Spectrophotometric Determination of Cobalt(II) in Water after Preconcentration by Sorption of Its Nitroso R Complex with Poly(chlorotrifluoroethylene) Resin[†]

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A simple and rapid method has been established for spectrophotometric determination of cobalt(II) in water after preconcentration by sorbing the nitroso R (sodium-1-nitroso-2-hydroxynaphthalene-3,6-disulfonate) complex of cobalt(II) on poly(chlorotrifluoroethylene) resin. The cobalt-nitroso R complex was quantitatively retained on the resin as an ion associate complex with tetrabutylammonium cation in the range of pH 5.5 to 8.5. The retention capacity was 41.6 μg (0.71 μmol) Co g^{-1} resin at a maximum flow rate of 30 ml min^{-1} . Cobalt retained on the resin column was completely extracted with 5 ml of methanol which was submitted to spectrophotometric measurement at 550 nm after 1 ml of 1.0 mol dm^{-3} nitric acid was added. The proposed method was applied to a river water sample.

Keywords Cobalt, preconcentration, nitroso-R salt, poly(chlorotrifluoroethylene) resin, spectrophotometry

In spite of recent advances in instrumental analysis, a direct determination of trace elements in complex matrices, such as environmental, biological, mineral, ore and high purity materials, seems still to be difficult because of insufficient sensitivity and selectivity of the methods. Thus, enrichment and separation of the analytes is important for the determination of cobalt, because of its extremely low concentration in natural water. Among a wide variety of methods proposed and used for preconcentration of cobalt, solvent extraction and column extraction using various sorbents have been most frequently used. The latter is superior to the former in its ability to treat a large volume of samples in a closed system free from contamination, with a high concentration factor.

The following three types of sorbents have been employed for concentration of trace metals including cobalt: (i) ligand-immobilized sorbents¹⁻³, (ii) ligand-impregnated sorbents⁴⁻⁷, and (iii) unloaded sorbents which collect the metal complex previously formed in an aqueous solution.⁸⁻¹² In the case of type (iii), Amberlite XAD resins have been used as column packings, combined with various kinds of ligands. On the other hand, the present authors have found that poly(chlorotrifluoroethylene) resin (PCTFE) effectively adsorbs some metal complexes. The metal retained on the polymer can be easily eluted with hydrochloric acid or methanol.^{13,14}

This polymer has some advantages over XAD resins: (i) excellent chemical and mechanical resistance making it possible to be used repeatedly, and (ii) no swelling in any solvent, which allows a high flow rate of the sample passage to be attained. Recently, this method has been satisfactorily applied to analysis of 8-quinolinol-Cu (fungicide) in the environmental water.¹⁵

A highly specific reagent for cobalt complexation, nitroso R salt which gives a water-soluble red complex, provides a very sensitive and selective method for the determination of traces of cobalt.¹⁶ However, the detection limit obtained by the direct spectrophotometric measurements using 1.0 cm cell was about 50 $\mu\text{g dm}^{-3}$, which is about 20 times that obtained with ICP-AES but not low enough for determining cobalt(II) in natural waters. Therefore, in the present study, a technique to preconcentrate cobalt by adsorbing its nitroso R complex onto PCTFE resin, was investigated in order to establish a simple and rapid method for spectrophotometric determination of cobalt in natural water.

Experimental

Apparatus

A Shimadzu Model UV-160 UV/VIS spectrophotometer with a 1.0 cm quartz cell was used for absorbance measurement. A small volume flow cell (ϕ 5 mm) mounted in a Nihonbunko Model U-best UV spectrophotometer and a Tokyo Rikakikai Model MP-3 peristaltic pump were used in the flow system for column experiments.

The column was a glass tube (10 mm i.d.) with a coarse sintered glass disc and a stop cock at the bottom.

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Reagents

All chemicals and solvents used were of analytical reagent or poisonous metal analysis grade. Methanol was a Nacalai Tesque brand high purity solvent.

Deionized distilled water (DDW) prepared with a Barnstead Nanapure system was used in all experiments.

A commercially available PCTFE (Neoflon, Daikin Kogyo, Osaka, molding powder) was sieved to 80–100 mesh and finer than 100 mesh sizes. Specific surface areas of the powders were measured by BET method and found to be $3.27 \text{ m}^2 \text{ g}^{-1}$ for the latter. Those powders were purified by washing with a mixture of hydrochloric acid and methanol (1:1 v/v), and then washed with DDW and stored in methanol prior to use.

