

Spectrophotometric Determination of Nickel with Chlorophosphonazo-III

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Abstract: The optimum conditions for spectrophotometric method for the determination of Ni²⁺ with chlorophosphonazo-III (CPA-III) were established and the nickel content in water samples has been successfully determined. In a pH 5.5 acetic acid-sodium acetate buffer medium, CPA-III and Ni²⁺ formed a 1:3 green blue complex and the maximum absorption wavelength of the complex is at 620 nm. Ni²⁺ content in a range of 0.1~3.5 µg/mL and absorbance shows a good linear relationship. The apparent molar absorption coefficient of method is $\epsilon_{620\text{nm}} = 1.40 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and the detection limit is 0.075 µg/mL.

Keywords: Nickel, Chlorophosphonazo-III, Spectrophotometry, Water sample

Introduction

Nickel is one of the most common sensitizing metals and about 20% of the people are allergic to nickel ion. In contact with the human body, nickel ion can penetrate inside the skin by pores and sebaceous glands, thus causes skin allergic inflammation and its clinical manifestations are dermatitis and eczema. The clinical manifestations of nickel allergic dermatitis are itching papular, papular or papulovesicular dermatitis, accompanying moss. Similar with other elements, nickel is regulated and controlled by the internal balance mechanism of body. Intake amount is too low, which will result in element deficiency symptom. Nickel is a trace element essential to the human body and it can make the increase of insulin and the blood glucose decrease. However, excessive intake will accumulate in the organism and acute, chronic poisoning appears and even the excessive nickel can become a potential carcinogen¹. Humans can absorb nickel through drinking water way *etc.* Therefore, development of an analytical method for the determination of nickel has a very important practical value.

Some methods for the determination of nickel have been proposed, which involved atomic absorption spectrometry², inductively coupled plasma-atomic emission spectrometry³

X-ray fluorescence spectrometry⁴, inductively coupled plasma-mass spectrometry⁵, *etc.* However, for these methods the instruments are expensive and the analysis costs are high. Spectrophotometry has the characteristic that instrument is cheaper, operation is simple and convenient and is a determination method of higher practical value. Chlorophosphonazo-III (abbreviated as: CPA-III), has been ever used as rare earths⁶, magnesium⁷ chromogenic agent. To the best of our knowledge, no study report on chromogenic reaction of the reagent and nickel(II) is seen. In this paper, color reaction of the reagent with nickel(II) was studied and successfully applied to the determination of nickel in water samples.

Experimental

Absorbance was measured on a 722S spectrophotometer (Shanghai Lenggunag Technique Co., Ltd., China) with 1 cm cells. The stock standard solution of nickel, 1 mg/mL, was prepared by dissolving 0.4784 g of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (Beijing Chemical Works, China) in an appropriate amount of water containing 2 mL of $\text{H}_2\text{SO}_4(1+1, \text{V/V})$ (Beijing Chemical Works, China) and then diluted to 100 mL with water. A 10 $\mu\text{g/mL}$ of working solution of nickel(II) was prepared by diluting the stock solution with water. Chlorophosphonazo-III (CPA-III, Shanghai Changke Research Institute of Reagent, China) solution, 1 g/L, was used. Buffer solution ($\text{pH} = 5.5$) was prepared by mixing 0.1 mol/L acetic acid (Beijing Chemical Works, China) and 0.1 mol/L sodium acetate (Beijing Chemical Works, China) according to the volume ratio of 1:20. Unless otherwise stated, all reagents used in the experiment were of analytical-reagent grade and the water was distilled.

General procedure

In a 10 mL calibrated flask, 20 μg Ni(II) working solution, 1.5 mL of chlorophosphonazo-III solution, 2.0 mL of buffer solution were added and diluted to the mark with water. After standing for 5 min, the absorbance was measured at 620 nm in a 1 cm cell against a reagent prepared in the same way but without Ni(II).

Results and Discussion

Absorption spectra

Chlorophosphonazo-III presents violet in $\text{pH} = 5.5$ HAc-NaAc medium, while it can form a green blue complex with nickel(II) under the condition. The maximum absorption wavelength of the complex against reagent blank is at 620 nm (Figure 1), while that of the reagent blank against water is at 550 nm. In this study, 620 nm was used as the determination wavelength in order to obtain maximum sensitivity.

