H. Zhang, Z. Li, S. Zhang, G. Yang, J. Yin,
S. Afr. J. Chem., 2004, **57**, 28–32,
<http://journals.sabinet.co.za/sajchem/>.

The Synthesis of QADMAA and its Application to the Solid Phase Extraction and Spectrophotometric Determination of Cobalt

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Received 3 February 2004; revised 29 February 2004; accepted 2 March 2004.

ABSTRACT

In this paper, the synthesis of a new chromogenic reagent, 2-(2-quinolylazo)-5-dimethylaminoaniline (QADMAA), is reported. A sensitive, selective and rapid method for the determination of cobalt based on the rapid reaction of cobalt(II) with QADMAA and the solid phase extraction of the Co(II)-QADMAA chelate with C_{18} membrane disks was developed. In the presence of a pH = 5.5 buffer solution and a cetyl trimethylammonium bromide (CTMAB) medium, QADMAA reacts with cobalt to form a violet complex with a molar ratio of 1:2 (cobalt to QADMAA). This chelate was enriched by solid phase extraction with C_{18} membrane disks and an enrichment factor of 50 was obtained. The molar absorptivity of the chelate is 1.32×10^5 L mol^{-1} cm^{-1} at 616 nm in the measured solution. Beer's law is obeyed in the range of 0.01~0.6 μg mL^{-1}. The relative standard deviation for eleven replicate sample at the 0.01 μg mL^{-1} level is 1.35%. The detection limit reached 0.02 μg L^{-1} in the original samples. This method was applied with good results to the determination of cobalt in environmental samples.

KEYWORDS

2-(2-Quinolylazo)-5-dimethylaminoaniline, cobalt, spectrophotometry, solid phase extraction.

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1. Introduction

Cobalt is an important element. It is important both for industry and 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 instruments, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, liquid chromatography, and the like have widely been applied to the determination of cobalt.[1–7] The spectrophotometric methods have, however, gained popularity for cobalt determination because of their simplicity and low operating costs. For these reasons, a wide variety of spectrophotometric methods for the determination of cobalt have been developed. The main chromogenic reagents are pyridylazo, thiazolylazo and benzothiazolylazo reagents, 8-aminoquinoline derivatives, porphyrins, nitroso dyes and the likes.[8–24] Each chromogenic reagents has its advantages and disadvantages with regard to sensitivity, selectivity and convenience.

In previous work, some 2-quinolylazophenol and 2-quinolylazobenzoic acid reagents were reported for the determination of metal ions.[25–30] These reagents have a higher sensitivity than pyridylazo reagents because of their larger conjugated system. However, the 2-quinolylazophenol and 2-quinolylazobenzoic acid reagents have also the disadvantage of poor selectivity because both the oxygen atoms and nitrogen atoms donate electrons to the metal ions. To select a more sensitive and selective reagent, in this work, 2-(2-quinolinylazo)-5-dimethylaminoaniline (QADMAA) was first synthesized, and its colour reaction with cobalt was studied. This reagent has a higher selectivity than 2-quinolylazo-phenol reagents because only nitrogen atoms donate electrons to metal ions.

The routine spectrophotometric methods are often not sensitive enough to determine a low concentration of cobalt ions in environmental samples, when cobalt ions may be only at the μg L^{-1} level. Consequently, a pre-concentration step is usually required. Solid phase extraction is an attractive technique because it presents notable advantages.[31–36] In this paper, based on the colour reaction of QADMAA with cobalt and the solid phase extraction of the coloured chelate with C_{18} disks, a highly sensitive, selective and rapid method for the determination of cobalt in environmental samples was developed.

