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Study on the Solid Phase Extraction of Co(II)-N,N′-Disalicylideneethylene diamine Chelate with C_{18} Disk and Its Application in Determination of Trace Cobalt

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A sensitive, selective and rapid method has been developed for the determination μg L^{-1} level of cobalt based on the rapid reaction of cobalt(II) with N,N′-disalicylidene-ethylenediamine (NNDED) and the solid phase extraction (SPE) of the coloured chelate with Waters Porapak Sep-Park C_{18} disk. The N,N′-disalicylidene-ethylenediamine can reacts with Co(II) in the presence of pH 4.2, acetic acid-sodium acetate buffer solution and cetyl trimethylammonium bromide (CTMAB) medium to form a violet chelate of a molar ratio 1:2 (cobalt to NNDED. This chelate can retained on Waters Porapak Sep-Park C_{18} disk quantitatively when they passed the disk as aqueous solution. After the enrichment finished, the retained chelate can be eluted from disk by 2.5 mL of ethanol (contain 5 % acetic acid). In the measured solution, the molar absorptivity of the chelate is 1.58×10^5 L mol^{-1} cm^{-1} at 635 nm and Beer's law is obeyed in the range of 0.01-0.4 μg mL^{-1}. The relative standard deviation for 11 replicate sample of 0.01 μg mL^{-1} level is 2.54 %. The detection limit is 0.01 μg mL^{-1} (in original samples). This method can be applied to the determination of μg mL^{-1} level of cobalt in drinking water with satisfactory results.

Key Words: Cobalt, Solid phase extraction spectrophotometry, N,N′-Disalicylidene-ethylenediamine.

INTRODUCTION

Cobalt is an important element, not only for industry but for biological systems as well. In rapidly expanding the analytical fields such as environmental, biological and material monitoring of trace metals, there is an increasing need to develop simple, sensitive and selective analytical techniques that do not use expensive or complicated test equipment. For this reason, a wide variety of spectrophotometric methods for the determination of cobalt have been reported. The main chromogenic reagents are pyridylazo reagents, thiazolylazo reagents, benzothiazolylazo reagents, 8-aminoquinoline derivatives, nitroso dyes, *etc.*[1-20]. But the study of 2-quinolylazo derivatives as chromogenic reagents for the determination of cobalt has received less attention. In previous work, some 2-quinolylazo derivatives were synthesized and applied to the determination of metal ion[21-24]. In this paper, we studied the colour reaction of N,N′-disalicylidene-ethylenediamine (NNDED) with cobalt (II)

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and the solid phase extraction (SPE) of the coloured chelate with Waters Porapak Sep-Park C_{18} disk. A high sensitive, selective and rapid method for the determination of cobalt was developed.

EXPERIMENTAL

A spectrophotometer (Model 722, Third Analytical Instrument Factory, China) equipped with 1 cm cells was used for all absorbance measurements. Waters SPE device, which can prepare 20 samples simultaneously, Waters Porapak Sep-Park C_{18} disk (1 mL per 30 mg, 30 mm) (Waters Corporation). The pH measurements were made with a Model pH S-2 C pH meter.

N,N′-Disalicylidene-ethylenediamine (NNDED): Synthesis and its spectral characteristics: The procedure for preparation of N,N′-disalicylidene-ethylenediamine (NNDED) is as follows: A mixture of 0.002 mol salicylaldehyde and 0.001 mol of ethylene diamine in 10 to 15 mL of absolute methanol was refluxed in a round bottom flask for 1 h. The solvent was then evaporated and the residue was crystallized from 95 % ethanol as a yellow precipitate. The precipitate was thereafter recrystallized in absolute ethanol and finally dried in vacuum. The specifications of the yellow crystals obtained as product were: m.p. 126-128 °C; IR (KBr, ν_{max}, cm^{-1}): 3050, 2932, 2901, 2870, 1636, 1497, 1283, 1149, 1042, 1021, 857, 749, 741; MS, m/z (%): 268 (M^+, 23); Anal. calcd. (%) for $C_{16}H_{16}N_2O_2$ (268.31): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.8; H, 6.05; N, 10.3. ^1H NMR (250.1 MHz, $DCCl_3$): δ 3.9 (s, 4H, CH_2), 6.8 (m, 4H), 7.3 (m, 4H), 8.3 (s, 2H), 13.2 (brs, 2H, Ar-OH) Fig. 1.

