



Research Article

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Study on the chromogenic reaction between nickel(II) and Dibromo-*p*-methyl-arsenazo by spectrophotometry

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ABSTRACT

A new method for the determination of nickel(II) with dibromo-*p*-methyl-arsenazo by spectrophotometry has been proposed. The apparent molar absorption coefficient of method is $\epsilon_{612\text{ nm}} = 1.01 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Beer's law is obeyed over the range of 0.10 ~ 3.5 $\mu\text{g} / \text{mL}$ for nickel content. The detection limit of method is 0.11 $\mu\text{g} / \text{mL}$. The present method has been satisfactorily applied to the determination of nickel in rain water.

Keywords: Nickel, dibromo-*p*-methyl-arsenazo, spectrophotometry.

INTRODUCTION

Nickel is widely used in iron and steel, ceramics, metallurgy, pharmaceutical, electroplating and atomic energy field. Nickel is also an essential microamount element that is necessary to a life body and can reduce anemia, accelerate the regeneration of red cells, which helps to improve the structure of cell membrane and other physiological functions [1]. Nickel deficiency or excess, can cause different damage to life body. When intake of nickel is excessive, acute, chronic poisoning appears. Nickel compounds are carcinogenic to humans. In the surrounding environment, source of nickel is wide, therefore, determination of trace nickel has an important significance.

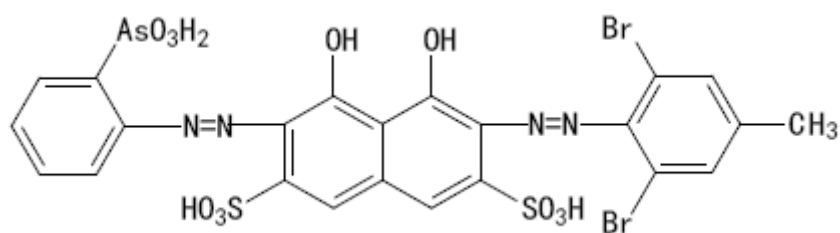


Fig.1: Structure of *p*-methyldibromoarsenazo

Although there are some methods for nickel determination at present, spectrophotometric method has the characteristics of simple equipment, convenient operation and practicability and this method is still an interesting method for the determination of nickel now. Although some chromogenic reagents have been proposed for the determination of nickel and 3, 5-dicarboxyl-phenyl diazoaminoazobenzene [2], *p*-nitrodiazoaminoazobenzene [3], 2-chloro-4-bromo -benzenediazoaminoazobenzene [4] were ever used for the study of nickel determination, most of the method selectivity is not ideal. A new spectrophotometric method for the determination of nickel still needs to be developed. *p*-Methyldibromoarsenazo (DBM-ASA) [5], whose structure is shown as Figure 1, has been used for the spectrophotometric determination of rare earth elements [5]. According to author's best knowledge, there is no research report on where spectrophotometric method is used for the determination of nickel with DBM-ASA. In this

article, the color reaction between this reagent and nickel (II) was studied, establishing the optimal experimental conditions for the determination of nickel. The method has been used in the determination of nickel in rain water with satisfactory results.

EXPERIMENTAL SECTION

Apparatus. Absorbance measurement was completed on a 722S spectrophotometer (Shanghai Linggunag Technique Co., Ltd., China) with 1-cm cells.

Reagents and solutions. The stock standard solution of nickel, 1 mg / mL, was prepared by dissolving 0.4784 g of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in an appropriate amount of water containing 2 mL of H_2SO_4 (1 + 1, V/V) and then diluted to 100 mL with water. The working standard solution of nickel(II), 10 μg / mL, was prepared by diluting the stock solution with water. Dibromo-*p*-methyl-arsenazo (DBM-ASA) solution, 0.5 g/L, was prepared by dissolving 0.05 g of DBM-ASA in 100 mL of water. Buffer solution (pH = 6.4): 45 mL of 0.02 mol / L NaOH solution was added to 100 mL of three acids (phosphoric acid, acetic acid, boric acid) mixed solution whose concentrations were all 0.04 mol/L for each acid. Unless otherwise stated, all reagents were of analytical-reagent grade and distilled water was used throughout the study.

General procedure: In a 10-mL volumetric flask, 15 μg of Ni(II) working solution, 2.0 mL of DBM-arsenazo solution and 1.0 mL of buffer solution, were added into a 10-mL calibrated flask, were consecutively added were added in turn. The solution was diluted to the mark with water. After 10 min, the solution was partially added to a 1-cm cell and the absorbance was determined at 612 nm using the blank solution without added Ni^{2+} as reference.

RESULTS AND DISCUSSION

Absorption spectra. The absorption spectra of the reagent and the complex are shown in Fig.2. At pH = 6.4, the reagent against water has a maximum absorption peak at 520 nm, whereas a maximum absorption peak of nickel complex against reagent blank is at 612 nm. A wavelength of 612 nm was selected for spectrophotometric determination of nickel in the present study in order to obtain maximum sensitivity.

