Analysis of nickel by solid-liquid separation after liquid-liquid extraction.
—Spectrophotometric determination of nickel after extraction of its nioxime complex with molten naphthalene—

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Nioxime reacts with nickel to form a water-insoluble red complex. This complex is quantitatively extracted into molten naphthalene at temperature above 81 °C. The solidified mixture of the complex and naphthalene is dissolved in chloroform at 50 - 60 °C, and the small amounts of nickel in the solution are determined spectrophotometrically. The factors such as pH, amounts of nioxime and naphthalene are studied, and the molar absorptivity, sensitivity and relative standard deviation are evaluated . The extracted complex is stable in both naphthalene and naphthalene-chloroform solution. The extraction of this complex into molten naphthalene is rapidly completed by contact with molten naphthalene or by slight shaking. This complex is mostly insoluble in chloroform, benzene, etc., but soluble in molten naphthalene. The mixture of the complex and naphthalene is insoluble in dimethylformamide, dimethylsulfoxide, acetonitrile, dioxane, isoamylacetate, chlorobenzene, etc., at 50 - 60 °C.

1. Introduction

Nioxime(1,2-cyclohexanedionedioxime) forms water-insoluble complexes with nickel and palladium and is used for the detection and gravimetric determination of these metals. These complexes formed cannot be almost extracted into organic solvents such as chloroform, benzene, etc., but done easily into molten naphthalene at high temperature above 81 °C. After extraction, the solidified crystals of the complex and naphthalene are separated from the solution and dissolved in chloroform at 50 - 60 °C. By measuring the absorbance of the solution, the trace amounts of metals are determined from the calibration curve.

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In this paper, nioxime was recommended as a new analytical extraction reagent for the spectrophotometric determination of nickel with naphthalene. Compared with the chloroform extraction method, the present method is characterized by the higher extraction rate and the higher solubility of the complex into molten naphthalene.

2. Experimental result

2.1 Apparatus

A Hitachi Model 200-20 double beam spectrophotometer was used for the absorbance measurement with a 10 mm glass cell.

The measurements of pH were made with a Toa-Dempa pH meter equipped with combined calomel and glass electrodes, Model HM-5A.

2.2 Reagents

Satndard nickel solution, 10 ppm. Prepared by diluting standard nickel stock solution(1000 ppm) to 1000 ml with doubly distilled water.

Nioxime solution, 0.5 %. Prepared by dissolving 0.5 g of nioxime in 100 ml of ethanol.

Buffer solution. Prepared from 1M acetic acid and 1M ammonium acetate solution, or 1M ammonia water and 1M ammonium acetate solution

All other solutions were prepared with analytical reagent grade chemicals by using doubly distilled water.

2.3 Procedure

To 30 ml of the sample solution containing 1-7 ml of 10 ppm standard nickel solution, in a 80 ml tightly stoppered Erlenmeyer flask, add 2.0 ml of acetic acid-ammonium acetate buffer solution and 1.5 ml of 0.5 % nioxime solution, and adjust the pH to about 4.6. Mix the solution well, and warm it on a steam-bath at around 90 °C. Add 2.0 g of naphthalene and warm the mixture in the steam-bath at 90 °C to melt naphthalene completely. Shake it vigorously till the naphthalene layer solidifies. Again warm and melt the very fine crystals slowly, and let them grow to give a coaser crystalline deposit. Collect the solidified deposit on a filter paper, wash with water, and blot the surplus water with a dry filter paper. Spread the crystals on a filter paper for air-drying. Then dissolve them with chloroform at 50-60 °C by vigorous shaking. After cooling, dilute to 10 ml. Dry the solution by addition of about 2 g of anhydrous sodium sulfate, transfer a portion into a 10 mm cell and measure its absorbance at 384 nm against a reagent blank prepared similarly. Calculate the amount of nickel from the calibration curve.

