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# Study on the Solid Phase Extraction and Spectrophotometric Determination of Cobalt with 2-(2-Quinolylazo)-5-Diethylaminoaniline

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A sensitive, selective and rapid method for the determination of cobalt based on the rapid reaction of cobalt(II) with QADEAA and the solid phase extraction of the Co(II)-QADEAA chelate with C<sub>18</sub> membrane disks was developed. In the presence of pH = 5.5 buffer solution and cetyl trimethylammonium bromide (CTMAB) medium, QADEAA reacts with cobalt to form a violet complex with a molar ratio of 1:2 (cobalt to QADEAA). This chelate was enriched by the solid phase extraction with C<sub>18</sub> membrane disks. An enrichment factor of 50 was obtained by elution of the chelate from the disks with a minimal amount of isopentyl alcohol. In isopentyl alcohol medium, the molar absorptivity of the chelate is  $1.43 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 625 nm. Beer's law is obeyed in the range of  $0.01 \sim 0.6 \mu\text{g mL}^{-1}$  in the measured solution. The relative standard deviation for 11 replicate samples of  $0.01 \mu\text{g mL}^{-1}$  level is 1.18%. The detection limit reaches  $0.02 \mu\text{g L}^{-1}$  in the original samples. This method was applied to the determination of cobalt in environmental samples with good results.

**Key Words:** 2-(2-quinolylazo)-5-diethylaminoaniline, cobalt, spectrophotometry, solid phase extraction.

## Introduction

Cobalt is an important element, not only for industry but also for biological systems. In rapidly expanding 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. Many sensitive techniques, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry and chemiluminescence have been widely applied to the determination of cobalt<sup>1-7</sup>. However, the spectrophotometric method still has the advantages of being simple and not requiring expensive or complicated test equipment. For this reason, a wide variety of spectrophotometric methods for the determination of cobalt have been developed. The

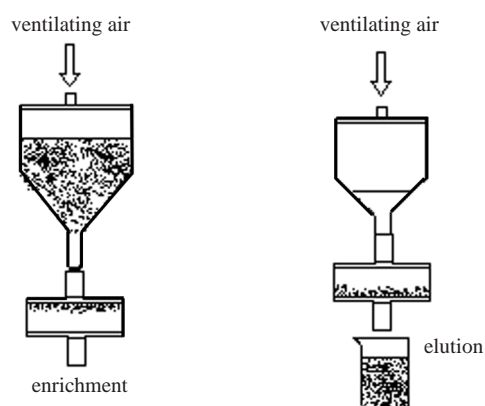
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main chromogenic reagents are pyridylazo reagents, thiazolylazo reagents, benzothiazolylazo reagents, 8-aminoquinoline derivatives, porphyrins, nitroso dyes etc<sup>8-19</sup>. Each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity.

In previous studies, various 2-quinolylazo-phenol reagents were reported for the determination of metal ions<sup>20-24</sup>. This kind of reagent has a higher sensitivity than that of pyridylazo reagents because of its larger conjugated system. However, the 2-quinolylazo-phenol reagent also has a disadvantage of poor selectivity because both the oxygen atoms and nitrogen atoms donate to the metal ions. To select a more sensitive and selective reagent, we synthesized 2-(2-quinolylazo)-5-diethylaminoaniline (QADEAA) and studied its color reaction with silver. This reagent has higher selectivity than that of 2-quinolylazo-phenol reagents because it only donates nitrogen atoms to metal ions<sup>25</sup>.

Routine spectrophotometric methods are often not sensitive enough to determine low concentrations of cobalt ions in environmental samples only at the  $\mu\text{g L}^{-1}$  level. Consequently, a preconcentration step is usually required. Solid phase extraction is an attractive technique because of its notable advantages<sup>26-29</sup>. In this paper, QADEAA was first used as a chromogenic reagent for cobalt. Based on the color reaction of QADEAA with cobalt and the solid phase extraction of the colored chelate with C<sub>18</sub> disks, a highly sensitive, selective and rapid method for the determination of cobalt in environmental samples was developed.



## Experimental

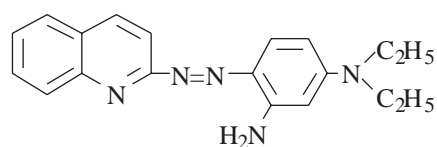
### Experimental apparatus

A UV-160 A spectrophotometer (Shimadzu, Japan) equipped with a 1 cm microcell (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman  $\Phi$ -200 pH meter. The extraction was performed on a Waters Solid Phase Extraction (SPE) device (that can prepare 20 samples simultaneously), and Zorbax C<sub>18</sub> membrane disks [47 mm (diameter)  $\times$  0.5 mm (thickness), 8  $\mu\text{m}$ , 50 mg] (Agilent Technologies, USA) were used. The samples were passed through the disks in a forward direction and the retained chelate was eluted from the disks in a reverse direction.

