

**PRECONCENTRATION AND DETERMINATION OF TRACES OF COBALT (II)
AS A THENOYLTRIFLUOROACETONE COMPLEX WITH
DIBENZO-24-CROWN-8 BY SYNERGISTIC EXTRACTION AND
GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY**

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A new solvent extraction technique for the enrichment and determination of traces of cobalt (II) in natural waters was developed by means of the synergistic action of thenoyltrifluoroacetone (TTA) and dibenzo-24-crown-8 (DB24C8) in *o*-dichlorobenzene combined with graphite furnace atomic absorption spectrophotometry. The composition of the resulting adduct was determined by slope analysis revealing a stoichiometric formula of $\text{Co}(\text{TTA})_2\text{DB24C8}$ with a stability constant ($\log \beta$) of 5.51. Calibration plots of cobalt (II) gave linear responses ($r^2 = 0.999$) with increasing concentration of the standards in the ng/mL range. The detection limit was 0.015 ng/mL. The analytical precision was less than 4% (RSD), and the spike recoveries of cobalt (II) was $\geq 89\%$ for the preconcentration factors up to 20-fold. The method was applied to the determination of the cobalt content in Kakehashi river (Komatsu City), Japan Sea (Uchinada Town) and tap water (Kanazawa University) samples and the results were found to be 5.82 ± 0.73 ng/mL, 0.097 ± 0.010 and < 0.015 ng/mL, respectively.

1. Introduction

The average concentration of cobalt in natural waters is 0.04 ng/mL in fresh waters and 0.05 ng/mL in sea waters¹⁾. However, higher concentrations can be expected with the use of cobalt in various industrial applications²⁾ such as in steels, alloys, pigment in paints, etc. Interest in cobalt analysis in environmental samples has grown due to reports of associated diseases like pulmonary fibrosis^{3, 4)} and idiopathic dilated cardiomyopathy⁵⁾ as recent studies have shown. This alarming biological impact therefore necessitates continuous monitoring.

Complex formation as a mechanism for the isolation and/ or preconcentration of cobalt has been explored extensively; 8-quinolinol and 1-nitroso-2-naphthol complexed with nickel as the carrier element has been used for co-precipitation of cobalt from seawaters in conjunction with a specialized miniature cup for the graphite furnace atomic absorption spectrophotometer⁶⁾; dialkyldithiophosphate of cobalt allows its selective C₁₈ sorbent extraction from coexisting cadmium, copper, lead and iron by flow injection⁷⁾ using synthetic solutions, while, a 99.5% recovery of cobalt (second circuit) as its Cyanex 272 complex from spent Ni-Cd batteries was obtained after previous separation of cadmium (first circuit) in solution⁸⁾. Several drawbacks to such methods can be seen such as the need for special gadgets, lack of real sample analysis and lengthy sample manipulation, respectively.

Recently, several papers have been published on the synergistic action of the β -diketone, thenoyltrifluoroacetone (TTA) and various crown ethers for the separation of traces of metals in waters coupled with atomic absorption spectrophotometry (AAS). The synergistic action of TTA and crown ethers via adduct formation has been known to be successful in the extraction of traces of Ba⁹⁾, Mn¹⁰⁾, Li¹¹⁾, Cd, Zn¹²⁾ and Pb¹³⁾ in waters. Several published papers were also found in the case of cobalt^{10, 14, 15)}, however, none of these reported practical applications to environmental samples.

The main objective of this research therefore is to investigate the applicability of the synergistic action of TTA and crown ethers through adduct formation for the enrichment and determination of traces of cobalt (II) in natural waters.

2. Experimental

2.1 Apparatus

A Hitachi Atomic Absorption Spectrophotometer equipped with a Zeeman Background Corrector, model Z-1600 for Flame-AAS (FAAS) and model Z-8270 for Graphite Furnace AAS (GFAAS); a Taiyo Recipro Shaker, model SR-II; a Tomy Seiko Swing Type Centrifuge, model CD-50R and a Hitachi-Horiba pH meter, model F-a2 were all used in this work.