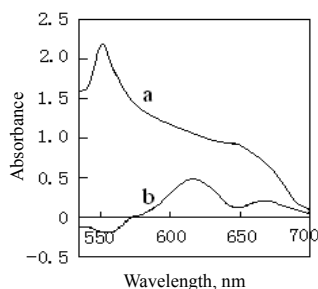


Figure 1. Absorption spectra: (a) Reagent blank (against water); (b) complex (against reagent blank); $[\text{Ni}^{2+}] = 3.4 \times 10^{-5} \text{ mol/L}$; $\text{pH} = 5.5$

Optimization of experimental variables

The results of acidity effect showed that a maximum and constant absorbance could be obtained over the pH 5.0-6.5. Thus, pH 5.5 was selected. In 10 mL of solution, 1.8-2.2 mL HAc-NaAc buffer solution gave a constant and maximum absorbance, therefore 2.0 mL is recommended.

With the addition of 1.0-2.0 mL of 1 g/L chlorophosphonazo-III solution, absorbance was maximum and the sensitivity was the highest. So determinations were carried out with 1.5 mL of chlorophosphonazo-III solution.

The experimental results displayed that the order of reagent addition had no effect on the absorbance of this system. This study used the order of Ni(II) + CPA-III + HAc-NaAc buffer solution.

Complex composition ratio and stability

By means of molar-ratio method and equimolar continuous variation method, the composition of the complex was determined to obtain the composition ratio of the complex as (CPA-III): Ni(II) = 3:1. At room temperature, the color reaction was immediately completed. When 2.0 µg/mL Ni(II) was determined, within 2 h the absorbance variation was less than 5% and the complex remain stable.

Working curve

At the maximum absorption wavelength of 620 nm, Ni²⁺ content in the range of 0.1~3.5 µg/mL and the absorbance A showed a good linear relationship and its linear regression equation is $A = 0.1647 C \text{ (g/mL)} + 0.0073$ with a correlation coefficient of 0.9993. The apparent molar absorption coefficient of method was $\epsilon_{620 \text{ nm}} = 1.40 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. According to the general procedure 11 parallel determinations of 2.00 µg/mL of Ni(III) were made and the average value determined was 2.03 µg/mL. The relative standard deviation of the determined results was 1.2%. For 11 determinations of reagent blank, based on $\rho = 3S / K$ (S is the standard deviation of eleven parallel determinations of reagent blank, K is the slope of working curve), the detection limit of the method was calculated to be 0.075 µg/mL.

Selectivity of method

An extensive study was made of the effect of foreign ions in the determination of 2.0 µg/mL Ni(II) under the optimum experimental conditions. The tolerance (5% error maximum) to foreign ions is as follows (W/W) : F⁻, Cl⁻, Br⁻, CH₃COO⁻, SiO₄²⁻, SO₄²⁻, PO₄³⁻ (100), B(III), I⁻ (50), Ag⁺, Cd²⁺ (15); Mg²⁺ (4), Cu²⁺, Al³⁺, Fe³⁺, Y³⁺, Zr⁴⁺ (0.5); Ce(IV), Mo(VI) (0.4); Cr(VI) (0.3); Fe²⁺, Zn²⁺, W(VI) (0.2); Ti(IV) (0.1); Co²⁺, Mn²⁺, MnO₄⁻ (0.05); Ca²⁺, Sr²⁺, Ba²⁺, La³⁺, Y³⁺ (0.02).

Sample analysis

500 mL of rain water was taken and heated for concentration to about 50 mL. After cooling, 5 mL of aqua regia was added to it. The contents were evaporated on an electric cooker to near dryness, dissolved by a small amount of water, transferred to a 10 mL calibrated flask and determined for nickel according to the general procedure. Meanwhile, atomic absorption spectrometry was used as contrast method for the determination of nickel content in the water sample. The above results are listed in Table 1.

Table 1. Analytical results of samples

Sample	Found (n = 11) μg/g	Relative standard deviation %	Added μg/g	Recovered μg/g	Recovery %	Atomic absorption spectrometry μg/g
No.1	37.9	2.3	5.000	5.002	100.04	37.9
No.2	45.2	1.9	5.000	4.998	99.96	45.3

Conclusion

A method for the spectrophotometric determination of nickel with chlorophosphonazo-III has been established. Beer's law was obeyed over the range of 0.1~3.5 μg/mL for Ni²⁺. The apparent molar absorption coefficient of method was $\epsilon_{620\text{ nm}} = 1.40 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ and the detection limit was 0.075 μg/mL. The recoveries for analyses of the rainwater samples obtained were 99.96%-100.04% and the relative standard deviations were 1.9%-2.3% with satisfactory results. The present method for determination of nickel is more convenient than the ones in literature²⁻⁵.

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