A 1000 mg dm^{-3} cobalt(II) stock solution was prepared by dissolving cobalt(II) nitrate reagent in 0.1 mol dm^{-3} hydrochloric acid.

A 0.2% nitroso R salt solution and a tetrabutylammonium chloride (TBAC) solution were prepared by dissolving each reagent in DDW. A citrate buffer solution was prepared by dissolving 21 g of citric acid and 11.8 g sodium hydroxide in 100 ml of DDW.

Preparation of PCTFE column

PCTFE powder was slurried with methanol by using an ultrasonic vibrator for 5 min (under the condition 1.0 g of 100 mesh resin became 2.2 ml), and then poured into the glass column. After the methanol level was brought to the column bed, the column was carefully washed with at least 50 ml of DDW without disturbing the resin bed. The prepared column was always filled with DDW in order to prevent the resin bed from drying.

General procedure

To an aliquot of Co^{II} solution were added 1 ml of citrate buffer solution, 2 ml of 0.2% nitroso R salt solution and 1 ml of TBAC solution as a counter ion reagent. The resulting solution (*ca.* pH 6.5) was passed through the PCTFE column at a given flow rate with the aid of a peristaltic pump. The cobalt retained on the column was eluted with 5 ml of methanol. After 1 ml of 1.0 mol dm^{-3} nitric acid was added, the absorbance of the effluent was measured by a spectrophotometer at 550 nm. The PCTFE column can be used repeatedly after washing with DDW.

The chromatographic characteristics of Co-nitroso R complex on PCTFE column were examined using a flow system. An aqueous complex solution containing TBAC and with pH adjusted to *ca.* 6.5 was passed through the PCTFE column connected to the system using a peristaltic pump. The absorbance of the effluent was continuously measured using a small volume flow cell.

Results and Discussion

Effect of pH on the retention of Co-nitroso R complex

The recovery of Co-nitroso R complex from an

aqueous solution was examined in the range of pH 3.0 to 11. A 100 ml portion of the complex solution ($\text{Co}: 10 \mu\text{g dm}^{-3}$) was passed through the column. The results are shown in Fig. 1. The quantitative recovery of cobalt is attained in the range of pH 5.5 to 8.5. This fact indicates that change in the pH of natural water is not a significant factor which would affect the recovery of the Co complex. The optimum pH of the solution was selected to be around 6.5 in all experiments.

Retention and elution of Co-nitroso R complex

The loading curves for different concentrations of Co-nitroso R complexes are shown in Fig. 2. An increase in

Fig. 1 Effect of pH on retention of cobalt-nitroso R complex.

Fig. 2 Loading curves of cobalt-nitroso R complex for different cobalt concentrations: (a) 0.025, (b) 0.05, (c) 0.1 and (d) 0.25 mg dm^{-3} .

Table 1 Retention capacity of PCTFE resin for cobalt-nitroso R complex as a function of cobalt(II) concentration

Co ^{II} concentration/ mg dm^{-3}	Retention capacity ^a / $\mu\text{g g}^{-1}$ ($\mu\text{mol g}^{-1}$)
0.025	38.6 (0.66)
0.05	39.2 (0.67)
0.10	43.0 (0.73)
0.25	45.4 (0.77)
Average	41.6 (0.71)

a. 0.5 g of PCTFE was used.

retention was observed with increase in Co^{II} concentration. The sorption capacity of Co-nitroso R complex by PCTFE resin for different concentrations of Co^{II} are listed in Table 1. The average retention capacity was calculated to be $41.6 \mu\text{g}$ ($0.71 \mu\text{mol}$) g^{-1} polymer. This relatively low capacity may be attributed to the small surface area of PCTFE resin ($3.27 \text{ m}^2 \text{ g}^{-1}$), but it is considered to be enough for the preconcentration of trace cobalt(II) in natural water. Moreover, the small surface area of the resin also minimizes the volume of eluent used, so that a higher concentration factor might be attained. Table 2 shows the retention capacity for Co-nitroso R complex (Co : 0.1 mg dm^{-3}) from the aqueous solution of different ionic strength. As can be seen from the table, with an increase in ionic strength of the aqueous solution the retention capacity decreases.

A complete elution of the complex from the PCTFE column was attained by passing 3 ml of methanol; however, 5 ml methanol was used to fill a 1.0 cm cell with the eluate.

Effect of nitroso R salt concentration

For an analytical method using nitroso R salt as a colorimetric reagent for cobalt, it is important to determine the concentration of the reagent to be used. Although, an excess of the reagent used would assure a complete complexation of cobalt in an aqueous solution, a high concentration of the reagent might cause a blank problem for the samples with very low Co^{II} concentration.

