

The Determination of Traces of Nickel(II) by Solid State Spectroscopy

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Traces of nickel(II) are determined by measurement of light absorption in the solid state after co-precipitation with a large excess of α -benzildioxime. The detection limit is $0.2 \mu\text{g}$ Ni and nickel can be recovered even from 1000 ml sample volumes (*i.e.* $<1 \text{ ng/ml}$ can be determined). Only a few foreign ions interfere.

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On détermine des traces de nickel(II) par mesure d'absorption de la lumière à l'état solide après co-précipitation avec un grand excès d' α -benzildioxime. La limite de la détection est de $0.2 \mu\text{g}$ de nickel et on peut même récupérer le métal à partir d'échantillons ayant des volumes de 1000 ml (*i.e.* on peut déterminer des quantités $<1 \text{ ng/ml}$). Seulement quelques ions étrangers interfèrent dans cette analyse.
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Introduction

In recent communications, methods have been described for the determination of trace metal ions by solid state fluorescence after preconcentration by co-precipitation. Two major principles were used: (1) co-precipitation with an inorganic carrier and subsequent activation by ignition to produce a phosphor (1-3); (2) co-precipitation of a fluorescent chelate with a large excess of a non-fluorescent, water insoluble chelating agent (4, 5).

While these methods exhibit a high sensitivity, because of the preconcentration effect, they often suffer from interferences. Since color-forming methods in solution are not usually subject to interferences to such a degree as fluorimetric methods, the potential of spectrophotometry in the solid state, based on chelate formation, was studied.

The basic requirements for a suitable chelating agent can be summarized as follows: (a) react to form a color with the metal ion of interest, (b) be selective, (c) have a low solubility

in water so that the method would be essentially independent of the sample volume, (d) have appreciable solubility in some organic, water miscible solvent.

One of the very selective color and, at the same time, precipitation reactions is that of α -dioximes with nickel(II). Among various dioximes α -benzildioxime shows a very low water solubility, dissolves readily in dimethylsulfoxide, and can be easily synthesized. The present paper describes the determination of nickel(II) at ng/ml levels using co-precipitation of the nickel chelate with α -benzildioxime and subsequent measurement of the light absorption of the precipitate.

Experimental

Apparatus and Reagents

All spectrophotometric measurements were made with a Farrand VIS-UV Chromatogram Analyzer or with a Zeiss Chromatogram Spectrophotometer. The sample cell was an aluminum sheet painted white with drilled holes (diameter 5 mm) and covered with a glass plate. It was packed with a sample powder which was held in place by masking tape; the glass was removed prior to measurement.

A stock solution containing 1000 $\mu\text{g/ml}$ of nickel(II) was prepared from nickel(II) chloride hexahydrate (BDH) and was standardized by EDTA titration using xylenol orange (6). The α -benzildioxime was synthesized according to the procedure given in the monograph by Diehl (7). Benzil (BDH) (40 g) was dissolved in 200 ml of hot methanol; 32 g of hydroxylamine hydrochloride (Baker) were added and the reaction mixture was boiled and stirred for 3 h. After cooling, the precipitate of dioxime was filtered off with suction, washed with hot water and then with 50% ethanol; 12 g of white, crystalline product were obtained after drying. It was used without further purification. The reagent solution was 1% (w/v) in dimethylsulfoxide (Fisher, Certified A.C.S.).

The buffer solution ($\text{pH} \sim 10$) was prepared by mixing 70 g of ammonium chloride with 570 ml of concentrated ammonia and diluting to 1 l with water.

The ammonium tartrate (Baker & Adamson) solution was 1 M.

Procedure

To 100 ml of solution containing 0.2–10.0 μg of nickel add 3 ml of ammonia buffer ($\text{pH} \sim 10$)¹, 1 ml of 1 M ammonium tartrate and, finally, 3 ml of the reagent solution with rapid stirring. Filter the precipitate through a filter crucible, wash with distilled water and dry in a vacuum desiccator for 1 h. Pack the cell (grinding of the powder causes electrostatic charge and thus packing difficulties) and measure the light absorption. Settings of the Farrand instrument: function SIG (single beam), λ , 435 nm (on both monochromators), excitation filter removed, filter 3–73, screen mesh reducer 0.625 and aperture 0.021 in the analyzer leg, range 1.0 (if measurement at 570 nm is desired use aperture 0.062).

Results and Discussion

The reflectance spectrum of the nickel chelate in the solid state (obtained with the Zeiss instrument) exhibits two absorption maxima at 435 and 570 nm, absorption at 435 nm being stronger and thus recommended for measurement. This is in agreement with the spectrum obtained in solution of the nickel chelate in amyl-alcohol.

Typical calibration curves are shown in Fig. 1 (two different runs); A, 0.2–2 μg Ni, B, 1–10 μg Ni. They do not pass through the origin because the plate background was selected as the base line (zero absorption). The relative standard deviation of six determinations of 2 μg Ni/100 ml (20 ng/ml) is $\sim 7\%$.