### Synthesis of QADEAA

2-Aminoquinoline (7.2 g) was dissolved in 500 mL of anhydrous ethanol, to which sodamide (2.0 g) was added, the solution was refluxed for 5 h in a boiling water bath, and then the isoamyl nitrite (7.4 mL) was

added. The solution was refluxed again for 30 min in a boiling water bath. The solution was cooled and placed over night under 0 °C. The diazo salt was obtained by filtering the precipitates with a yield of 95%. The diazo salt was dissolved in 200 mL of anhydrous ethanol, and *m*-diethylaminoaniline (5.7 g) was added. The carbon dioxide was ventilated into the solution by stirring until the pH reached about 8.0. The solution was for 2 days, and then diluted with 400 mL of water and extracted with chloroform, we then evaporated the chloroform and re-crystallized the residue with 25% ethanol. QADEAA was obtained with a yield of 35%. The structure was verified by elemental analysis, IR, <sup>1</sup>HNMR and MS. Elemental analysis: C<sub>19</sub>H<sub>21</sub>N<sub>5</sub> found (calculated); C 71.12 (71.45), N 21.87 (21.93), H 6.68 (6.63). IR (KBr) (cm<sup>-1</sup>): 3310 (ν<sub>N-H</sub>); 1615, 1575, 1500, 1426 (ν<sub>C=C, N=N</sub>); 1375, 1326 (ν<sub>C-N</sub>); 2920, 2873 (ν<sub>C-H</sub>); 1465, 1380 (δ<sub>C-H</sub>); 3060, 3015 (σ<sub>Ar-H</sub>); 1175, 1120, 865, 780, 720 (δ<sub>Ar-H</sub>). <sup>1</sup>HNMR (solvent: d<sub>6</sub>-acetone) (δ ppm): 1.25 (t 6H, C-CH<sub>3</sub>); 2.75 (q 4H, N-CH<sub>2</sub>-), 3.60 (s 2H, -N-H<sub>2</sub>); 6.86~7.85 (m 9H, Ar-H). MS: 319 (M<sup>+</sup>). All these show that the structure of QADEAA is as follows:



## Reagents

All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Isopentyl alcohol (Fisher Corporation, USA) was used. The QADEAA solution ( $5 \times 10^{-4}$  mol L<sup>-1</sup>) was prepared by dissolving the QADEAA with 95% ethanol. A stock standard solution of cobalt (1.0 mg mL<sup>-1</sup>) was obtained from the Chinese Standard Center, and a working solution of 1.0 μg mL<sup>-1</sup> was prepared by diluting this solution. The buffer solution of 0.5 mol L<sup>-1</sup> acetic acid-sodium acetate (containing 5% of Zn-EGTA and 5% of NaF) was prepared by dissolving 30 g of acetic acid, 50 g of sodium fluoride and 50 g of glycoetherdiamine tetraacetic acid zinc salt (Zn-EGTA) in 600 mL of water. We then adjusted the pH to 5.5 with sodium hydroxide solution and diluted this solution to a volume of 1000 mL with water. Cetyl trimethylammonium bromide (CTMAB) solution (1.0%) was prepared by dissolving the CTMAB with 10% ethanol. All chemicals used were of analytical grade unless otherwise stated.