2.2 Materials

TTA of reagent grade was purchased from Dojindo Chemicals Ltd. Japan. Dibenzo-24-Crown-8

(98% pure) was purchased from Kanto Chemicals Ltd., Japan and *o*-dichlorobenzene from Ishizu Seiyaku Ltd., Japan. All other chemicals were of guaranteed grade and were used without further purification.

Standard solutions of cobalt were prepared by dilution of a 1,000 $\mu\text{g/mL}$ stock solution of $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in dilute HNO_3 ($f = 1.00$, Ishizu Seiyaku Ltd.) to the working range using distilled-deionized water (Nanopure system, Barnstead Ltd. USA).

2.3 Procedures

Solvent Extraction The aqueous phase consisted of a 5 mL sample solution containing cobalt (10 ng/mL) and buffer (0.25 mL of 0.2 mol/L phthalate buffer) which was previously adjusted to the desired pH by the addition of either 0.05 mol/L HCl and/or 0.05 mol/L NaOH. The organic phase was a 5 mL solution of 0.1 mol/L TTA and 0.01 mol/L DB24C8 in *o*-dichlorobenzene. Both phases were contacted in a 30-mL centrifuge tube and were shaken on a shaking machine for 2 min. Phase separation was carried out by centrifugation at 2,000 rpm for 10 min, followed by filtration on a special filter paper (TOYO 2S, 90 mm in diameter), which allowed only the organic phase to pass through. The resulting pH (extraction pH) of the aqueous phase was then measured.

Back-extraction The cobalt-loaded organic phase (5 mL) was shaken with 5 mL of 0.05 mol/L HCl solution for 2 min. The concentration of cobalt back-extracted into the aqueous phase was determined by FAAS (in the preliminary investigations) and by GFAAS (in the analytical studies) at 240.7 nm under the manufacturer's recommended conditions.

3. Results and Discussion

3.1 Synergistic effect

The conditions adopted for the preliminary experiments were taken from the initial investigations on cobalt by Billah et al.¹⁰⁾. The synergistic effect of TTA and crown ethers in different solvents was initially optimized. *o*-Dichlorobenzene was selected on the basis of low solubility in water at the same time allowing for the quantitative extraction of cobalt. The variation in extraction behavior of cobalt with TTA and various crown ethers in *o*-dichlorobenzene with pH was also investigated. Significant variation of the extraction efficiency (% E) as a function of pH occurs in the region 3.0 to 4.75 for all crown ethers. The extractability of cobalt gave the following order: DC18C6 < DB24C8 < 15C5 < 18C6 < DB18C6 < 12C4 < B12C4 with increasing pH. DB24C8 was chosen as the optimum crown ether because of an observed higher extraction efficiency of cobalt in the pH region > 4.5 as compared to DC18C6, which was reported to have various conformational structures^{16,17)}.

The extraction of cobalt using TTA, DB24C8, and TTA-DB24C8 in *o*-dichlorobenzene exhibited different behaviors as shown in Table 1. The extraction of cobalt with TTA alone was accompanied by

precipitate formation; small yellowish opaque solids were collected on the filter paper. The extraction of cobalt was not observed at any pH region when using DB24C8 alone. The combination of TTA and DB24C8 in solution achieved 100% extraction of cobalt in the acidic region, which prevented the hydrolysis of the cobalt (II) ion.

