

Liquid-liquid extraction and spectrophotometric determination of nickel(II) with pyridine-2-acetaldehyde salicyloyl hydrazone

S H Sinha & A D Sawant*

Department of Chemistry, The Institute of Science, 15, Madam Cama Road, Bombay 400 032

Received 4 September 1990; revised and accepted
22 January 1991

A new spectrophotometric method for the determination of nickel(II) at the trace level has been developed. Pyridine-2-acetaldehyde salicyloyl hydrazone (PASH) reacts with nickel(II) forming a yellow coloured complex in the pH range 4-7 (λ_{\max} 395nm), which is extractable into chloroform. The molar absorptivity and Sandell sensitivity are $8513.3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and 6.8 ng/cm^2 . Beer's law is obeyed in the concentration range 0.5-5 ppm. The validity of the method has been checked by estimating nickel in a variety of samples.

Several methods of determination of microgram amounts of nickel have been reported based on various reagents such as xanthates¹, isonitrosoacetophenone², dimethylglyoxime⁴, 1,1,1-trifluoro-4-mercaptopent-3-en-2-one⁷, 4-benzyl-3-methyl-1-phenylpyrazoline-5-one⁸, 3-methoxy-7-methylphenothiazine¹⁰, purpurin¹¹ and 2-thioortoc acid¹². Among these, dimethylglyoxime is preferred for routine work. However, the extraction with dimethylglyoxime occurs mostly in the alkaline pH range. Of the remaining reagents, xanthate is highly photosensitive and studies on its extractive parameters are not reported. Extraction with isonitrosoacetophenone occurs mostly in the alkaline pH range and the complex is stable for 5 hr. In the case of purpurin and 3-methoxy-7-methylphenothiazine, the complex is stable for 2.5 and 4 hr respectively and extraction occurs at fixed pH. Nickel(II) has been extracted quantitatively with 4-benzyl-3-methyl-1-phenylpyrazoline-5-one into chloroform, but it takes 6 hr for the quantitative extraction; with TBP the extraction takes about 30 min. Therefore, these methods are time consuming.

In the present note we report the use of the reagent pyridine-2-acetaldehyde salicyloyl hydrazone (PASH) for the determination of nickel(II). PASH extracts nickel quantitatively into chloroform (99.95%) from aqueous solution in a wide pH range

(from 4 to 7) and in addition to this the extracted complex is stable for more than 48 hr and it has a reasonably high ϵ value.

Experimental

A Bausch and Lomb Spectronic-20 model spectrophotometer was used for absorbance measurements. A digital ELICO pH meter type LI-120, was employed for pH measurements.

All the reagents and chemicals used were of AR quality. The stock solution of Ni(II) was prepared by dissolving appropriate quantity of nickel acetate in doubly distilled water. Solutions of ions used for interference studies were prepared by dissolving the corresponding salts in distilled water or dilute hydrochloric acid. PASH was synthesized by the method reported in the literature⁹. Sodium acetate-acetic acid buffer of the pH 5 was used for subsequent studies.

Procedure

To an aliquot containing $30 \mu\text{g}$ of nickel, 5 ml of buffer solution (pH 5) was added and the volume was made up to 10 ml. The solution was equilibrated with 10 ml of chloroform containing 0.1% reagent solution in DMF-chloroform for two minutes. The organic extract was collected in a 10 ml standard flask and made up to the mark with chloroform, if necessary. The absorbance of the solution was measured at 395 nm against a reagent blank. A calibration curve was prepared. Unknown amount of nickel(II) was determined from the calibration curve.

The optimum extraction conditions were established by studying the effects of pH, reagent concentration and period of equilibration. Tolerance of diverse ions was also studied.

Results and discussion

The absorption spectrum of Ni-PASH complex in chloroform showed an intense peak at 395 nm. The system was found to obey Beer's law over the concentration range of 0.5 to 5 ppm Ni(II). The sensitivity of the method as defined by Sandell was found to be 6.8 ng/cm^2 at 395 nm and the molar absorptivity was $8513.3 \text{ l mol}^{-1} \text{ cm}^{-1}$. The colour stability of extracted complex was $> 48 \text{ hr}$.

Effect of pH and reagent concentration

The effect of the pH on the extraction of the complex was studied in pH range 1-10. The extraction was greater than 99.5% in the pH range 4-7. Hence,

the subsequent studies were carried out at pH 5. The equilibration time maintained was 2 min which was predetermined.

The concentration of PASH was varied from 0.01 to 0.15% keeping concentration of nickel as 30 μg .

The studies showed that for 30 μg of nickel at pH 5, 0.4 to 1 ml of 0.1% of PASH solution was sufficient for complete colour development and quantitative extraction of nickel(II).