2. Experimental

2.1. Synthesis of QADMAA

The QADMAA was synthesized according to the following procedure: 2-aminoquinoline (6.9 g) was dissolved in a 500 mL anhydrous ethanol. Sodamide (2.0 g) was added to this and the mixture was refluxed on a boiling water bath for 5 h, followed by the addition of isoamyl nitrite (7.4 mL). The solution was refluxed for 30 min on a boiling water bath. The solution was cooled and stored overnight under 0°C. The diazo salt was obtained by filtering this solution with an isolation yield of 95%. Then the diazo salt was dissolved in 200 mL anhydrous ethanol, followed by the addition of *m*-dimethylaminoaniline (5.7 g). The carbon dioxide was sparged into the solution with stirring until the pH reached about 8.0. The solution stood for two days, and evaporated to dryness. The residue was re-crystallized with 30% ethanol, and the QADMAA was obtained with a 36% yield.

The structure of QADMAA was verified by elemental analysis,

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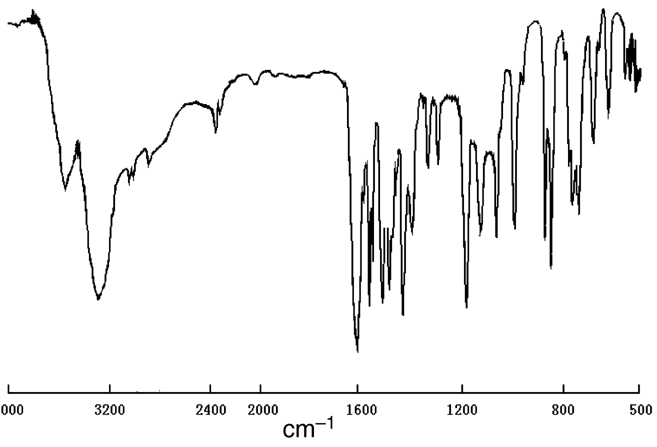

Figure 1 The infrared spectrum of QADMAA.

IR (Fig. 1), ^{1}HNMR (Fig. 2), and MS (Fig. 3). IR (KBr) (cm^{-1}): 3300 ($\nu_{N\text{-}H}$), 1600, 1560, 1505, 1426 ($\nu_{C=C,\ N=N}$), 1380, 1323 ($\nu_{C\text{-}N}$), 2850 ($\nu_{C\text{-}H}$), 1465 ($\nu_{C\text{-}H}$), 3050, 3015 ($\nu_{Ar\text{-}H}$), 1175, 1120, 865, 780, 720 ($\nu_{Ar\text{-}H}$). ^{1}HNMR (solvent: d_6-acetone) (δ ppm): 2.28 (s, 6H, N-CH$_3$), 3.69 (s, 2H, -N-H$_2$); 6.86~7.85 (m, 9H, Ar-H). MS: 291 (M$^+$). Elemental analysis: $C_{17}H_{17}N_5$ found (calculated) C 69.82 (70.08), N 23.83 (24.04), H 6.04 (5.88). All these show that the QADMAA has the structure given in Fig. 4.

The QADMAB is a deep red grain. The melting point of QADMAA is 224–226°C. It dissolves readily in polar solvents such as methanol, ethanol, acetonitrile, tetrahydrofuran, acetone and the like. It is a little soluble in water, low polar solvents such as *n*-hexane and petroleum ether. It is stable in ethanol solution for just over two month.

2.2. Experimental Apparatus

A UV-160A spectrophotometer (Shimidzu, Japan) equipped with 1 cm microcells (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman ϕ-200 pH meter. The extraction was performed on a Waters Solid Phase Extraction (SPE) device (it can prepare 20 samples simultaneously), and Zorbax C_{18} membrane disks [47 mm (diameter) × 0.5 mm (thickness), 8 μm, 50 mg] (Agilent Technologies, USA) were used.

2.3. Reagents

All 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. QADMAA solution (5 $\times 10^{-4}$ mol L^{-1}) was prepared by dissolving QADMAA with 95% ethanol. A stock standard solution of cobalt (1.0 mg mL^{-1}) was obtained from the Chinese Standards Center, and a working solution of 1.0 μg mL^{-1} was prepared by diluting this solution. The buffer solution of 0.5 mol L^{-1} acetic acid–sodium acetate (containing 5% Zn-EGTA and 5% NaF) was prepared by dissolving 30 g acetic acid, 50 g sodium fluoride and 50 g glycoletherdiamine tetraacetic acid zinc salt (Zn-EGTA) in 600 mL water, then the pH of the solution was adjusted to 5.5 with a sodium hydroxide solution, and this in turn was diluted to a volume of 1000 mL with water. The 1% cetyl trimethylammonium bromide (CTMAB) solution was prepared by dissolving a suitable volume of CTMAB with 10% of ethanol. All chemicals used were of analytical grade unless otherwise stated.