Table 2 Retention capacity of PCTFE resin for cobalt-nitroso R complex from solutions of different matrices

Matrix ^a	Retention capacity ^b / $\mu\text{g g}^{-1}$
DDW	43.0
1.4% NaCl	40.1
3.5% NaCl	36.5

a. Citrate buffer was added (pH 6.5).

b. 0.5 g of PCTFE resin was used.

Fig. 3 Effect of nitroso R salt concentration on retention of cobalt-nitroso R complex.

The recovery of cobalt complex was examined as a function of concentration of nitroso R reagent using $20 \mu\text{g dm}^{-3}$ Co^{II} solution at pH 6.5. The results shown in Fig. 3 indicate that the recovery of cobalt is highly dependent on the reagent concentration. The retention recovery steeply increased from 1 to $10 \mu\text{mol dm}^{-3}$ in the reagent concentration, then gradually increased to reach quantitative retention at the concentration of $16 \mu\text{mol dm}^{-3}$. Thus, the reagent concentration of $16 \mu\text{mol dm}^{-3}$, i.e. about 50 times that of cobalt(II), was selected because it gave a reasonably high recovery of cobalt.

Effect of ion association reagent

Because nitroso R salt forms an water-soluble negatively charged complex with cobalt(II) ion, which shows strong polarity, cobalt was not adsorbed on non-polar PCTFE resin. However, by the addition of an ion association reagent such as TBAC, the complex anion was quantitatively retained on the polymer. This fact indicates that the formation of an ion associate between Co-nitroso R complex anion and TBA^+ cation gives a less polar bulky complex leading to an increase in retention ability of cobalt on the PCTFE column.

The effect of TBAC concentration on retention of the complex was investigated with 100 ml of $20 \mu\text{g dm}^{-3}$ Co-nitroso R complex solution at pH 6.5. The results are shown in Fig. 4. A quantitative retention of cobalt(II) was attained at a TBAC concentration above $9 \mu\text{mol dm}^{-3}$. The adsorption of the cobalt complex with TBAC on PCTFE column is described by the following equation:

$$K = \frac{[\text{Co-NRS}(\text{TBA}^+)_n]_{(\text{aq})}}{[\text{Co-NRS}][\text{TBA}^+]^n} \quad (1)$$

$$K_D = \frac{[\text{Co-NRS}(\text{TBA}^+)_n]_{(\text{resin})}}{[\text{Co-NRS}(\text{TBA}^+)_n]_{(\text{aq})}} \quad (2)$$

Fig. 4 Effect of tetrabutylammonium chloride concentration on retention of cobalt-nitroso R complex.

$$D = \frac{\Sigma C_{\text{resin}}}{\Sigma C_{\text{aq}}} = \frac{[\text{Co-NRS}(\text{TBA}^+)_n]_{(\text{resin})}}{[\text{Co-NRS}]_{(\text{aq})}} \quad (3)$$

where ΣC_{aq} and ΣC_{resin} are the total concentration of cobalt in aqueous phase and PCTFE resin phase, respectively, NRS represents nitroso R salt, and D is a distribution coefficient for the ion associate complex.

If we combine Eqs. (1) and (2) into Eq. (3), the distribution coefficient D can be expressed by the following equation:

$$D = K \cdot K_D (\text{TBA}^+)^n \quad (4)$$

or

$$\log D = \log K + \log K_D + n \log (\text{TBA}^+) \quad (5)$$

Therefore, according to Eq. 5, $\log D$ should increase linearly with the concentration of TBA^+ with a slope of n . The value of n was determined from the slope of the $\log D$ vs. $\log(\text{TBA}^+)$ plot shown in Fig. 5 and found to be 2. This fact indicates that a molecule of Co-nitroso R complex is associated with TBA^+ in the ratio of 1:2. Since the produced bulky complex may become more hydrophobic than the Co-nitroso R complex, the adsorbability on the hydrophobic polymer is significantly increased. Since the Co-nitroso R complex is regarded to be charged -3 , the value of n would be expected to be 3 to form a neutral complex. However, in the case of Cu^{II} -8-quinolinol-5-sulfonate complex, $[\text{Cu}^{\text{II}}\text{-SO}_3]^{2-}$, it was found that the complex was associated with TBA^+ in the ratio of 1:1 and was quantitatively retained on PCTFE resin. Moreover, tetraphenylporphine tetrasulfonate and humic acid were also effectively adsorbed on the polymer from sodium acetate/acetic acid buffer solution. In these cases, the sodium ion seemed to be the counter ion which associates to the above-mentioned bulky anions. In the present study the sodium ion also would associate with the Co-nitroso R-TBA complex anion, and the ion-associate complex was adsorbed on the resin.