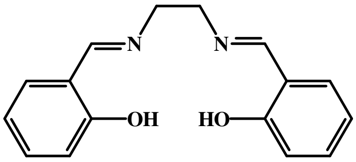

Fig. 1. Molecular structure of N,N′-disalicylidene-ethylenediamine (NNDED)

All of the solutions were prepared with ultrapure water obtained by a Milli-Q50 SP reagent water system (Millipore Corporation). High purity ethanol (Fisher corporation), NNDED was prepared as described in paper[26], a 2.5×10^{-4} mol L^{-1} of solution was prepared by dissolving NNDED with ethanol. A stock standard solution of Co(II) (1.0 mg mL^{-1}) was prepared by dissolving appropriate amount of $Co(NO_3)_2 \cdot 6H_2O$ with water and adjusting the volume to 500 mL in a 500 mL calibrated flask, then standardized by EDTA titration, a work solution of 0.2 mg mL^{-1} was prepared by diluting this solution. Acetic acid/sodium acetate buffer solution, pH 3.8. Cetyl trimethyl ammonium bromide (CTMAB) solution: 2.0 %, dissolving with 10 % of ethanol. Glycoletherdiamine tetraacetic acid zinc salt (Zn-EGTA) solution: 5 %. NaF solution: 10 %. All chemical used were of analytical grade unless otherwise stated.

Procedure: To a standard or sample solution containing not more than 1.0 mg of Co(II) in a 250 mL of flask. 10 mL of acetic acid-sodium acetate buffer solution, with pH 3.8, 5.0 mL Zn-EGTA solution, 5.0 mL NaF solution, 5.0 mL of NNDED solution and 5.0 mL of CTMAB solution were added. The mixture diluted to volume of 250 mL and mixed well. After 10 min, the solution was passed through Waters Porapak Sep-Park C_{18} disk at a flow rate of 50 mL min^{-1}. The coloured chelate would be retained on the disk. After the enrichment finished, eluted the retained chelates from the disk with 2.5 mL of ethanol (contain 5 % acetic acid) at a flow rate 5 mL min^{-1} in reverse direction. The absorbance of this solution was measured at 635 nm in a 1 cm cell against a reagent blank prepared in a similar way without cobalt.

RESULTS AND DISCUSSION

Absorption spectra: In the measured solution, the absorption spectra of NNDED and its Co(II) chelate are shown in Fig. 2. The absorption peaks of NNDED and its Co(II) chelate are located at 478 and 635 nm.

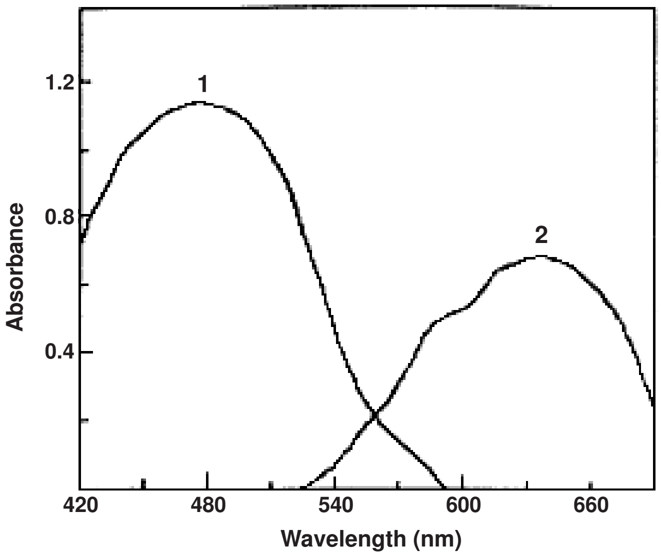

Fig. 2. Absorption spectra of NNDED and its Co(II) chelate: (1) NNDED-CTMAB blank against water; (2) NNDED Co(II)-CTMAB complex against reagent blank

Effect of acidity: Results showed that the optimal pH for the reaction of Co(II) with NNDED was 2.5-5.2. A pH 4.2 was recommended as the addition of 5-15 mL of the acetic acid-sodium acetate buffer solution (pH 4.2) per 250 mL of final solution was found to give a maximum and constant absorbance. The use of 10 mL of buffer was recommended.

