is selected for the present investigation. A 69-fold molar excess of the reagent is required for full development of colour intensity.

The nickel(II)-HCFM complex exhibits maximum absorption at 362–368 nm, where the reagent and nickel(II) under similar conditions do not absorb appreciably. Beer's law is obeyed in the range 0.02–2.2 ppm of nickel(II) with an optimum concentration range 0.1–2.1 ppm. For  $\log I_0/I = 0.001$ , the sensitivity of the reaction as calculated from Beer's law data is 2.7 ng cm<sup>-2</sup>. The molar absorptivity is  $2.16 \times 10^4$  l mole<sup>-1</sup> cm<sup>-1</sup>. The colorimetric measurement of pure nickel solutions containing 1.0–1.5 µg of Ni/ml was found to be better than 2% (IS;  $n = 10$ ). The absorbance readings remained constant in the temperature range 6°–50°C. The order of addition of reagents was not critical.

The equilibrium shift method<sup>4</sup> and Asmus' method<sup>5</sup> indicate the formation of 1:1 complex between nickel(II) and HCFM with a log  $K$  value of 4.67 at 27°C. The ion-exchange experiments showed that nickel(II)-HCFM complex is cationic in nature.

The effect of diverse ions on the absorbance readings of the complex was investigated and many cations like Cu(II), Co(II), Ag(I), Ru(III), Rh(III),

TABLE I  
Determination of nickel in nickel-aluminium alloy

Certified composition, (%) <sup>*</sup>	Certified value of nickel, ppm	Nickel content of solution found †, ppm	
		DMG method	Present method
Ni, 50; Al, 50	0.2	0.20	0.20
	0.4	0.40	0.39
	0.7	0.70	0.71
	0.8	0.81	0.81
	1.0	1.00	1.01
	1.2	1.20	1.18
	1.6	1.63	1.62
	1.8	1.79	1.79
	2.0	2.01	2.00

\* Values are supplied by Rober-Johnson Company.

† The results quoted as "found" are the means of ten determinations on each solution.

Os(VIII), Os(VI), Au(III), Pt(IV), Pd(II), Ir(III), Ti(IV) and Hg(II) interfere considerably and the anions like  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $CH_3COO^-$ , tartrate, phosphate, thiosulphate do not interfere (to an extent of 4000 ppm). The interference of certain metals could be reduced by using tartrate, citrate, fluoride and phosphate as masking agents.

About 0.1 g of the alloy is weighed in a 50 ml beaker and treated with 3 ml of concentrated nitric acid and heated gently. After the alloy is dissolved, the excess of nitric acid is removed by heating with 6 ml of concentrated HCl and evaporated to dryness on a steam bath after each addition. The residue is dissolved in distilled water and diluted to 500 ml. An aliquot of the solution was then treated with the reagent, the volume made up to 25 ml and the absorbance measured at 366 nm. The results of the analysis in table 1 are in good agreement with those obtained by dimethylglyoxime method<sup>2</sup>.

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## A NEW COLLECTION OF FOSSILS FROM THE PRECAMBRIAN VINDHYAN SUPERGROUP OF CENTRAL INDIA

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ALTHOUGH the sediments of the Vindhyan Supergroup of central India are well suited for the preservation of organic remains, few macrofossils have been found in them, and there is considerable controversy regarding their exact systematic position, affinities and ages. Among them the most significant is *Fermoria*<sup>1,2</sup>. It occurs in the Suket Shale formation of the Semri Group around Rampura town in the Neemuch district of Madhya Pradesh. A new

collection has been made from the cuttings from a newly dug well in Jamalpura village near Rampura, and it includes several species not recorded from the Suket Shale or any other Vindhyan formation so far. Their occurrence has important bearing on the age of this supergroup and evolution of life in the Precambrian. This is a preliminary note on the findings; the collection is under detailed study and systematic descriptions will be published elsewhere. The collection is deposited in the Northern Region of the Geological Survey of India, Lucknow, under registration No. NRP-1/72.

The collection consists of several thousand individual bodies made up of several species, most of which are being reported for the first time from the Precambrian Vindhyan sediments. They occur closely packed together along partings of thinly laminated and fissile shale. They are mostly embedded on the upper surface of the shale layers; the lower surface may also have a few that may have accidentally adhered there while splitting the shale. The shale is of two kinds: one is compact, hard, and dark grey in colour; the other is olive green in colour and softer. The fossils are much more abundantly distributed in the dark variety than in the green.

The species could be broadly divided into two main habits, viz., rounded and elongated. All the species occur together randomly mixed up without any apparent segregation.

The most abundant fossil is *Fermoria*, which is also identified in the past variously as *Protoboella*, *Vindhyanella*, and *Krishnania* by different investigators<sup>1-3</sup>. A reassessment of these forms has shown that all of them are congeneric with *Chuarla* Walcott 1899 according to Ford and Breed<sup>4</sup>. This conclusion is confirmed by the study of the present material<sup>5</sup>. The *Chuarla* in the new collection is mostly 2-3 mm in diameter, but smaller specimens up to 1 mm are also seen, though larger than 3.5 mm are extremely rare. There are evidently two species of *Chuarla* in this collection, though some authors<sup>4,6</sup> consider that all forms should be assigned to a single species, *C. circularis*. One species (type No. NRP-1/72/1) is dark coloured, chitinous, and has distinct wrinkles along its borders (figure 1A). The other (type No. NRP-1/72/2) is greyish, much lighter in colour, and does not show any ornamentation (figure 1B). The number of specimens of the first type is much fewer than the second. Since both occur together on the same slab of shale, the difference in their morphology is apparently not due to any difference in the condition of their preservation which could give dissimilar appearance to the same species, but because they represent different and separate species. The dark form with wrinkles