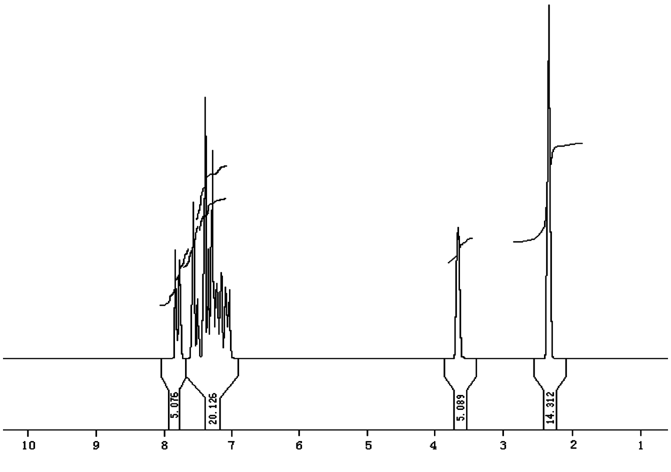

Figure 2 The ^{1}H nuclear magnetic resonance spectrum of QADMAA.

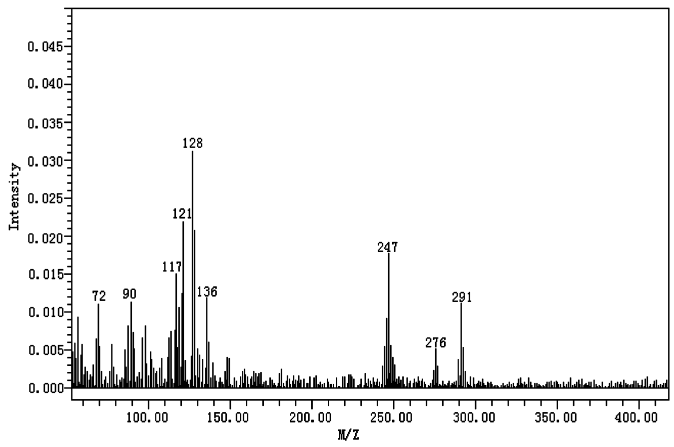

Figure 3 The mass spectrum of QADMAA.

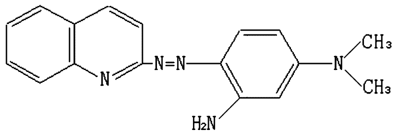

Figure 4 The structure of QADMAA.

2.4. 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^{-1} acetic acid–sodium acetate buffer solution (containing 5% Zn-EGTA and 5% NaF) with pH 5.5, 6 mL of 5 × 10^{-4} mol L^{-1} QADMAA 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_{18} disks at a flow rate of 50 mL min^{-1}. After enrichment had been completed, the retained chelates were eluted from the disks with 4 mL isopentyl alcohol at a flow rate of 5 mL min^{-1}. The absorbance of the eluant was measured in a 1 cm cell at 616 nm against a reagent blank prepared in a similar way but without cobalt.

3. Results and Discussion

3.1. Absorption Spectra

The absorption spectra of QADMAA and its Co(II) complex in isopentyl alcohol medium are shown in Fig. 5. The absorption peaks of QADMAA and its complex are located at 462 nm and 616 nm.

