

GRAVIMETRIC DETERMINATION OF NICKEL WITH CYCLOHEXYLIDINE-AMMONIUM-2-AMINOCYCLOHEXYLIDINE-1-CYCLOHEXENE-1-DITHIOCARBOXYLATE

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Abstract

Cyclohexylidene-ammonium-2-aminocyclohexylidene-1-cyclohexene-1-dithiocarboxylate (CCCD) is employed for the gravimetric determination of Ni (II). In neutral or ammoniacal solutions, the metal forms a violet precipitate with the reagent which can be weighed as $\text{Ni}(\text{C}_{13}\text{H}_{18}\text{NS}_2)_2$ after drying at $115 - 120^\circ\text{C}$. Using this procedure, the nickel content of steel samples can also be determined accurately. The purity of the precipitate and complete removal of interferences are confirmed by differential pulse polarography.

Introduction

Cyclohexylidene-ammonium-2-aminocyclohexylidene-1-cyclohexene-1-dithiocarboxylate (CCCD) was first prepared by Takeshima et al. [1]. This ligand forms an intense violet complex with nickel which is insoluble in water. This instantaneous intensive colour formation upon addition of the ligand to nickel (II) solutions permits determination of trace amounts of nickel by spectrophotometric methods [2]. In this paper, we take advantage of the insolubility of the complex in aqueous media which forms the basis of developing an accurate gravimetric method for the determination of nickel. Nickel in steel samples can also be measured by the proposed method.

Results and Discussion

The errors of the method were in the range of $\pm 0.02 - 0.36\%$ (20 - 6 mg). For smaller samples (less than 6 mg) errors up to 0.7% were observed.

The complex is soluble in mineral acids and in acetic or ethanolic solutions containing more than 60% ethanol or acetone by volume. Hence a large excess of the reagent solution should be avoided to prevent any solvation of the complex. The precipitation is generally affected by the addition of the reagent to a warm, weakly acidic nickel solution and then bringing the pH of the solution to 8.5 - 9.5 by adding ammonia. In this way a more easily filtered precipitate is obtained. Filtration is usually rapid and efficient, despite the tendency of the precipitate to creep up the wall of the crucible. The precipitate is usually dried at $115 - 120^\circ\text{C}$ for about 1.5 h, but it remains unchanged in composition up to 170°C .

Nickel is determined as above, without interferences in the presence of known amounts of Fe^{2+} , Fe^{3+} , Al^{3+} , Cr^{3+} , Zn^{2+} , Ca^{2+} , Mg^{2+} , K^+ , citrate, tartarate, CO_3^{2-} , NO_3^- , I^- , Cl^- and SO_4^{2-} (Table 1). However, Cu^{2+} , CO^{2+} , Ag^+ , Hg^{2+} , Pd^{2+} , Cd^{2+} and PO_4^{3-} do interfere.

The interference of copper (II) can be conveniently removed by the addition of thioacetamide in the presence of acetic acid-acetate buffer (pH = 5) and precipitation of CuS prior to the addition of the reagent. The interference from cobalt (II) can be removed by its precipitation with 1-nitroso-2-naphthol before addition of the reagent. Ag^+ and Hg^{2+} interferences are removed by their precipitation with ammonium thiocyanate.

The purity of the precipitate and the complete removal of copper and cobalt interferences were confirmed by differential pulse polarography. For this purpose after applying the procedure for removal of Cu^{2+} and Co^{2+} , 0.01g of $\text{Ni}(\text{CCCD})_2$ precipitate was dissolved in 20ml of 6M HCl and 10ml acetone. The solution was then diluted to 100 ml with distilled deionized water. 3ml of this solution was added to 18.5 ml of 0.5M $\text{NH}_3\text{-NH}_4\text{Cl}$ in a polarographic cell. The solution was deaerated for 10 minutes with pure nitrogen and the polarogram was recorded (Fig. 1.). Only one peak was obtained due to the presence of nickel and none due to traces of Cu^{2+} (at -0.4V) or Co^{2+} (at -1.3V) were observed. This shows that the recommended procedures for the removal of copper and cobalt were successful in removing all Cu^{2+} and Co^{2+} originally presented (15 mg of each ion was present initially).