Effect of flow rate on retention of cobalt(II)

Fig. 5 Relationship between $\log D$ and $\log [\text{TBAC}]$.

The effect of flow rate on recovery of cobalt(II) was examined by passing 100 ml of $20 \mu\text{g dm}^{-3}$ Co-nitroso R complex solution through the PCTFE column at pH 6.5. A quantitative and reproducible retention of the complex was attained at flow rates between 6 and 30 ml min^{-1} .

Effect of the volume of sample solution on retention of cobalt(II)

The recovery of cobalt(II) was examined using different volumes of sample solution ranging from 100 to 1000 ml. The results shown in Table 3 indicate that there is little change in recoveries of the element over the volume range described above. In the present study, since only 5 ml of an eluent is enough to completely extract cobalt from the PCTFE column, high concentration factor could be easily achieved by using a larger volume of a sample in the case of low concentration cobalt.

Selection of wavelength for measuring absorbance

The wavelength of maximum absorbance of the Co-nitroso R complex was found to be 415 nm, as shown in Fig. 6-a. However, the absorbance by the reagent itself was also very high at this wavelength (Fig. 6-b). Therefore, in this study, the absorbance of cobalt complex was measured at wavelength 550 nm, at which the absorbance of the reagent is negligibly low. The absorbance difference between the complex and the reagent is nearly equal to that measured at wavelength 415 nm.

Effect of foreign ions and removal of interference

Interferences with the spectrophotometric determina-

Table 3 Effect of sample volume on the recovery of cobalt

Sample volume/ ml	Co ^{II} concentration/ $\mu\text{g dm}^{-3}$	Recovery ^a , %
100	10	94.3
250	10	96.2
500	10	98.3
1000	5	97.6

a. Average of three runs.

Fig. 6 Absorption spectra of (a) cobalt-nitroso R complex and (b) nitroso R salt in methanol.

Table 4 Interference of foreign ions

Ion	Concentration/ mg dm ⁻³	Absorbance ^a	
		Absorbance ^b	
Co ^{II}	0.05	0.042	0.042
Fe ^{III}	5.0	0.194	0.002
Cu ^{II}	0.5	0.059	0.002
Cr ^{VI}	0.1	0.001	—
Ni ^{II}	1.0	0.002	—
Mn ^{II}	1.0	0.002	—
VO ₂ ⁺	1.0	0.002	—

a. Methanol effluent.

b. Methanol effluent added 1.0 ml of 1.0 mol dm⁻³ HNO₃.Table 5 Analysis of river-water for cobalt(II)^a

Sample volume/ml	Co ^{II} /μg dm ⁻³		Recovery, %
	added	found	
250	—	1.5 ₂	—
	1.0	2.4 ₆	94±5
	5.0	6.3 ₂	96±7
500	—	1.4 ₈	—
	2.5	3.9 ₃	98±6
	5.0	6.1 ₃	93±5

a. Average of three runs.

tion of cobalt(II) as its nitroso R complex had been reported for Fe^{III}, Cu, Cr^{IV}, Ni, VO₃⁺, and Mn^{II}.¹⁷ However, interferences with Cr^{IV}, Mn^{II} and VO₃⁺ were negligible in concentrations of 2, 20 and 20 times that of cobalt. The interferences by the other ions which may form their complexes with the reagent could be minimized by adding 1 ml of 1.0 mol dm⁻³ nitric acid to the methanol effluent prior to absorbance measurement. By this treatment, the complexes of these metals might dissociate. The results summarized in Table 4 indicate that interferences by Fe^{III} and Cu become negligibly small up to concentrations 100 and 10 times that of cobalt, respectively. Then, the proposed method can be regarded as highly selective and sensitive for determination of cobalt.

Analysis of river water for cobalt(II)

To confirm the usefulness of the proposed method,

concentration of cobalt(II) in a sample of river water (Tatsumi canal flowed from Sai-river, Kanazawa City) was measured. Replicate results for 250 ml and 500 ml of the water samples are given in Table 5. The satisfactory results of recovery were obtained and the average concentration of cobalt(II) was 1.5±0.2 μg dm⁻³.

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