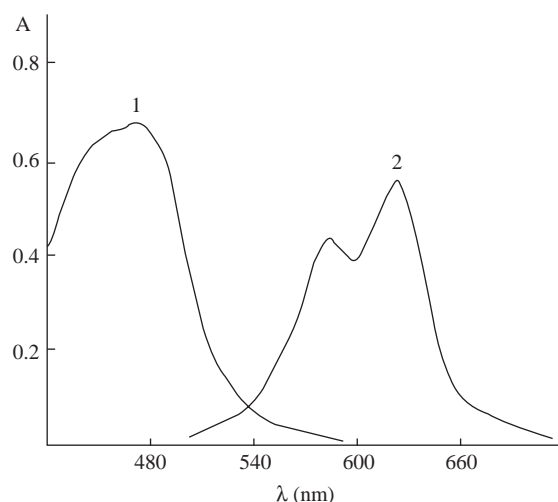
## General procedure

To a standard or sample solution containing no more than 2.4 μg of Co(II) in a 200 mL calibrated flask, 10 mL of 0.5 mol L<sup>-1</sup> acetic acid-sodium acetate buffer solution (containing 5% Zn-EGTA and 5% NaF) at pH 5.5, 6 mL of  $5 \times 10^{-4}$  mol L<sup>-1</sup> QADEAA solution and 5.0 mL of 1.0% CTMAB solution were added. The mixture was diluted to a volume of 200 mL and mixed well. After 10 min, the solution was passed through the C<sub>18</sub> disks at a flow rate of 50 mL min<sup>-1</sup>. After the enrichment had finished, the retained chelates were eluted from the disks with 4 mL of isopentyl alcohol at a flow rate of 5 mL min<sup>-1</sup>. The absorbance of the eluant was measured in a 1 cm cell at 625 nm against a reagent blank prepared in a similar way without cobalt.

## Results and Discussion

### Absorption spectra

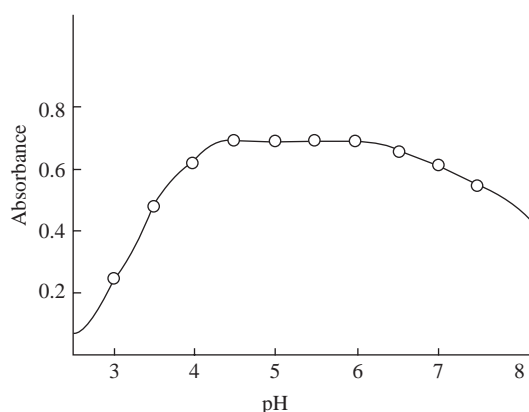
The absorption spectra of QADEAA and its Co(II) complex in isopentyl alcohol medium are shown in Figure 1. The absorption peaks of QADEAA and its complex are located at 470 nm and 625 nm.



**Figure 1.** Absorption spectra of QADEAA and its Co(II) complex: (1) QADEAA-CTMAB blank against water; (2) QADEAA-Co(II)-CTMAB complex against reagent blank

### Effect of acidity

The results showed that the optimal pH (Figure 2) for the reaction of Co with QADEAA is 4.2.~6.8. A pH 5.5 acetic acid-sodium acetate buffer solution was recommended to control the pH. The use of 6 ~ 15 mL of buffer solution per 200 mL was found to give a maximum and constant absorbance. Therefore, 10 mL of buffer solution was recommended. In this work, the routine ions Ni(II), Cu(II), Zn(II) and Fe(III) react with QADEAA to cause serious positive interference. According to the literature<sup>30,31</sup>, in the determination of cobalt with pyridylazo reagent, the interference of Fe(III) can be masked by NaF, and the interference Ni(II), of Cu(II), Zn(II) can be masked by Zn-EGTA. Therefore, experiments containing an appropriate amount of Zn-EGTA and NaF in buffer solution to mask Ni(II), Cu(II), Zn(II) and Fe(III) ions were performed. The results showed that levels of 4 ~ 6% Zn-EGTA and 3 ~ 10% NaF in buffer solution can greatly enhance the tolerance limits of Ni(II), Cu(II), Zn(II) and Fe(III) and do not affect the sensitivity of this method. Levels of 5% Zn-EGTA and 5% NaF in the buffer solution were recommended to mask the Ni(II), Cu(II), Zn(II) and Fe(III) ions.



**Figure 2.** Effect of pH on the formation of Co(II) complex, Co(II) concentration was  $5.0 \times 10^{-6}$  mol.L $^{-1}$ , other conditions as the general procedure.

### Effect of surfactants

The Co-QADEAA complex has poor solubility in water solution. It is required to add a suitable amount of surfactants to enhance the solubility of the complex. The experiments showed that all the anionic surfactants, nonionic surfactants and cationic surfactants are effective in enhancing solubility. In addition to enhancing solubility, in the nonionic surfactants and cationic surfactants medium, the sensitivity of the Co-QADEAA chelates was also increased markedly. The effect of the nonionic surfactants and cationic surfactants on improving sensitivity is shown in Table 1. The results showed that CTMAB was the best additive and that the use of 3.0 ~ 8.0 mL of CTMAB gave constant and maximum absorbance. Accordingly, 5.0 mL of CTMAB solution was recommended.