3. Result and discussion

3.1 Absorption spectra

According to the recommended procedure, nickel in the sample solution containing 50 μg of nickel and 1.5 ml of 0.5 % nioxime solution was extracted into molten naphthalene as nickel-nioxime complex at pH ca. 5.5. The extracted naphthalene mixture was dissolved in chloroform at 50 - 60 °C. The absorption spectra of the solution was measured at various wavelengths in the range of 340 to 500 nm. Fig.1 shows absorption spectra for the reagent and the nickel complex in naphthalene-chloroform solution, measured against water. The nickel complex has the absorbance maximum at 384 and 440 nm. The reagent blank shows strong absorption below 360 nm. Beyond this wavelength, there is practically a negligible absorption due to the reagent blank. Therefore, all the absorbance measurements were performed at 384 nm throughout this experiment.

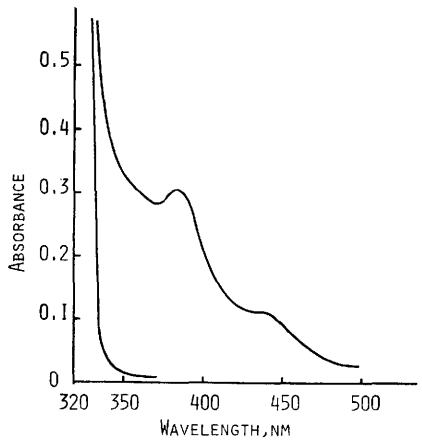

FIG. 1 ABSORPTION SPECTRA OF NIOXIME AND NICKEL COMPLEX IN NAPHTHALENE-CHLOROFORM SOLUTION
(1) 0.5 % NIOXIME : 1.5 ML ; PH : 4.6
(2) NI : 50 μG ; 0.5 % NIOXIME : 1.5 ML ; PH : 4.6
REFERENCE : WATER

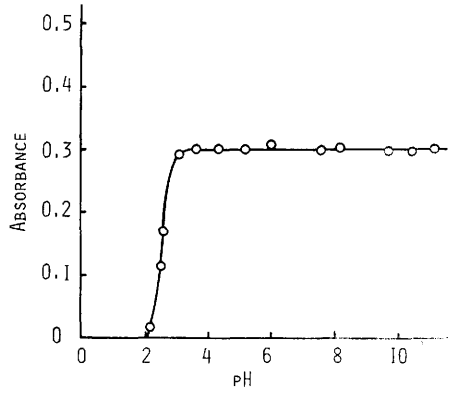

FIG. 2 EFFECT OF PH ON ABSORBANCE
NI : 50 μG ; 0.5 % NIOXIME : 1.5 ML ;
WAVELENGTH : 384 NM ; DIGESTION TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.2 Effect of pH on absorbance

The sample solution was prepared that contained 50 μg of nickel, 2.0 ml of the respective buffer solution and 1.5 ml of 0.5 % nioxime solution in total volume of approximately 34 ml. The extraction was carried according to the recommended procedure. The pH values of the solution after extraction were measured at room temperature. Fig.2 shows the effect of pH on the absorbance of the nickel complex in

naphthalene-chloroform solution. The extraction of the complex starts from pH 2.0, increases sharply with the increase of pH at pH 2.0 to 3.2, and becomes constant and maximum at pH 3.2 to 11.2. Therefore, The pH of the solution was adjusted to 4.6 throughout further experiment.

3.3 Effect of reagent concentration on absorbance

To the sample solution containing 50 μg of nickel and 2.0 ml of the acetate buffer solution(pH4.6) in total volume of approximately 32 ml, 0.01 - 5.0 ml of 0.5 % nioxime solution was added, and the extraction was carried out according to the recommended procedure. Fig. 3 shows the effect of addition of nioxime solution on the absorbance of the complex. From this, the absorbance increased with increasing amounts of nioxime up to 0.06 ml of 0.5 % nioxime solution, whereas addition of 0.06 - 5.0 ml of it gave definite absorbance. Therefore, 2.0 ml of 0.5 % nioxime solution were taken throughout this experiment.