Table 1. Synergistic effect of TTA and DB24C8 in *o*-dichlorobenzene

Reagent	pH	%E
TTA	4.33	0.0
	4.73	4.8
	5.07	4.8
	5.38	0.020
DB24C8	4.05	0.0
	5.16	0.0
	6.04	0.0
TTA – DB24C8	4.73	100
	5.25	100

TTA: 0.1 mol/L; DB24C8: 0.01 mol/L; Co: 8 μ g/mL; Solvent: *o*-Dichlorobenzene; Shaking time: 10 min

3.2 Effect of the shaking time and concentration factor

Examination of the recovery data in Table 2 as a function of shaking time (15 sec - 10 min) showed that attainment of synergistic extraction equilibrium was relatively fast for cobalt. A 100% recovery of cobalt was obtained for either forward or backward extraction within 1 min. Therefore a 2 min shaking time ensures quantitative recovery and lessens sample manipulation time.

Preconcentration was carried out by extracting traces of cobalt (8 μ g/mL) at pH 5.0, from a large volume of sample solution into a small volume of organic solvent to improve the sensitivity of the method. It was then found that quantitative recovery of cobalt could be achieved up to a preconcentration factor ($V_{aq}/V_{org} = 10:0.5$) of 20-fold. %E was calculated from the difference between the cobalt concentration in the aqueous phase before and after equilibration and thus back-extraction is unnecessary for the present purpose. For practical application of a 20-fold preconcentration, 80 mL of sample was extracted with 4 mL organic and back-extracted by 4 mL of stripping reagent. Extraction efficiency was found to decrease (< 95%) at higher enrichment factors.

Table 2. Effect of shaking time on the recovery of cobalt

Time	Forward extraction	Back-extraction
	Recovery (%)	Recovery (%)
15 sec	100	59.76
30 sec	100	70.47
1 min	100	100
2 min	100	100
4 min	100	100
6 min	100	100
8 min	99.75	100
10 min	100	99.00

TTA: 0.1 mol/L; DB24C8: 0.01 mol/L; Co: 8 μ g/mL; Solvent: o-Dichlorobenzene; pH: 5

3.3 Effect of pH

Cobalt was extracted with equal volumes of the immiscible phases in the region above pH 3.0 as shown in Fig. 1. Extractions of cobalt greater than 95% were obtained in a pH range of 4.5 to 5.9 in the presence of phthalate buffer (previously investigated). The influence of pH on the extraction efficiency of other metals was also investigated. Quantitative recovery was attainable in the pH range of 2.0 – 5.6 for Cu(II), 2.7 – 6.1 for Fe(III), 4.2 – 5.5 for Ni(II), 4.7 – 5.6 for Zn(II), 5.0 – 5.7 for Mn(II) and 5.0 – 5.8 for Cd(II).

