

Solid Phase Extraction and Determination of Nickel Ions in Samples of Steel and Hydrogenated Oils Using Modified Cellulose

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2-Pyridyliminosalicyl cellulose has been used for the adsorption and estimation of nickel by both column and batch techniques. The distribution coefficient has been determined for nickel ions. Methods have been developed to estimate nickel in steel and hydrogenated oil samples.

Key Words: Nickel, 2-Pyridyliminosalicyldehyde, Cellulose, Pre-concentration.

INTRODUCTION

Recently cellulose immobilized with phosphoric acid and carboxymethyl group,^{1,2} dithiocarbamate and 2,2'-diaminoethylamine³ have been used for the preconcentration of lead, cadmium and some transition metals. From literature it is apparent that Schiff bases have been largely used in the past to synthesize various stable transition and non-transition metal complexes.⁴⁻⁶ 2-Pyridyliminosalicylaldehyde has also been reported to form stable complexes with various transition metal ions. The present work describes a novel method developed for the preconcentration and estimation of nickel ions in various samples. In the technique both batch and column methods have been employed.

EXPERIMENTAL

All chemicals and solvents used were of analytical reagent grade. Distilled deionized water was used throughout the investigation. Acetate buffer solutions were prepared by mixing 0.2 M acetic acid and 0.2 M sodium acetate in suitable proportions. A digital pH-meter 5651 A and a Shimadzu AA-640-13 atomic absorption spectrophotometer were used. A glass tube of 100 mm length and 7 mm i.d. was used as a chromatographic column.

Preparation of immobilized cellulose

2-Aminopyridine was immobilized onto cellulose in two separate steps as follows:

Step-1: Cellulose (10 g) was suspended in a 100 mL M solution of 2-hydroxy-5-bromobenzaldehyde (HBB) in dry ether. The mixture was refluxed on a water bath for 2 h in the presence of triethylamine; the resulting product HBB-cellulose (HBBC) was filtered, washed consecutively with ether, ethanol and acetone and then heated at 60°C for 8 h in vacuum.

Step-2: HBBC (5 g) was reacted with 50 mL of 1 M 2-aminopyridine in dry diethyl ether with constant stirring in the presence of an acid. The solid product 2-pyridyliminosalicylcellulose (PSC) was filtered, washed and dried by heating in a vacuum.

Procedure for analysis: Immobilized cellulose (0.08 g) was equilibrated with 10 mL (10 ppm) solution of nickel ion in a 100 mL pyrex conical flask. Solutions of nickel ions were maintained at pH 6.5 by sodium acetate. The total volume of the solution was made to 20 mL. The solution was maintained at 40°C for 20 min in a thermostat. Immobilized cellulose was allowed to settle. Supernatant solution was separated and nickel ions in supernatant solution were determined by atomic adsorption spectrophotometric technique.

Glass columns were packed with 0.08 g of modified cellulose to a height of about 10 mm. Then 10 mL (10 ppm) solution of nickel ions, maintained at the required pH 6.5 with sodium acetate-acetic acid buffer, were passed through the column at a flow rate of 2 mL/min. Adsorbed nickel ions were then eluted from the column using 20 mL of 0.1 N HNO₃. Nickel ions were then determined by atomic absorption spectrophotometry. The time required for the solid-liquid system to attain the equilibrium condition was determined at a definite temperature by placing 10 ml (10 ppm) of metal ions in a conical flask and shaking it with 0.08 g of immobilized cellulose. The supernatant solution from the flask was separated off at different time intervals. The time intervals were studied between 2 to 20 min. Unextracted nickel ions was determined with atomic adsorption spectrophotometry.

RESULTS AND DISCUSSION

The speed with which the solid phase adsorbs nickel ions from the solution and attains the equilibrium condition is of considerable importance. It was found that the time required to reach the equilibrium is 12 min. The percentage extraction of 10 ppm of nickel ion by immobilized cellulose was best found with 0.08 g of PSC and it was maintained throughout the study. Retention of metal ion on a column packed with immobilized cellulose was studied as a function of pH. For that pH of the solution nickel ions were adjusted to different pH values and passed at a rate of 2 mL/min through the column. The adsorbed nickel ions were eluted from the column with 0.1 N HNO₃ and determined by AAS. It was found that the maximum adsorption occurred in the pH range 6.5–7.2. For adsorption isotherms, the distribution coefficient *D*, calculated for nickel in mL/g, is found as 3.8×10^2 . Adsorption of metal ion is affected by temperature. The equilibrium constant of the complexation reaction has been found to decrease with the decrease in temperature. It has been observed that adsorption increases with increase in temperature up to 35°C and practically remains constant after that. The dependence of uptake nickel ions on the flow rate was studied at pH 6.5 where maximum adsorption took place. The flow rate varied from 1 to 5 mL/min, and 2 mL/min was found to be the most suitable. In order to investigate preconcentration and recovery results, column method was employed. When the volume of eluent was kept 20 mL the percentage recovery was found in the range 98–99%.

The effect of various electrolytes such as sodium chloride, potassium nitrate and potassium chloride on the adsorption of nickel ions on modified cellulose was investigated. Electrolytes had no effect on the adsorption of metal ion by the immobilized cellulose.

Determination of nickel in steel solution

Steel (0.2 g) was taken in a 250 mL calibrated flask; water (10 mL) and conc. H_2SO_4 (4 mL) was then added to it. This solution was then boiled with 2.5 mL nitric acid. Any solid that appeared at this point redissolved in the next step. The flask was cooled and then 5 mL conc. H_2SO_4 , 5 mL 85% phosphoric acid, 2 mL 0.1 M silver nitrate and 60 mL H_2SO_4 were added in this order. Following this, 5 g of potassium persulphate was added. This solution was swirled until most of the salt dissolved. This solution was again boiled for 5 min, cooled and then 0.5 g potassium periodate was added. Again this solution was boiled and cooled to room temperature and diluted to 250 mL. Nickel solution then passed through the column filled with immobilized cellulose. Nickel ion was eluted from the column using 0.01 N HCl. The amount of nickel ion was then determined by atomic adsorption spectrophotometry (Table-1).

TABLE -1
ANALYSIS OF NICKEL IN STEEL

Name of sample	Certified value (%)	Observed value (%)	RSD (%)
JSS 503-4 (Ni-Cr Steel)	1.24	1.19	1.07
JSS 645-7 (Stainless steel)	20.33	20.25	1.18
JSS 655-4 (Stainless steel)	11.48	11.35	1.31
NBS SRM 679 (Zinc alloy)	0.0075	0.0072	0.97

Each value is the mean of five simultaneous determinations.

Determination of nickel in partially hydrogenated vegetable oils

40 g of the sample oil was transferred into a 100 mL Erlenmeyer flask. It was digested several times with nitric acid and sulphuric acid. Most of the acid was evaporated and the rest was neutralized with 1% NaOH solution. Finally the total volume was made up with distilled water. The solution then passed through a column filled with immobilized cellulose. Nickel ion was eluted from the column using 0.01 N HCl. The amount of nickel ion was then determined by atomic adsorption spectrophotometry (Table-2).

TABLE-2
DETERMINATION OF NICKEL IN HYDROGENATED OIL

Sample	Ni added ($\mu\text{g/mL}$)	Ni determined ($\mu\text{g/mL}$)	% Recovery
A	—	0.38	—
	0.10	0.47	97.9
B	—	0.58	—
	0.10	0.67	98.5
C	—	0.28	—
	0.10	0.37	97.3

Each value is the mean of five simultaneous determinations.

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