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THE NICKEL(II)-DIMETHYLGLYOXIME COMPLEX: A NEW USE FOR AN OLD COMPOUND

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ABSTRACT: The nickel(II)-dimethylglyoxime complex can be used to standardize EDTA solutions. The conditions required for the preparation and purification of the complex are described in this paper. In addition, the results of quantitative experiments using the complex are compared with those obtained using more conventional methods of EDTA standardization. The method described is quick, economical, and easy to incorporate into an undergraduate analytical chemistry laboratory.

INTRODUCTION

Nickel is an element of interest, especially in undergraduate inorganic chemistry courses, where it is used in demonstrations of both qualitative and quantitative analysis. The strawberry-colored nickel(II)-dimethylglyoxime complex is used to demonstrate a selective reaction, precipitation from a homogeneous solution, solubility equilibria, and so on.

The nickel-dimethylglyoxime complex, with the formula $NiC_8H_{14}N_4O_4$, continues to be used for the gravimetric determination of nickel. The complex precipitates from a mildly alkaline solution and is very insoluble in water. To be a satisfactory material for use in gravimetric determinations, a precipitate must have the following properties:

1. It must be insoluble in the medium from which it is ultimately to be precipitated;
2. It must be resistant to air oxidation;
3. It must be heat stable to temperatures of 120° C;
4. It must be easily filterable after precipitation;
5. Its final form must be one of constant stoichiometry; and
6. It must be produced in a highly pure form.

Occasionally, some compromises are made in the above specifications: solubility (e.g., potassium perchlorate) and drying (e.g., calcium oxalate monohydrate). However, most common gravimetric materials encountered possess these six properties.

The nickel-dimethylglyoxime complex is such a material, and it can be used as a primary standard against which EDTA solutions may be standardized. This paper explores some possibilities with regard to using the complex as a standard material and outlines the experimental details of doing so.

MATERIALS AND METHODS

Preparation of the Nickel-Dimethylglyoxime Complex. Nickel sulfate hexahydrate (4.0 g) was dissolved in 150 mL of distilled water at about 50° C in a 400-mL beaker. Dimethylglyoxime solution (10% w/v in 50:50 methanol-isopropanol solvent) was added in sufficient quantity to ensure complete precipitation, when the solution was made alka-

Table 1. Results of the microanalysis of the nickel-dimethylglyoxime complex.

Element	Expected %	Found %
C	33.26	33.28
H	4.88	4.88
N	19.39	19.41
Ni	20.32	20.30

line (pH 9 to 10) with aqueous ammonia. The solution was stirred well and kept at 50° C to 60° C for about one hour to aid precipitation. The resulting mixture was then filtered through fluted filter paper, washed several times with distilled water, and dried in an oven at 150° C for two to three hours. The elevated temperature ensured that any free dimethylglyoxime was removed by volatilization. Prior to use, the complex was dried for one hour at 120° C, after which the complex was stored in a brown glass, screw-capped bottle. The results of microanalysis for carbon, hydrogen, nitrogen, and nickel are given in Table 1.

Solubility Testing. This testing was performed with the objective of producing a solution which could be buffered appropriately for titration. Several solvents were tested: cyanide solutions worked well but seemed unnecessarily toxic, while strongly alkaline solutions were difficult to buffer effectively. Mineral acid was the most effective solvent. However, nitric acid could not be used, because traces of nitrate apparently oxidize the titration indicator, resulting in poor titration end-points.

The following procedure was finally settled upon. Dry the complex in an oven for one hour at 120° C, allow the complex to cool, and then accurately weigh about 1.7 g into a 400-mL beaker. Add 100 mL of distilled water, and heat to boiling. Place a medium sized glass powder funnel into the mouth of the beaker to reduce spattering, and then introduce, dropwise, concentrated sulfuric acid until the solid material just dissolves (3 mL or less). Quantitatively transfer this solution to a 250-mL volumetric flask, and dilute to the mark with distilled water. This solution was found to be stable for at least 24 hours, although a slight haze was noticed with some solutions. After longer periods of time, white, needle-like crystals may precipitate. The crystals were found to be dimethylglyoxime (based on IR spectrum and melting point data).

Performing the Titration. Place about 10 mL of the nickel solution (graduated cylinder) into a small beaker. Add 1N sodium hydroxide solution dropwise until the solution pH reaches 3, as indicated with pH paper. Count the number of drops used. **THE SOLUTION MUST BE MIXED CAREFULLY TO AVOID LOCALIZED HIGH pH.**

Pipette 25 mL of the nickel solution into a 250 mL Ehrlenmeyer flask, add, with mixing, 2.5 times as many drops of 1N sodium hydroxide solution as were added to the 10 mL nickel solution sample. Then, add 15 mL of acetic acid (5M)/sodium acetate (anhydrous, 11.3 g/L) buffer to adjust the pH to about 3.5. Add four drops of copper(II)/EDTA solution (mix equal volumes of 0.1M solutions of EDTA and copper(II) sulfate) and enough PAN indicator (0.1 g in 100 mL of ethanol) to produce a rose/violet color (Flaschka and Abdine, 1956). Heat the mixture to boiling, and titrate with approximately 0.1M EDTA solution to a yellow-with-green tint end-point. This end-point requires a little practice to identify correctly. The color sequence prior to the endpoint is: rose/violet to true violet to a grayish intermediate color with a slower reaction time towards end-point to a greenish/

Table 2. Titration results (EDTA molarity). In each case, fifteen determinations were made.

	Nitric Acid Digest	Sulfuric Acid Preparation
	0.05744	0.05746
	0.05744	0.05745
	0.05748	0.05745
	0.05751	0.05747
Average	0.05748 ± 0.00004	0.05747 ± 0.00004

yellow end-point. As the end-point is approached, the titrant must be added slowly. The process can be speeded up considerably after the first titration by adding most of the titrant at the beginning, returning the solution to boiling, and completing the titration dropwise.

RESULTS AND CONCLUSIONS

The results of several titrations of the EDTA into nickel solutions prepared using two different methods are given in Table 2. The method of dissolving the nickel-dimethylglyoxime complex in a sulfuric acid medium is compared with the more conventional method of dissolving it in concentrated nitric acid. The results (Table 2), representing only a few of those actually obtained while testing the titration, exemplify the quality of the preparation method. A statistical comparison of the two sets of results showed that they are identical, and further titration data using solutions prepared independently from highly purified nickel foil also agreed with those in Table 2.

No major difference between the two sets of results was found that would set them apart from one another, except for the time taken for solution preparation. The sulfuric acid preparation takes approximately 20 minutes, while the nitric acid digest takes about 80 minutes. What is clear, however, is that the nickel(II)-dimethylglyoxime complex can be used as a standard material. It is stable and easily stored and dried, it exists in a weighable form, and it is produced in a pure form during the course of a classical gravimetric analysis for nickel. At the very least, it could be used as the basis of an exercise in quantitative analysis.

LITERATURE CITED

Flaschka, H. and H. Abdine. 1956. EDTA titrations using copper-PAN complex as indicator. Chemist-Analyst 45(3): 58-61.