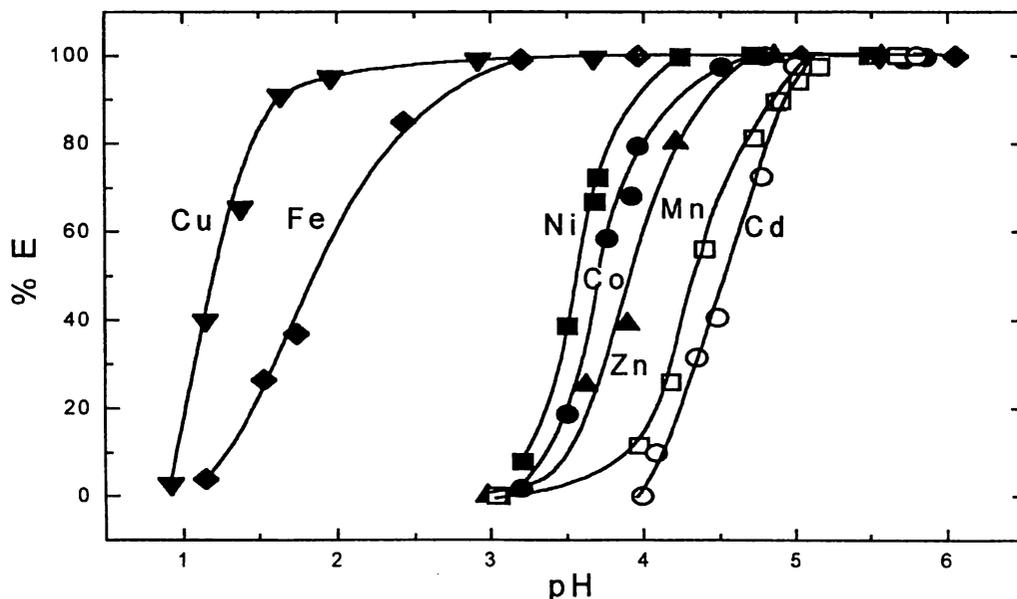


Fig. 1. Effect of pH on the extraction of cobalt and other heavy metals: ∇ Cu, \blacklozenge Fe, \blacksquare Ni, \bullet Co, \blacktriangle Zn, \square Mn and \circ Cd (TTA: 0.1mol/L; DB24C8; 0.01mol/L; Solvent: o-Dichlorobenzene; Shaking time: 2min)

3.4 Composition of extracted species

The composition of the extracted species was estimated by slope analysis; the plot of $\log D$ vs. $\log [\text{TTA}]_{\text{org}}$ at pH 3.8 (approx. equal to the pH of 50% extraction) and 0.01 mol/L DB24C8 (Fig. 2) gave a straight line with a slope of 1.96. This suggests the formation of a complex of $\text{Co}(\text{TTA})_2$ as expressed in equation (1). On the other hand, Fig. 3 indicates the variation of $\log D/D_0$ with increasing $\log [\text{DB24C8}]_{\text{org}}$. The slope of the line is unity at concentrations greater than 1×10^{-4} mol/L which indicates that the cobalt-TTA chelate forms a stable adduct with a stoichiometric formula of $\text{Co}(\text{TTA})_2 \cdot \text{DB24C8}$ having a stability constant ($\log \beta$) of 5.51. D and D_0 can be expressed as $D = \{[\text{Co}(\text{TTA})_2]_{\text{org}} + [\text{Co}(\text{TTA})_2 \cdot n\text{DB24C8}]_{\text{org}}\} / [\text{Co}^{2+}]$ and $D_0 = \{[\text{Co}(\text{TTA})_2]_{\text{org}}\} / [\text{Co}^{2+}]$, assuming negligible amounts of cobalt complexes in the aqueous phase due to the limited solubility of DB24C8 in water¹⁸. Here, D and D_0 are the distribution ratios of cobalt with or without DB24C8. D_0 was derived from the 5% E of cobalt using TTA only (Table 1) at pH 4.8. The adduct formation is expressed in equation (2). These results were found consistent with the independent results of Khalifa et al.¹⁴) and Aly et al.¹⁵). The adduct is assumed to have the structure described in Fig. 4.

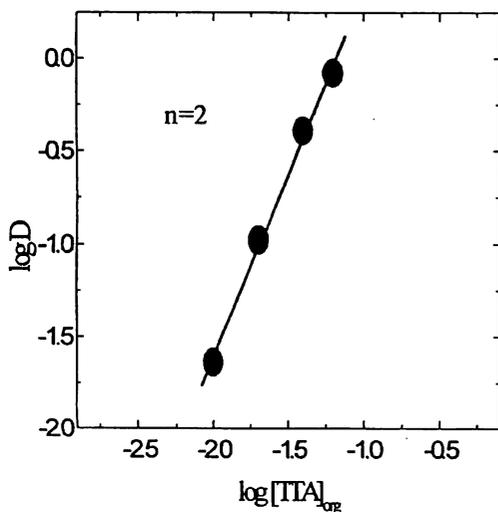
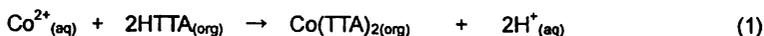


Fig. 2. Effect of TTA on the distribution ratio of cobalt with 0.01 mol/L DB24C8 in *o*-dichlorobenzene at pH 3.8