**Table 1.** The effect of surfactants on the Co-QADEAA chromogenic system.

| Surfactant   | Absence | CTMAB | CPB  | TritonX-100 | Emulsifier-OP | Tween-80 | Tween-20 | Tween-60 |
|--|---------|-------|------|-------------|---------------|----------|----------|----------|
| $\lambda$ max (nm)                                       | 590     | 625   | 620  | 610         | 605           | 610      | 615      | 610      |
| $\epsilon$ ( $\times 10^4$ )<br>L.mol $^{-1}$ cm $^{-1}$ | 8.12    | 14.3  | 11.5 | 9.26        | 9.87          | 11.8     | 9.08     | 8.96     |

### Effect of QADEAA concentration

For up to 2.4  $\mu$ g of Co(II), the use of about 5 ~ 10 mL of  $5 \times 10^{-4}$  mol L $^{-1}$  of QADEAA solution was found to be sufficient for a complete reaction. Accordingly, 6 mL of QADEAA solution was added in all further measurements.

### Stability of the chromogenic system

After mixing the components, the absorbance reached its maximum within 6 min at room temperature and remained stable for 6 h in aqueous solution. The chelates were stable for at least 20 h when extracted into the isopentyl alcohol medium.

### **Solid phase extraction**

Both the enrichment and the elution were carried out on a Waters SPE device (capable of preparing 20 samples simultaneously). The flow rate was set to 50 mL min<sup>-1</sup> when enriching and 5 mL min<sup>-1</sup> when eluting.

Some experiments were carried out in order to investigate the retention of QADEAA and its Co(II) chelate on the disks. It was determined that the QADEAA and its Co(II) chelate were retained on the disks quantitatively when they passed the disks as an aqueous solution. The capacity of the disks for QADEAA was 31 mg and that for its Co(II)-chelate was 22 mg in 200 mL of solution. In this experiment, the disks were of sufficient capacity to enrich the Co(II)-QADEAA chelate and the excessive QADEAA.

In order to choose a proper eluant for the retained QADEAA and its Co(II) chelate, various organic solvents were studied. The effect of the various organic solvents was in the following sequence: isopentyl alcohol > acetone > acetonitrile > ethanol > methanol. Isopentyl alcohol was therefore selected as the eluant. The experiment showed that it was easier to elute the retained QADEAA and its Co(II) chelate in a reverse direction than in a forward direction, and it is necessary to upturning the disks when eluting. In addition, 4.0 mL of isopentyl alcohol was sufficient to elute the QADEAA and its Co(II) chelate from the disks at a flow rate of 5 mL min<sup>-1</sup>. A volume of 4.0 mL of eluant was selected.

### **Calibration curve and sensitivity**

The calibration curve show that Beer's law is obeyed in the concentration range of 0.01 ~0.6  $\mu\text{g Co(II)}$  per mL, The linear regression equation obtained was  $A = 2.48 C(\mu\text{g mL}^{-1}) + 0.0108$ , ( $r = 0.9991$ ). The molar absorptivity was calculated to be  $1.43 \times 10^5 \text{L mol}^{-1} \text{cm}^{-1}$  at 596 nm. The detection limit, based on the 3 times of the standard deviation of the blank, was  $0.02 \mu\text{g L}^{-1}$  in the original samples. The relative standard deviation at a concentration level of  $0.2 \mu\text{g Co(II)}$  per mL (11 repeat determinations) was 1.18%.

### **Composition of the complex**

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

### **Interference**

The selectivity of the proposed method was investigated by the determination of  $2.0 \mu\text{g Co(II)}$  in 200 mL of solution in the presence of various ions within a relative error of  $\pm 5\%$ , and the results are given in Table 2.

### **Application**

The proposed method was successfully applied to the determination of cobalt in biological samples and water.

For biological samples, 0.20 g of sample was weighed accurately into a Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). Then 2.5 mL of concentrated nitric acid and 2.5 mL of 30% hydrogen peroxide were added. The bombs were sealed tightly and then positioned on the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 6.0 min. The digest was evaporated

to near dryness. The residue was dissolved with 1% hydrochloric acid, and the cobalt contents were analyzed according to the general procedure. The results are shown in Table 3.

**Table 2.** Tolerance limits in the determination of 2.0  $\mu\text{g}$  of Co with QADEAA (relative error  $\pm 5\%$ ).