Factors Affecting the Method

It is necessary to have the reagent solution as concentrated as possible so that the minimum amount of solvent is introduced, together with the reagent, into the sample solution. The solu-

¹If the buffer is insufficient, due to the original acidity of the sample solution, adjust pH to ~ 10 by addition of 1:1 ammonia.

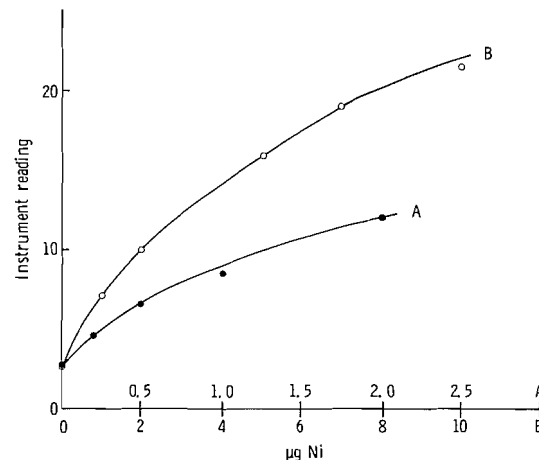


FIG. 1. Calibration curves for nickel. A, 0.2–2.0 μg ; B, 1.0–10.0 μg .

bility of the resulting precipitate is thus kept low and dependence on the sample volume is minimized. Dimethylsulfoxide has been selected as a solvent since at least a 1% solution of the reagent could be prepared. Three ml of this solution added to 100 ml of water are sufficient to produce enough precipitate (~ 30 mg) to fill a hole in the measuring cell.

While at $\text{pH} \sim 5$ there is virtually no difference in absorption between the precipitates separated from solution containing nickel- and respective blank, the absorption of the precipitates from nickel containing solutions increases sharply with increasing pH up to ~ 8 , and then remains essentially unchanged up to $\text{pH} \sim 10$. For better masking, $\text{pH} \sim 10$ was selected for further work.

There is no appreciable dependence of light absorption or quality of the precipitate upon the rate of addition of the reagent solution. Essentially the same readings are obtained for precipitates filtered immediately after their precipitation and those allowed to stand for various periods of time (up to 1 h) before filtration.

The light absorption of the powder increases with increasing sample volume (containing 2 μg Ni) from 10 to 100 ml and remains virtually constant with further increase of volume up to 1 l. This fact makes it possible to increase the sensitivity of the method by an order of magnitude if a large volume of sample is available. Lower readings for sample volumes under 100 ml can be attributed to the increased solubility of the precipitate (due to the higher concentration

of organic solvent) and thus lower effectiveness of co-precipitation of the nickel chelate.

When the precipitation is performed at elevated temperatures progressively lower readings are obtained. Precipitation at the room temperature is, therefore, recommended.

The presence of 1 mmol of ammonium tartrate in the solution does not have an appreciable effect on the calibration curve. Tartrate is, therefore, included in the procedure to mask some metal ions which would otherwise precipitate in basic medium, particularly iron(III).

The method is independent of many variables: pH (within 8–10), volume (100–1000 ml), rate of reagent addition, time of standing before filtration (up to 1 h at least), presence of a large amount of tartrate.

It has been observed that the precipitates become paler in color upon drying. If the light absorption is measured while still wet a stronger signal is obtained making possible the determination of even 0.1 $\mu\text{g Ni}/100\text{ ml}$; however the uncertainty in water content, especially during the measurement in the instrument, results in poorer reproducibility.

At least a 1000-fold weight excess of the following ions is without interference in the determination of 2 $\mu\text{g Ni}$ in 100 ml of water: aluminum(III), bismuth(III), cadmium(II), calcium(II), iron(III), lead(II), magnesium(II), manganese(II), mercury(II), palladium(II), potassium(I), silver(I), sodium(I), tin(IV), zinc(II), acetate, borate, bromide, citrate, fluoride, iodide, nitrate, perchlorate, phosphate, sulfate, sulfide, and thiocyanate. A 50-fold excess of cobalt(II) and a 10-fold excess of chromium(III), copper(II), iron(II), and EDTA are also without interference. Cyanide can be tolerated only at a 1:1 ratio.

Iron(III) does not interfere even at 10 000-fold

excess (20 mg Fe) provided 2 mmol of tartrate are present and the pH is adjusted to ~ 10 with ammonia. For still higher amounts of iron(III), the higher concentration of tartrate necessary to keep iron in solution results in a decrease of the signal.

Since the detection limit of the method is 0.2 $\mu\text{g Ni}$, it should be possible to determine 0.2 $\mu\text{g Ni}$ in 20 mg iron. For example, the method was applied to the determination of nickel in a sample of mild steel (British Chemical Standards, #324). After dissolution of the sample in diluted hydrochloric and nitric acids, tartrate was added and the solution was neutralized with concentrated ammonia. Aliquots were taken and, after dilution, the regular precipitation procedure was performed. The average nickel content given was 0.050%, found 0.049%; the results demonstrate the potential of the method in a relatively complex matrix.

The simplicity, sensitivity, and reproducibility of the method should lead to many applications for the determination of very small amounts of nickel.

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