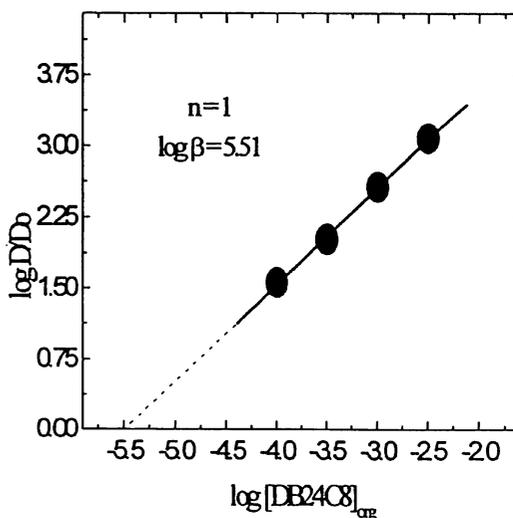


Fig. 3. Effect of DB24C8 on the distribution ratio of cobalt with 0.1 mol/L TTA in *o*-dichlorobenzene at pH 4.8

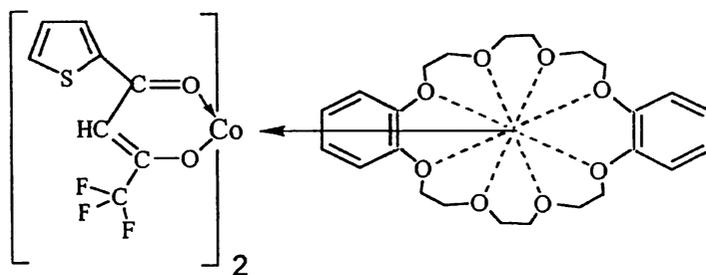


Fig. 4. Co – TTA - DB24C8 adduct

3.5 Effect of foreign ions

Foreign ions in increasing concentrations were spiked individually in 10 ng/mL cobalt solutions before extraction. The tolerance limit was defined as the maximum allowable concentration of the foreign ion in which a 100 % recovery of cobalt can be attained within a deviation of $\pm 5\%$. The results are summarized in Table 3. It can be seen that copper, iron, nickel and lead gave the lowest tolerance limit of about 250 times. This can be explained by the fact that copper, iron and nickel are extracted at lower pH values compared to cobalt (Fig. 1). The same phenomenon was considered in the case of lead¹³⁾, however, additional investigations are advised for confirmation. At the outset, the presence of most foreign ions (≥ 900 times) has an insignificant effect on the recovery of cobalt.

Table 3. Foreign ion effect on the extraction of cobalt

Foreign ion	Tolerance limit (times that of cobalt)	Recovery of cobalt, %
Na ⁺	> 1000	100
K ⁺	> 1000	100
Mg ²⁺	> 1000	100
Ca ²⁺	> 1000	100
Sr ²⁺	> 1000	100
Ba ²⁺	> 1000	100
Cu ²⁺	300	100
Fe ³⁺	250	100
Zn ²⁺	> 1000	100
Cd ²⁺	> 1000	100
Mn ²⁺	900	96
Pb ²⁺	250	95
Ni ²⁺	250	96
CO ₃ ⁻²	> 1000	100
NO ₃ ⁻²	> 1000	100
SO ₄ ⁻²	> 1000	100
Cl ⁻	> 1000	100

TTA: 0.1 mol/L; DB24C8: 0.01 mol/L; Solvent: o-Dichlorobenzene; Co: 10 ng/mL; pH: 5; Shaking time: 2 min

3.6 Analytical performance

The atomic absorption signal of cobalt was measured under the default settings of the GFAAS instrument and was found to be satisfactory. Increasing concentrations of cobalt (0 – 25 ng/mL Co in 0.05

mol/L HCl) gave a proportional increase in its absorption intensity. A linear calibration plot was obtained from five data points ($r^2 = 0.999$) as shown in Fig. 5. Absorption was measured as the area under the absorbance peak and all determinations were made in triplicate. The detection limit (D.L.), calculated as the average of the blank value plus three times its standard deviation, was 0.015 ng/mL. D.L. was also corrected for the method's ability to perform preconcentration up to 20-fold. Table 4 outlines both precision and recovery data obtained in the extraction of cobalt from representative samples. Analytical precision was excellent with relative standard deviation (RSD) falling below 4%. Good recovery was observed in both tap water and sea water, which indicates the efficiency of the method for cobalt determination regardless of sample complexity.