Effects of surfactants: Both the NNDED and the Co(II)-NNDED chelate have a poor solubility in water solution. It is need to add surfactants to enhance the solubility of Co(II)-NNDED system. Experiment shows that all the anionic surfactants, non-ionic surfactants or cationic surfactants have good effect to enhance the solubility. But in the presence of the anionic surfactants SDS, SDBS medium, the Co(II)-NNDED chromogenic system give a low absorption, whereas in the presence of non-ionic surfactants or cationic surfactants, the absorption of the chromogenic system increases markedly. Various nonionic surfactants and cationic surfactants enhance the absorbance in the following sequence: CTMAB > Tween-80 > CPB > Tween- 20 > Triton-X-100. Accordingly, CTMAB is the best additive. The addition of 4.0-8.0 mL of CTMAB solution give a constant and maximum absorbance and the use of addition 5.0 mL were recommended.

Effect of NNDED concentration: The addition of about 5.0 mL of 2.5×10^{-4} mol L^{-1} of NNDED solution has been found to be sufficient for a complete reaction. Accordingly, 5.0 mL of NNDED solution was added in all further measurement.

Stability of the chromogenic system: After mixing the components, the absorbance reaches its maximum within 5 min at room temperature and remains stable for at least 8 h in water solution. When extracted into the ethanol medium, the chelate remain stable at least for 15 h.

Solid phase extraction: Both the enrichment and the elution were carried out on a Waters SPE device, which can prepare 20 samples simultaneously. The flow rate was 50 mL min^{-1} when enrichment and 5 mL min^{-1} when elution. Some experiments were carried out in order to investigate the retention of NNDED and its Co(II) chelate on the disk. It was found that the NNDED and its Co(II) chelate could be retained on disk quantitatively when they pass through the disk as aqueous solution. The capacity of the disk for NNDED was 25 mg and its Co(II) chelate was 20 mg in a 250 mL of solution. Under the circumstance of this experiment, the disk has adequate capacity to enrich the Co-NNDED chelate and the excessive NNDED. In order to choose a proper eluant for the retained NNDED and its Co(II) chelate, various organic solvents were studied. It was found that the tetrahydrofuran, acetone, acetonitrile, ethanol and methanol could elute the NNDED and its Co(II) chelate from disk quantitatively. Ethanol has a low volatility, toxicity and economic, so ethanol was selected. Co(II)-NNDED chelate has a good stability in weak acid medium. In presence of 3-10 % of acetic acid in ethanol could increase the stability of the Co(II)-NNDED chelate in the course elution. So ethanol (containing 5 % of acetic acid) was selected as eluant. Experiment shows that it was easier to elute the retained NNDED and its Co(II) chelate in reverse direction than in forward direction, so it is necessary to upturned disk when elution. Ethanol (2.5 mL, contains 5 % of acetic acid) was sufficient to elute the NNDED and its Co(II) chelate from disk at a flow rate of 5 mL min^{-1}. The volume of 2.5 mL eluant was selected.

Calibration curve and sensitivity: The calibration curve (Fig. 3) shows that Beer's law is obeyed in the concentration range of 0.01-0.4 mg Co(II) min^{-1} in the measured solution. The linear regression equation obtained was: A= 2.475C (mg L^{-1}) + 0.008, (r = 0.9999). The molar absorptivity in the five measured solution was calculated to be 1.58×10^5 L mol^{-1} cm^{-1} at 635 nm and the Sandell sensitivity was 3.67×10^{-4} mg cm^{-2}. The relative standard deviation at a concentration level of 0.01 mg mL^{-1} of Co(II) mL^{-1} (11 repeat determination) was 2.54 %. The detection limit is 0.01 mg mL^{-1} (in original samples).