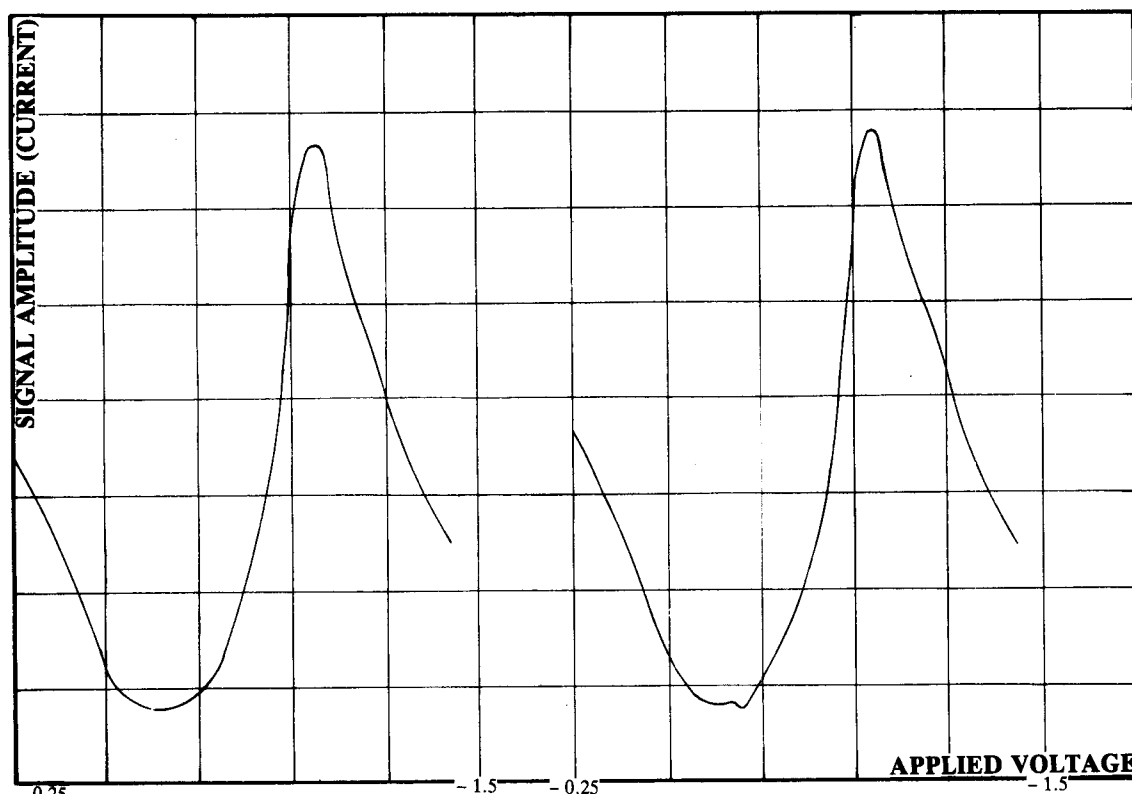


Fig. 1. Differential pulse polarogram of Ni (CCCD)₂ complex after removal of Cu & CO interferences. Voltage range -0.25 to -1.5V, pulse amplitude 25 mv, drop time 0.5 sec.

Conclusion

In the alkaline solutions, the violet insoluble Ni (C₁₃H₁₈NS₂)₂ can be used to determine as little as 6 mg of nickel accurately. The advantage of the proposed method over Ni-dimethylglyoxime precipitation is its much more favourable gravimetric factor (0.104 compared to 0.203 for Ni-DMG) and ease of formation. Moreover, the precipitation procedure is free from interferences. Because the precipitate is so bulky, only small amounts of nickel can be handled conveniently.

Experimental Section

Reagents

CCCD: Prepared and recrystallized by the procedure of Takeshima et al. [2]

1% solution of this reagent in ethanol was used.

The solutions used for the removal of some of the interferences were 1% (1-nitroso-2-naphtol) in ethanol. 1M thioacetamid and acetic acid buffer (pH = 5) was used. All other reagents were prepared from analytical-grade chemicals.

Apparatus: An electrochemistry system model 170, (PAR) was used.

Recommended Procedure. Weigh accurately 0.1g of nickel nitrate (Ni (NO₃)₂·6H₂O). Dissolve it in water, add a few

drops of 6M hydrochloric acid and dilute the solution to approx. 300ml with water. Heat the solution to 50 – 60 °C

Foreign ion added (mg)	mg Ni taken	mg Ni obtained	Error mg	% Relative Error
S ₂ O ₄ ²⁻ (200)	7.373	7.350	- 0.023	0.31%
Cl ⁻ (303)	5.979	5.999	+ 0.020	0.33%
I ⁻ (400)	6.000	5.990	- 0.010	0.16%
NO ₃ ⁻ (1000)	6.000	5.980	- 0.020	0.33%
CO ₃ ²⁻ (150)	5.478	5.510	+ 0.032	0.58%
tartarate (200)	8.441	8.411	- 0.030	0.36%
citrate (100)	10.096	10.069	- 0.027	0.27%
Na ⁺ (200)	5.970	5.990	+ 0.020	0.33%
K ⁺ (120)	6.000	5.990	- 0.010	0.16%
Mg ²⁺ (200)	6.200	6.18	- 0.020	0.32%
Ca ²⁺ (100)	6.000	5.988	- 0.012	0.2%
Al ³⁺ (100) ^a	9.434	9.406	- 0.028	0.3%
Cr ³⁺ (50) ^a	6.000	5.978	- 0.022	0.36%
Zn ²⁺ (50) ^a	9.430	9.399	- 0.031	0.33%
Fe ²⁺ (15) ^b	14.540	14.510	- 0.030	0.2%
Co ²⁺ (15) ^b	14.810	14.800	- 0.010	0.06%
Cu ²⁺ (15) ^b	12.253	12.233	- 0.020	0.16%
Fe ²⁺ , Co ²⁺ , ^b				
Cu ²⁺ (15 mg each)	14.130	14.160	+ 0.03	0.2%

a) Working pH = 6 – 7

b) After removal of interferences using the suggested method.

Table 1: Effect of foreign ions on gravimetric determination of nickel

and then add about 15ml of 1% solution of reagent in ethanol for every 10 mg of nickel present, followed by the dropwise addition of diluted ammonia to adjust the pH to 8.5 - 9.5. Allow the solution to stand for 30 min. Test the supernatant solution for complete precipitation by adding more reagent. Digest on a hot water bath for 1hr. Cool the solution to room temperature. Allow to stand for another 30 min. Filter the precipitate on a M.size sintered glass crucible. Wash the precipitate with cold distilled water until free from chloride. Dry the precipitate at 115 - 120°C and weigh as $\text{Ni}(\text{C}_{13}\text{H}_{18}\text{NS}_2)_2$.

For determination of the nickel content of steel

samples, weigh individual samples containing between 20 - 30 mg of nickel. Dissolve in 20 ml 6F nitric acid. Boil the solution to expel oxides of nitrogen. Add 10 - 15 ml of 20% tartaric acid to prevent interferences from iron. Heat the solution to 50 - 60°, and proceed as above.

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References

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