When a 5 mL seawater sample spiked with 10 ng/mL Co^{2+} was extracted with an equivalent volume of organic solvent, the extraction pH (4.18) was only slightly lower than optimum pH (5.0). An 89% recovery of cobalt is expected in the pH region immediately below 4.5 as can be seen in Fig. 1. HTTA (acid form), with its reported versatility in solvent extraction of many metal ions¹⁹, was apparently complexed with numerous metals from the sea water and released a considerable number of protons (H^+) as in the manner shown in equation (1). The observed phenomenon eventually disappeared at higher preconcentration factors due to the dispersion of H^+ to larger aqueous volumes, giving an insignificant pH lowering.

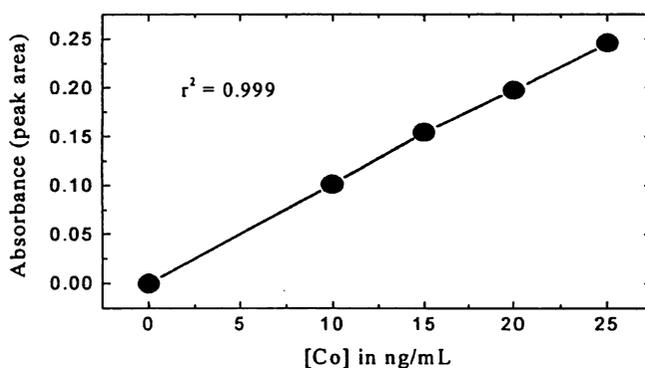


Fig. 5. Cobalt standard calibration curve

Table 4. Precision and recovery of cobalt spiked in natural waters

Sample	Preconcentration factor	Cobalt added (ng/mL)	Cobalt found (ng/mL) ^a	Recovery (%)	RSD (%)
Tap Water (Kanazawa University)	1	10	10.29 ± 0.40	103	3.89
	10	1	9.82 ± 0.33	98	3.36
Sea Water (Uchinada Town)	1	10	8.90 ± 0.17 ^b	89	1.93
	10	1	10.44 ± 0.18	104	1.72

TTA: 0.1 mol/L; DB24C8: 0.01 mol/L; Solvent: o-Dichlorobenzene; pH: 5; Shaking time: 2 min

^a Mean value of 3 determinations

^b Extraction pH= 4.18

3.7 Determination of cobalt in natural waters

Water samples were collected from different sites. The tap water was collected directly from the Analytical Laboratory of the Department of Chemistry, Kanazawa University. The fresh water sample was collected from the Kakehashi River that flows at the base of the abandoned Ogoya Copper Mine in Komatsu City. The saline water was collected from the Japan Sea in Uchinada Town. All sample solutions were passed through a $0.45 \mu\text{m}$ Millipore filter before being placed in polyethylene bottles. Samples were preserved by acidification to pH 1.0 with the addition of conc. HNO_3 . Additional recovery studies were made in parallel with the samples to check for matrix effects and to establish the credibility of the proposed method. The resulting analytical data using the recommended procedure (Fig. 6) is presented in Table 5. The cobalt content in the samples was corrected for the corresponding spike recovery, dilution (addition of buffer and acid/ base for pH adjustment) and preconcentration factor. As exemplified in the values shown, the method gave satisfactory results even for the complicated matrix of the sea water sample. The result for tap water, indicates that the adopted 20-fold preconcentration was insufficient and was not due to failure of the method as proven by the 96% spike recovery in Table 5. The analytical results for cobalt (Table 5) proved the efficiency of the combined action of TTA and DB24C8 via Co-TTA-DB24C8 adduct formation as the mechanism for the isolation, preconcentration and determination of cobalt at ppb to sub-ppb levels in natural waters.