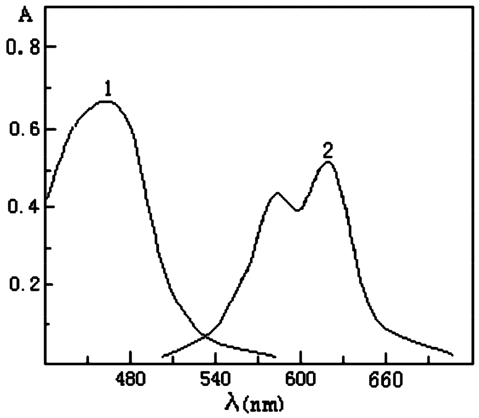

Figure 5 Absorption spectra of QADMAA and its Co(II) complex: (1) QADMAA-CTMAB blank against water; (2) QADMAA-Co(II)-CTMAB complex against reagent blank.

3.2. Effect of Acidity

The results show that the optimal pH (Fig. 6) for the reaction of Co with QADMAA 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 25 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 QADMAA to cause a serious positive interference. For the determination of cobalt with pyridylazo reagent, the interference of Fe(III) can be masked with NaF, and the interferenceof Ni(II), Cu(II), Zn(II) can be masked with Zn-EGTA, according to the literature[37,38]. Accordingly, experiments to obtain an appropriate amount of Zn-EGTA and NaF in buffer solutions to mask Ni(II), Cu(II), Zn(II) and Fe(III) ions were performed. The results showed that 4~6% of Zn-EGTA and 3~10% of NaF in the 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. The use of 5% Zn-EGTA and 5% NaF in the buffer solution were recommended to mask Ni(II), Cu(II), Zn(II) and Fe(III) ions.

3.3. Effect of Surfactants

The Co-QADMAA complex has poor solubility in a water solution. One needs to add a suitable amount of surfactants to enhance the solubility of the complex. Experiments showed that all the anionic surfactants, nonionic surfactants and cationic surfactants enhance the solubility. In addition to enhancing the solubility, the sensitivity of the Co-QADMAA chelates was increased markedly in the nonionic surfactants and cationic surfactants medium too. The effect of the nonionic surfactants and cationic surfactants for the improving the sensitivity is shown in Table 1. The results show that CTMAB is the best additive and the use of 3.0~8.0 mL of CTMAB gives a constant and maximum absorbance. Accordingly, a 5.0 mL CTMAB solution was selected.

3.4. Effect of QADMAA Concentration

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

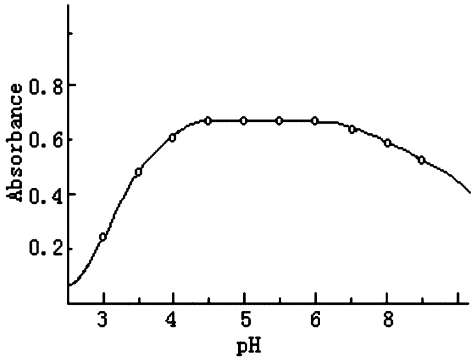

Figure 6 Effect of pH on the formation of Co(II) complex, Co(II) concentration was 5.0 × 10^{-6} mol L^{-1}, other conditions as general procedure.

3.5. Stability of the Chromogenic System

After mixing the components, the absorbance reaches its maximum within 6 min at room temperature and remains stable for 6 h in aqueous solution. The QADMAA and it cobalt chelate are stable for at least 20 h when it was extracted into the isopentyl alcohol medium.

3.6. Solid Phase Extraction

Both the enrichment and the elution were carried out on a Waters SPE device (the device can prepare twenty samples simultaneously). The flow rate was set to 50 mL min^{-1} when enriching and 5 mL min^{-1} when eluting.

Some experiments were carried out to investigate the retention of QADMAA and its Co(II) chelate on the disks. It was found that the QADMAA and its Co(II) chelate were retained on the disks quantitatively when they pass the disks as aqueous solutions. The capacity of the disks for QADMAA was 31 mg and for its Co(II)-chelate was 22 mg in 200 mL of solution. In this experiment, the disks had adequate capacity to enrich the Co(II)-QADMAA chelate and the excessive QADMAA.