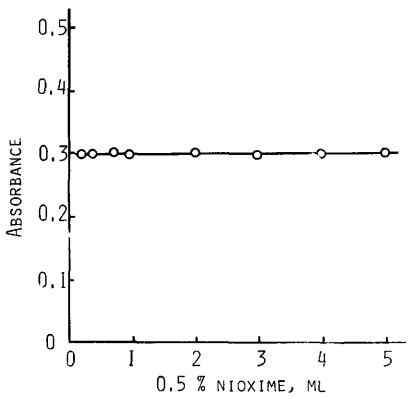

FIG. 3 EFFECT OF REAGENT CONCENTRATION ON ABSORBANCE
Ni : 50 μg ; WAVELENGTH : 384 nm ; pH : 4.6 ; DIGESTION TIME : 10 min ; STANDING TIME : 10 min
REFERENCE : REAGENT BLANK

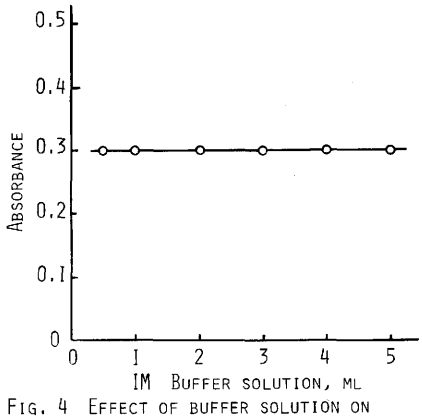

FIG. 4 EFFECT OF BUFFER SOLUTION ON ABSORBANCE
Ni : 50 μg ; WAVELENGTH : 384 nm ; pH :4.6 ; 0.5 % NIOXIME : 1.5 ml ; STANDING TIME : 10 min ; SOLVENT : CHLOROFORM(50 °C)
REFERENCE : REAGENT BLANK

3.4 Effect of buffer solution on absorbance

Fig. 4 shows the effect of addition of the acetate buffer solution (pH4.6) on the absorbance of complex. The addition of 0.5 - 5.0 ml of buffer solution gave no effect on the absorbance at 384 nm. Therefore, 2.0 ml of the buffer solution were taken throughout this experiment.

3.5 Effect of digestion time on absorbance

The nickel complex in the solution containing 50 μg of nickel was digested on a steam-bath at 90 °C, and the extraction was performed

according to the recommended procedure. Fig. 5 shows the effect of digestion time on the absorbance. From this, the formation of the complex was very fast owing to high temperature and the digestion was found to be unnecessary.

3.6 Effect of naphthalene on absorbance

The varying amounts of naphthalene were added to the solution containing 50 μg of nickel, 2.0 ml of the acetate buffer solution and 2.0 ml of 0.5 % nioxime solution and the extraction of the nickel complex was carried out according to the recommended procedure. Fig. 6 shows the effect of addition of naphthalene on the absorbance. The addition of 0.5 to 3.0 ml of naphthalene gave little effect on the absorbance. Therefore, 2.0 g of naphthalene were taken throughout this experiment.

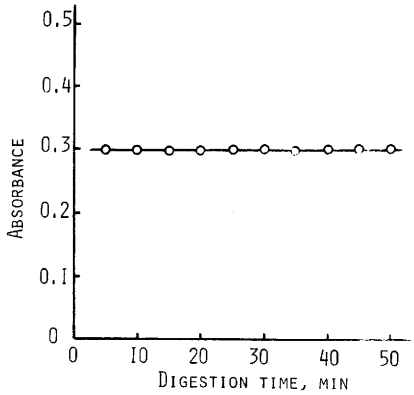

FIG. 5 EFFECT OF DIGESTION TIME ON ABSORBANCE
Ni : 50 μg ; 0.5 % NIOXIME : 1.5 ML ; pH : 4.6
BUFFER SOLUTION : 2.0 ML ; NAPHTHALENE : 2.0 G ; STANDING TIME : 10 ML
REFERENCE : REAGENT BLANK