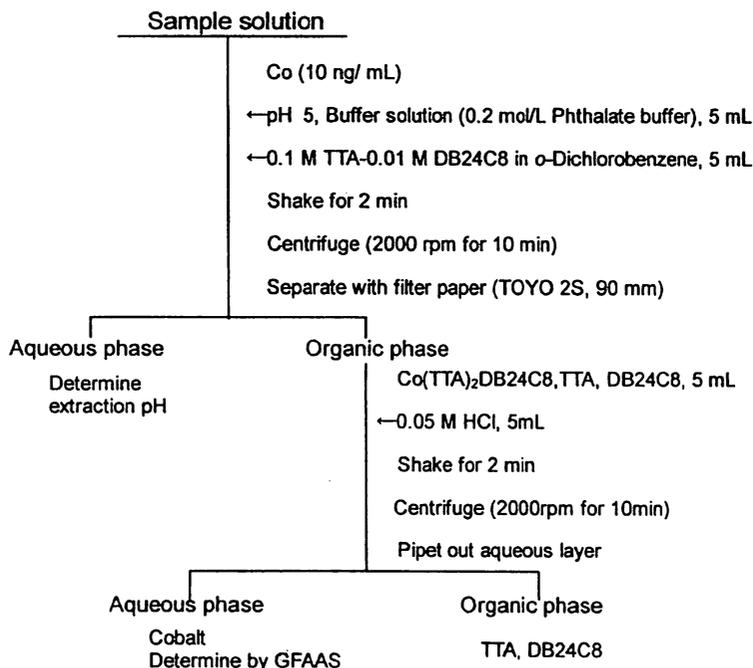


Fig. 6. Analytical scheme for the determination of cobalt in natural water samples

Table 5. Analytical results of cobalt in natural waters

Sample	Preconcentration factor	Cobalt added (ng/mL)	Cobalt found (ng/mL) ^a	Recovery (%)	Content (ng/mL)
River Water (Komatsu City)	1	-	3.90 ± 0.63	-	5.82 ± 0.73
	1	10	13.61 ± 0.14	97	
Sea Water (Uchinada Town)	20	-	1.68 ± 0.18	-	0.097 ± 0.010
	20	0.5	11.18 ± 0.10	95	
Tap Water (Kanazawa University)	20	-	< 0.015	-	BDL
	20	0.5	9.56 ± 0.53	96	

TTA: 0.1 mol/L; DB24C8: 0.01 mol/L; Solvent: o-Dichlorobenzene; pH: 5.0; Shaking time: 2 min

^a Mean value of 3 determinations

BDL: below detection limit

4. Conclusion

The synergistic action of TTA and DB24C8 in o-dichlorobenzene resulted in the quantitative extraction of cobalt in the acidic region. The stoichiometric formula of the adduct was determined by slope analysis and was found to be $\text{Co}(\text{TTA})_2\text{DB24C8}$ with a stability constant ($\log \beta$) value of 5.51. The optimum conditions involved only a few steps and short equilibration times. Interference studies revealed a high tolerance (≥ 900 times) of the proposed method for most foreign species investigated. When applied to real samples, the method gave satisfactory results regardless of sample matrix complexity and thus overcame the limitation of most analytical methods for cobalt determination in saline matrices. Moreover, the preconcentration step eliminates the need for highly sensitive instruments for detection. The analysis of real samples also confirmed the efficiency and suitability of the synergistic action of TTA and DB24C8 through adduct formation for the enrichment and determination of trace amounts of cobalt. The recommended procedure therefore offers a simple, fast and reliable new analytical technique for trace cobalt determination in natural waters.

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