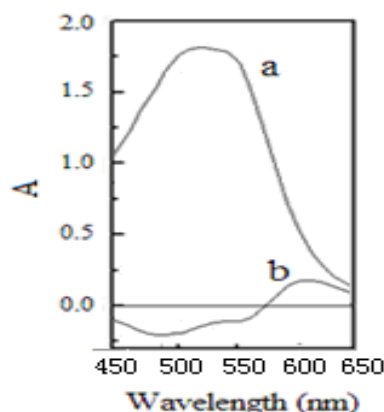


Fig.2: Absorption spectra of (a) Reagent blank (against water); (b) complex (against reagent blank); $[\text{Ni}^{2+}] = 2.56 \times 10^{-5}$ mol / L; pH = 6.4

Optimal conditions for nickel determination. The effect of pH ranging from 1 to 14 on the absorbance of complex was investigated. The results showed that the sensitivity was found to be larger and stable over the range pH 5.4 ~ 7.4. Outside this range, the sensitivity of the determination of nickel is lower. In the experiments, pH 6.4 was selected as the optimum acidity. The experiments showed that when the amount of buffer solution was 0.8 - 2.0 mL, the absorbance was a maximum and stable. The buffer solution amount selected was 1.0 mL.

The effect of DBM-arsenazo amount on the absorbance was investigated. As DBM-ASA amount increased, the absorbance gradually increased. When DBM-ASA amount was 1.8 ~ 2.3 mL, the absorbance was a maximum. In the experiments, 2.0 mL of 0.5 g/L DBM-ASA solution was selected.

Complex composition and stability. Ni^{2+} and DBM-ASA form a blue complex under the present experimental condition. Molar ratio method and equal molar continuous variation method were respectively used to determine the composition ratio of complex to be $n_{(\text{DBC-ASA})} : n_{\text{Ni(II)}} = 3 : 1$.

At room temperature nickel complex formed immediately and the absorbance reached a maximum. Within 2 h a variation of absorbance of the complex was less than 5% and the complex kept stable.

Working curve and analytical characteristics. The results showed that when nickel (II) content was 0.10 ~ 3.5 $\mu\text{g} / \text{mL}$, Beer's law was obeyed. Its linear calibration equation is: $A = 0.1778 C (\mu\text{g}/\text{mL}) + 0.0053$ with a correlation of 0.9993, where A is the absorbance determined at 612 nm and C is the concentration of Ni^{2+} in the sample solution in $\mu\text{g} / \text{mL}$. According to the working curve, the apparent molar absorptivity calculated is $\epsilon_{612 \text{ nm}} = 1.01 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The relative standard deviation (R. S. D.) for determination of 2.0 $\mu\text{g} / \text{mL}$ of Ni^{2+} was 1.3% ($n = 11$), indicating that the precision of the method is good. The limit of detection, defined as $C_L = 3S_b / m$, where C_L , S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was 0.11 $\mu\text{g} / \text{mL}$.

Selectivity of method. Under the optimum experimental conditions, $\pm 5\%$ deviation from absorbance value was considered as the criterion of the interference. The allowable amounts of coexisting substances for the determination of 2.5 $\mu\text{g}/\text{mL}$ Ni (II) are as follows (multiple in mass, m/m): F^- , Cl^- , Br^- , I^- , SO_4^{2-} , PO_4^{3-} (1500); Ag^+ , Cd^{2+} , Hg^{2+} , Mn^{2+} , Zn^{2+} , B(III) , CH_3COO^- (200); W(VI) , Mo(VI) , Br^- (50); Cu^{2+} , Al^{3+} (10); Sr^{2+} , Ba^{2+} , Fe^{2+} , Co^{2+} , Fe^{3+} , Zr^{4+} (2); Ca^{2+} , La^{3+} , Y^{3+} , Ti^{4+} (1), triethanolamine (200); hydroxylamine hydrochloride (40); ammonium tartrate (20); ascorbic acid (10); oxalic acid (5). The selectivity of the present method is better compared with that of the literature [2-4].

Application. Nickel in rain water was determined by the new method proposed by this article. 1.000 L of rain water was accurately taken, placed in a beaker, evaporated on an electric cooker until it was concentrated to a small amount and a few drops of 6 mol / L HNO_3 were added. The contents were filtered and the filtrate was placed in a 25-mL calibrated flask, diluted to the mark with water. 2 mL of the above sample was taken and placed in a 10-mL calibrated flask and the remainder was the same as the general procedure for the determination of nickel content. The result of atomic absorption spectrometry was used as contrast result.

The determined results were 251.2, 249.0, 249.0, 251.2, 250.1, 251.2, 251.2, 249.0, 249.0, 250.1, 250.1 ng / g, respectively. The average value of method was 250.1 ng / g and the relative standard deviation was 0.39%. The recovery of standard addition for method was 99.89%. The result of atomic absorption spectrometric contrast method was 250.0 ng / g. The analysis results of present method were satisfactory.

CONCLUSION

In this paper a new spectrophotometric method has been established for the determination of nickel with dibromo-*p*-methyl-arsenazo. The apparent molar absorption coefficient of method is $\epsilon_{612 \text{ nm}} = 1.01 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. Nickel content in 0.10 ~ 3.5 $\mu\text{g} / \text{mL}$ range obeys Beer's law with a detection limit of 0.11 $\mu\text{g} / \text{mL}$. When it was used for the determination of nickel in rain water, very good results were obtained.

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