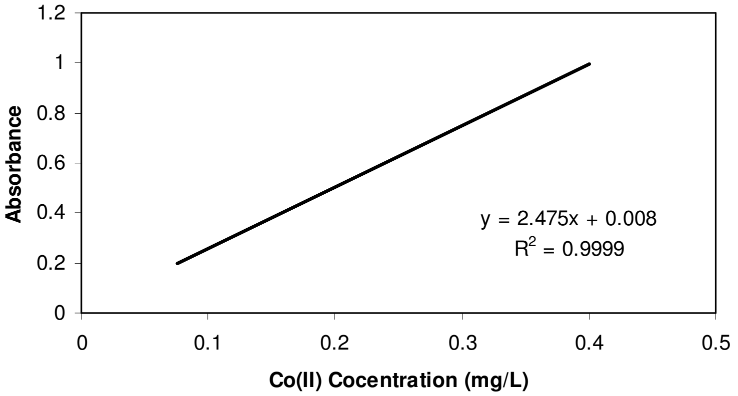

Fig. 3. Calibration curve

Composition of the complex: The composition of the complex was determined by continuous variation and by molar ratio method. Both showed that the molar ratio of Co(II) to NNDED is 1:2.

Interference: The selectivity of the proposed method was investigated by the determination 1.0 mg Co(II) in the presence of various ions within a relative error of ± 5 % are given in Table-1. Result show that masked with Zn-EGTA and NaF, most foreign ions did not interfered with the determination. This method is highly selective.

TABLE-1
TOLERANCE LIMITS IN THE DETERMINATION OF
1 mg OF Co(II) WITH NNDED (RELATIVE ERROR ± 5 %)

Tolerate (mg)	Ion added
100	SCN^-, tartrate, thiourea, NO_3^-, Cl^-, Na^+, K^+, borate oxalate, citrate,
40	benzoate, succinate, ascorbate, SO_4^{2-}, NH_4^+
25	Li^+, Al^{3+}, PO_4^{3-}
10	F^-, Br^-, ClO_4^-, Ca^{2+}, Mg^{2+}
3	Sr^{2+}, Ce^{4+}, Ba^{2+}, Zr^{4+}
1	Mn^{2+}, W^{6+}, Mo^{6+}, Zn^{2+}
0.5	Ti^{4+}, Bi^{3+}, V^{5+}, Cr^{6+}, Zr^{4+}, Ni^{2+}, Th^{4+}, Fe^{3+}
0.2	Ti^{3+}, Ag^+, Cd^{2+}, Cr^{3+}, Fe^{2+}, La^{3+}, Sn^{4+}, Pb^{2+}, Cu^{2+}
0.1	Ru^{3+}, Bi^{3+}, Hg^{2+}, Sb^{3+}, Pd^{2+}, Sn^{4+}
0.04	Se^{4+}, U^{6+}, Te^{4+}, Au^{3+}, Pt^{2+}
0.005	Os^{8+}, Ir^{4+}, Sb^{3+}

Application: The proposed method has been successfully applied to the determination of cobalt in three real drinking water samples (tap water of Saveh, pure water (TWT Corporation of Varamin) and well water of Varamin). The results were shown in Table-2, together with results of a recovery test by added known amounts of silver in water sample. A standard method with ICP-MS has also been used as reference method.

TABLE-2
DETERMINATION OF SILVER IN THE REAL SAMPLE

Recovery	RSD (%) (n = 2)	This method ($\mu g\ g^{-1}$)*	Reference method ($\mu g\ L^{-1}$)*	Sample
102	3.3	10.4	11.4	Tap water
101	2.3	6.03	5.25	Pure water
95	3.2	19.3	18.6	Well water

*Average of five determinations.

Conclusion

This method is high selectivity and high sensitivity. NNDED is one of the most sensitive and selective spectrophotometric reagents for cobalt. The molar absorptivity of the chelate reach 1.58×10^5 L mol^{-1} cm^{-1}. Most of the foreign ions do not interfere with the determination when masked with NaF and Zn-EGTA. By SPE with Waters Porapak Sep-Park C_{18} disk, the NNDED-Co(II) chelate in 250 mL solution can be concentrated to 2.5 mL. The detection limit is 0.01 μg L^{-1} (in original samples) and μg L^{-1} level cobalt in drinking water can be determined with satisfactory results. The consuming of organic solvents in this method is much lower than those consumed in liquid-liquid extraction method. Since the ethanol has a lower volatility and toxicity, this method is more safe than methods that using other organic solvents. By Using Waters SPE device, 20 samples can be prepared simultaneously. This method is rapid for simultaneously preparing large amount of sample.

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