| Ion added   | Tolerance (mg) |
|---|----------------|
| Zn-EGTA, $\text{F}^-$ , $\text{SCN}^-$ , tartrate, thiourea, $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{Na}^+$ , $\text{K}^+$ , borate              | 50             |
| $\text{SCN}^-$ , tartrate, thiourea, $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{Na}^+$ , $\text{K}^+$ , borate                                      | 50             |
| oxalate, citrate, benzoate, succinate, ascorbate, $\text{SO}_4^{2-}$ , $\text{NH}_4^+$  | 20             |
| $\text{Li}^+$ , $\text{Al}^{3+}$ , $\text{PO}_4^{3-}$   | 10             |
| $\text{F}^-$ , $\text{Br}^-$ , $\text{ClO}_4^-$ , $\text{I}^-$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$  | 5              |
| $\text{Sr}^{2+}$ , $\text{Ce(IV)}$ , $\text{Ba}^{2+}$ , $\text{Zr(IV)}$ , $\text{Zn}^{2+}$ , $\text{Fe}^{3+}$                                     | 2              |
| $\text{Mn}^{2+}$ , $\text{W(VI)}$ , $\text{Mo(VI)}$ , $\text{Cu}^{2+}$  | 1              |
| $\text{Ti(IV)}$ , $\text{Bi(III)}$ , $\text{V(V)}$ , $\text{Cr(VI)}$ , $\text{Zr(IV)}$ , $\text{Ni}^{2+}$ , $\text{Th(IV)}$                       | 0.5            |
| $\text{Tl(III)}$ , $\text{Ag}^+$ , $\text{Cd}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{2+}$ , $\text{La}^{3+}$ , $\text{Sn(IV)}$ , $\text{Pb}^{2+}$ | 0.2            |
| $\text{Ru(III)}$ , $\text{Bi(III)}$ , $\text{Hg}^{2+}$ , $\text{Sb}^{3+}$ , $\text{Pd}^{2+}$ , $\text{Sn(IV)}$ , $\text{Sb(III)}$                 | 0.1            |
| $\text{Se(IV)}$ , $\text{U(VI)}$ , $\text{Te(IV)}$ , $\text{Au}^{3+}$ , $\text{Pt}^{2+}$  | 0.03           |

**Table 3.** Determination of cobalt in the certified standard biological samples.

| Samples                  | Standard value ( $\mu\text{g g}^{-1}$ )   | By this method<br>( $\mu\text{g g}^{-1}$ ) | RSD %<br>(n = 5) |
|--------------------------|---|--|------------------|
| Human Hair<br>(GBW07601) | As(0.28), B(1.3), Bi(0.34), Ca(2900), Cd(0.11), Ce(1.2), Co(0.71), Cr(0.37), Cu(10.2), Fe(54), Hg(0.36), Mg(360), Mn(6.3), Mo(0.073), Ni(0.83), Pb(8.8) | 0.726                                      | 2.4              |
| Tea Leaf<br>(GBW08505)   | As(0.191), Ba(15.7), Ca(2840), Cd(0.032), Co(2.2), Cr(0.8), Cu(16.2), Fe(373), Hg(0.004), Mg(2240), Mn(766), Ni(7.61), Pb(1.06), Se(0.041), Zn(38.7)    | 2.08                                       | 2.6              |

For water samples, these were acidified with hydrochloric acid and filtrated by 0.45  $\mu\text{m}$  filter. The cobalt contents were analyzed according to the general procedure. The results are shown in Table 4, together with the results of a recovery test. A standard method using ICP-MS<sup>32</sup> was used as reference method. The results are also shown in Table 4.

**Table 4.** Determination of cobalt in the water sample.

| Samples     | Reference method<br>( $\mu\text{g L}^{-1}$ ) | Found *<br>( $\mu\text{g L}^{-1}$ ) | RSD %<br>(n = 5) | Recovery (%)<br>(n = 5)<br>(Add 0.5 $\mu\text{g}$ cobalt) |
|-------------|--|-------------------------------------|------------------|---|
| River water | 61.2   | 58.8                                | 2.2              | 96  |
| Lake water  | 43.5   | 44.1                                | 2.8              | 104   |
| Tap water   | 31.2   | 32.8                                | 2.1              | 93  |

## Conclusion

In this study, a highly sensitive and selective reagent for cobalt was used. The experiment showed that the molar absorptivity of the Co(II)-QADEAA-CTMAB chelate reaches  $1.43 \times 10^5 \text{L.mol}^{-1}.\text{cm}^{-1}$  in the measured solution. Most foreign ions do not interfere with the determination in the presence of sodium



thiosulfate and sodium fluoride medium. By solid phase extraction with C<sub>18</sub> disks, an enrichment factor of 50 was achieved. The detection limit reached 0.02 μg L<sup>-1</sup> in the original samples, and low concentrations of cobalt in samples can be determined with good results. The consumption of organic solvents in this method is much lower than that in the liquid-liquid extraction method. By using a Waters SPE device, 20 samples can be prepared simultaneously. This method is a rapid means of simultaneously preparing large amounts of sample.

## Acknowledgement

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