In order to choose a proper eluant for the retained QADMAA and its Co(II) chelate, various organic solvents were studied. The effect of various organic solvents was found to follow the sequence: isopentyl alcohol > acetone > acetonitrile > ethanol > methanol. Isopentyl alcohol was therefore selected as eluant. It was found that it is easier to elute the retained QADMAA and its Co(II) chelate in the reverse direction than in the forward direction, so it is necessary to turn the disks over during elution. Four millilitres of isopentyl alcohol was sufficient to elute the QADMAA and its Co(II) chelate from disks at a flow rate of 5 mL min^{-1}. A volume of 4.0 mL eluant was therefore selected.

3.7. Calibration Curve and Sensitivity

The calibration curve (Fig. 7) show that Beer's law is obeyed in the concentration range 0.01~0.6 μg Co(II) per mL. The linear regression equation obtained was: $A = 2.28\,C$ (μg/mL) + 0.0115, ($r = 0.9991$). The molar absorptivity was calculated to be 1.32 ×

Table 1 The effect of surfactants on Co-QADMAA chromogenic system.

Surfactant	Absence	CTMAB	CPB	TritonX-100	Emulsifier-OP	Tween-80	Tween-20	Tween-60
λmax (nm)	584	616	608	600	595	606	608	608
ϵ (×10^4) L mol^{-1} cm^{-1}	8.01	13.2	10.2	8.85	9.17	10.4	8.56	8.68

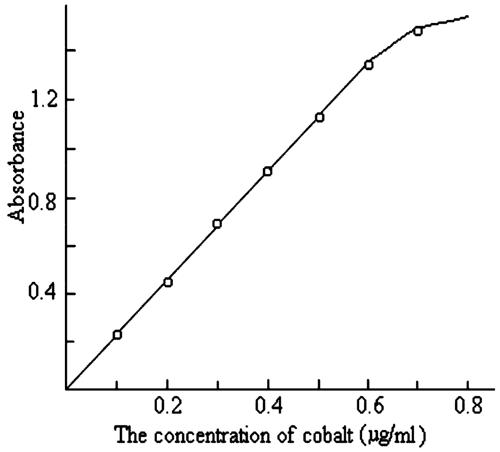

Figure 7 The calibration curve.

Table 2 Tolerance limits in the determination of 5 μg of Co with QADMAA (relative error ±5%).

Ion added	Tolerance (mg)
Tartrate, thiourea, NO_3^-, C^-, Na^+, K^+, borate,	50
Oxalate, citrate, benzoate, succinate, ascorbate, SO_4^{2-}, NH_4^+	20
Li^+, Al^{3+}, PO_4^{3-}	10
F^-, Br^-, ClO_4^-, I^-, Ca^{2+}, Mg^{2+}	5
Sr^{2+}, Ce(IV), Ba^{2+}, Zr(IV), Zn^{2+}, Fe^{3+}	2
Mn^{2+}, W(VI), Mo(VI), Cu^{2+}	1
Ti(IV), Bi(III), V(V), Cr(VI), Zr(IV), Ni^{2+}, Th(IV)	0.5
Tl(III), Ag^+, Cd^{2+}, Cr^{3+}, Fe^{2+}, La^{3+}, Sn(IV), Pb^{2+}	0.2
Ru(III), Bi(III), Hg^{2+}, Sb^{3+}, Pd^{2+}, Sn(IV), Sb(III)	0.1
Se(IV), U(VI), Te(IV), Au^{3+}, Pt^{2+}	0.03

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

Samples	Standard value (μg g^{-1})	By this method (μg g^{-1})	RSD% (n = 5)
Human hair (GBW07601)	Cd(0.11), Co(0.71), Cr(0.37), Cu(10.2), Fe(54), Hg(0.36), Ni(0.83), Pb(8.8)	0.715	2.8
Tea leaf (GBW08505)	Cd(0.032), Co(2.2), Cr(0.8), Cu(16.2), Fe(373), Hg(0.004), Ni(7.61), Pb(1.06)	2.31	2.5

Table 4 Determination of cobalt in the water sample.