Effect of foreign ions

Interference due to a number of ions in the determination of 30 μg of nickel by the recommended procedure was studied. Cations were added in the form of chlorides, sulphates or nitrates to the extent of a maximum of 10 mg/ml; anions were added in the form of sodium or potassium salts. Masking agents were used whenever absorption varied by ± 0.02 optical density. Chloride, bromide, iodide, perchlorate, bromate, iodate, sulphate, sulphite, thiosulphate, persulphate, pyrophosphate, thiocyanate, urea and thiourea did not interfere upto 300-fold excess. 150-fold excess of Co(II), Pb(II), Tl(I), Cd(IV), fluoride and tartrate did not interfere. Fifty-fold excess of Pd(II), Pt(IV), W(VI), Hg(II), Zn(II), Bi(II) and permanganate showed no interference. The interference from Fe(II) was removed by masking it with 200 $\mu\text{g}/\text{ml}$ hydrogen peroxide. Mo(VI), As(III), Cd(II), Mn(II), Cr(III), U(VI), Ti(II) and Sn(II) did not interfere upto 30-fold excess. Cu(II) interference was removed by masking it with thiosulphate. Fifteen-fold excess of Fe(III), Th(IV) and Te(IV) did not interfere. Interference due to EDTA could be removed by strongly heating the mixture with concentrated HNO_3 .

Nature of the extracted species

The composition of the complex was determined by Job's continuous variation method^{3,6}. A series of solutions was prepared by mixing 0.25 to 4.75 ml of $9.5 \times 10^{-4} M$ nickel (II) solution with 4.75 to 0.25 ml of $9.5 \times 10^{-4} M$ PASH solution, such that the volume of each of the mixture solution was 5 ml. Each solution was then extracted as described above. The plot of absorbance against $M/(M+R)$ ratio showed 1:2 (metal to reagent) composition at 395 nm. The composition was verified by mole ratio method⁵ using the equimolar solutions ($5 \times 10^{-4} M$) of metal and reagent by keeping constant metal concentration. The plot of absorbance at 395 nm against the ratio of mole fraction showed a break at 2, indicating 1:2 ratio of Ni-PASH complex.

Application of the method for determination of nickel at trace level

Various synthetic mixtures containing nickel were

Table I—Determination of nickel(II) in synthetic mixtures and standard samples

Sr. No.	Sample	Ni(II) found*	
		Present method	Dimethyl glyoxime method
<i>Synthetic mixtures†</i>			
1	Co(II) (50); Ni(II) (50).	49.95	50.10
2	Pd(II) (50); Ni(II) (50).	50.00	50.00
3	Zn(II) (40); Ni(II) (60).	60.00	59.85
4	Pt(IV) (25); Ni(II) (25).	25.00	25.00
<i>Standard Samples††</i>			
5	Brass alloy**		
	Sn (5.23); Ni (0.35); Cu (94.41); P (0.008)	0.35	0.35
6	S.S. Steel		
	Mn (0.60); Ni (1.75); Cr (1.27); Mo (0.06).	1.74	1.73

* An average of three determinations

** Cu masked with thiosulphate

† Values in μg

†† Values in %

prepared and each was analysed according to recommended procedure and the results were tested by known method. Ni-PASH extract did not show traces of associated metals at the working pH.

Similarly, the method was employed for the determination of nickel in Brass Sample No.1248 (Ita Lab.) and steel sample. Masking agents were used whenever necessary. Results obtained are summarized in Table I. They show a good agreement between the amounts added and estimated. The proposed method is simple and selective.

The average of eight determinations with 30 μg of nickel in 10 ml solution was 29.99 μg and 30.1 μg at 95% confidence limit.

References

- Hall D, *J Am chem Soc*, 44 (1922) 1462.
- Krohnke F, *Ber dt Chem Ges*, 60 (1927) 527.
- Job P, *Ann Chim*, 9 (1928) 113.
- Scott W W, *Standard methods of chemical analysis*, Vol I (D Von Nostrand, New York), 1939.
- Yoe J H & Jones A L, *Ind Eng Chem Anal Edn*, 16 (1944) 111.
- Irving H & Pierce T B, *J chem Soc*, (1959) 2565.
- Barrat R S, Belcher R & Stephen W I, *Anal chim Acta*, 58 (1972) 107.
- Joshi S N, Enanova E K & Peshkova V M, *Indian J Chem*, 11 (1973) 78.
- Garcia-Vargas M & dela Guardia M, *Analyst*, 105 (1980) 965.
- Jain R K & Mital R L, *J Inst Chem*, 53 (1981) 38.
- Roman Galan T, Arrebola Ramirez A & Roman Ceba M, *Microchem J*, (1982) 27.
- Shrivastava M & Pandey G S, *Indian J Chem*, 23A (1984) 357.