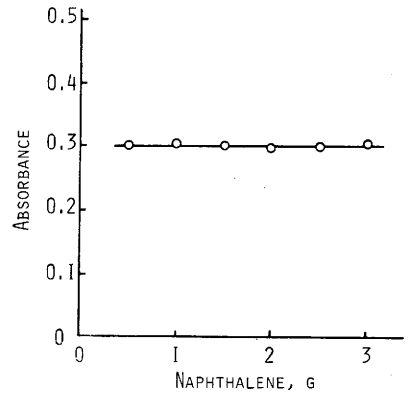

FIG. 6 EFFECT OF NAPHTHALENE ON ABSORBANCE
Ni : 50 μg ; WAVELENGTH : 384 nm ; pH : 4.6 ;
DIGESTION TIME : 10 MIN ; SOLVENT : CHLOROFORM
REFERENCE : REAGENT BLANK

3.7 Effect of standing time on absorbance

The mixture of the nickel complex and naphthalene was dissolved in chloroform at 50 - 60 °C,and the stability of color of the complex in naphthalene-chloroform solution was investigated. Fig. 7 shows the effect of the stability of color of the complex on the absorbance. The complex was very stable in both naphthalene and naphthalene-chloroform solution for a long time.

3.8 Calibration curve,sensitivity and reproducibility

Based on the optimum conditions obtained from the experimental results described above, the calibration curve for nickel determination

was established at the wavelength of 384 nm against the reagent blank. It was linear over the range of 8 - 70 μg of nickel in 10 ml of chloroform. The molar absorptivity was estimated to be 3.7×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$, the sensitivity 0.016 μg of nickel per cm^2 for the absorbance of 0.001. An average of ten determinations on 50 μg of nickel gave a mean absorbance of 0.309 with standard deviation of 1.25×10^{-3} (relative standard deviation, 0.58 %).

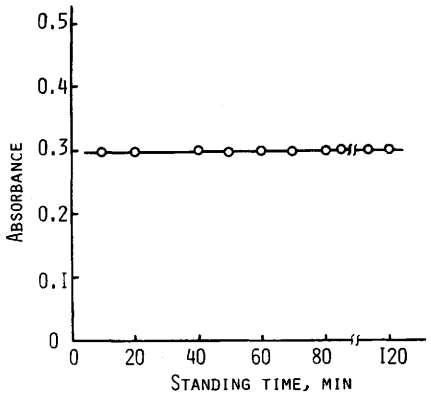

FIG. 7 EFFECT OF STANDING TIME ON ABSORBANCE
Ni : 50 μg ; 0.5 % NIOXIME : 1.5 ML ;
WAVELENGTH : 384 NM ; DIGESTION TIME :
10 MIN ; NAPHTHALENE : 2.0 G
REFERENCE : REAGENT BLANK

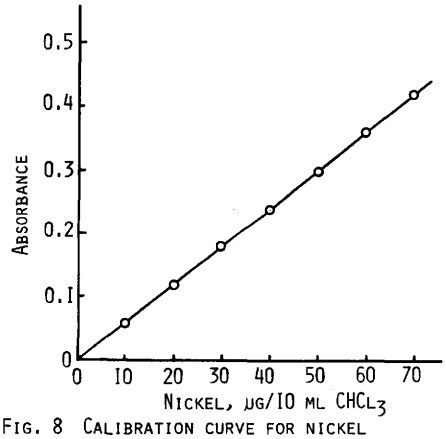

FIG. 8 CALIBRATION CURVE FOR NICKEL
WAVELENGTH : 384 NM ; 0.5 % NIOXIME : 1.5 ML ;
pH : 4.6 ; BUFFER SOLUTION : 2.0 ML ; DIGESTION
TIME : 10 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.9 Choice of solvent

An examination was made of various solvents to dissolve the mixture of the nickel complex and naphthalene. as a result, chloroform was found to be a suitable solvent for this complex containing up to 50 μg of nickel at room temperature and 70 μg at 50 - 60 °C. However, this complex is insoluble in most organic solvents such as benzene, dioxane, dimethylformamide, dimethylsulfoxide, acetonitrile, chlorobenzene, etc. at 50 - 60 °C.