Samples	Reference method (μg L^{-1})	Found (μg L^{-1})	RSD% (n = 5)	Recovery (%) (n = 5) (add 0.5 μg cobalt)
River water	61.7	63.4	2.4	93
Lake water	45.8	46.2	2.8	105
Tap water	34.5	35.6	2.5	97

10^5 L mol^{-1} cm^{-1} at 616 nm. The relative standard deviation at a concentration level of 0.2 μg Co(II) per mL (11 repeat determination) was 1.35%.

3.8. Composition of the Complex

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

3.9. Interference

The selectivity of the proposed method was investigated by the determination of 2.0 μg 200 mL^{-1} of Co(II) in the presence of various ions within a relative error of ±5% (Table 2).

3.10. Application

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

For biological samples, 0.20 g of sample was weighted accurately into the 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 in 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. Each digested sample was evaporated to near dryness. The residue was dissolved with 1% hydrochloric acid, and the cobalt contents were analysed according to the general procedure. The results are shown in Table 3.

For the water sample, the samples were acidified with hydrochloric acid and filtrated through a 0.45 μm filter. The cobalt contents were analysed according to general the procedure. The results are shown in Table 4, together with the results of a recovery test. A standard method using ICP-MS has also been used as reference method. The results are also shown in Table 4.

4. Conclusion

A comparison of the power of QADMAA with those of other methods for the determination of cobalt is given in Table 5. In this work, a highly sensitive and selective reagent for cobalt was synthesized. The molar absorptivity of the Co(II)-QADMAA-CTMAB chelate reaches 1.32 × 10^5 L mol^{-1} cm^{-1} in the measured solution. Most foreign ions do not interfere with the determination in the presence of the sodium thiosulfate and sodium fluoride medium. By solid phase extraction with C_{18} disks, an enrichment factor of 50 was achieved. The detection limit reached 0.02 μg L^{-1} 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 in the liquid–liquid extraction method. By using a Waters SPE device, 20 samples can prepared simultaneously. This method is rapid for simultaneously preparing a large number of sample.

Table 5 Comparison of reagents for spectrophotometric determination of cobalt.

Reagent	Medium/solvent	λmax (nm)	ϵ ($\times 10^4$) (L mol^{-1} cm^{-1})	Linear range (μg mL^{-1})	Ref.
1-(2-Pyridylazo)-2-naphthol	Aqueous (Triton X-100)	620	1.9	0.4–3.2	8
4-(2-Pyridylazo)-resorcinol	CHCl$_3$	520	6.4	–	9
4-(2-Thiazolylazo)-resorcinol	Aqueous	510	6.0	0.2–2	12
2-(2-Benzothiazolylazo)-2-p-cresol	Aqueous (Triton X-100)	615	1.62	0.08–1.06	14
Sodium diethyldithiocarbamate	CCl$_4$	322	2.33	–	15
1-Nitroso-2-naphthol	Aqueous (Triton X-100)	420	3.18	0.2–3	16
2-Hydroxybenzaldehyde-5-nitro-pyridylhydrazone	Aqueous(CTMAB), separation by IRC-718 resin	470	6.5	0.02–2	17
α-Benzilmonoxime	CHCl$_3$	380	2.55	0.08–2.2	18
5-[o-Carboxyphenylazo]-2,4-dihydroxybenzoic acid	Aqueous (Tween-80)	550	1.64	0.1–3.5	19
5-(4-Sulfophenylazo)-8-aminoquinoline	Aqueous (CTMAB)	560	6.42	0.1–2	20
Nitroso-R Salt	CHCl$_3$	420	3.30	0.1–2	21
2-(3,5-Dibromo-2-pyridylazo)-5-dimethylamino-benzoic acid	CH$_2$Cl$_2$	673	15.5	0.0–0.35	22
2-(3,5-Dibromo-2-pyridylazo)-diaminotoluene	pH 4–8	590	13.4	0.01–0.4	23
5,10,15,20-Tetrakis-(4-sulfophenyl)-porphine	pH 4.0	426	35.4	0.0–0.2	24
2-(2-Quinolylazo)-5-dimethyl aminoaniline	Aqueous (CTMAB)	616	13.2	0.01–0.6	This work

Acknowledgement

The project was supported by Natural Science Foundation of Yunnan Province (0111143)

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