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# ICP-OES Determination of Cobalt in Natural Water Using a Flow Injection System After Preconcentration on Activated Carbon

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## ABSTRACT

An on-line cobalt preconcentration system is described for the ICP-OES determination of cobalt in drinking water in a flow injection system. The methodology developed is simple and rapid. Trace amounts of cobalt were pre-concentrated by sorption on a conical mini column packed with activated carbon (AC) at pH 9.5, with retention of 95%. The cobalt was removed from the conical mini column with 20% (v/v) nitric acid. An enrichment factor of 95-fold for a sample volume of 50 mL was obtained. The detection limit for the preconcentration method proposed was found to be 20 ng $L^{-1}$. The precision for 10 replicate determinations at the 5-µg $L^{-1}$ Co level was 2.7% relative standard deviation, calculated from the peak heights obtained. The calibration graph preconcentration method for cobalt species was linear with a correlation coefficient of 0.9994 at levels near the detection limits up to at least 100 µg $L^{-1}$. The method was successfully applied to the determination of cobalt in natural water samples.

## INTRODUCTION

The toxicity of cobalt is low and is considered an essential trace element, required in human diet in the form of vitamin B12-(cyanocobalamin). For this reason, cobalt has been used in the treatment of anemia (1). However, the ingestion or inhalation of large doses may lead to toxic effects (2,3).

Since one of the routes of incorporation of cobalt into the human body is by ingestion (4), its determination in natural water becomes very important. Because the cobalt concentration levels are very low in water samples, sensitive analytical techniques are required to obtain low detection limits.

Within the last decade, inductively coupled plasma mass spectrometry ( ICP-MS) has proved ideally suited as an alternative approach for the determination of cobalt in various matrices (5–7). ICP-MS is used for the determination of Co because of its high sensitivity, high selectivity and high sample throughput. Nevertheless, the cost of instrumentation may be prohibitive to many laboratories.

Atomic absorption spectrometry with electrothermal atomization (ETAAS) has become the most appropriate technique for the determination of Co (8–11), but the detection limit of this method is not sufficient when the concentrations are too low. Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely recognized as a suitable technique for the determination of trace elements. However, the low level of Co in natural waters is not compatible with the detection limit of this technique. In order to achieve accurate, reliable, and sensitive results, preconcentration and separation are needed when the concentrations of analyte elements in the original material or the prepared solution are too low to be determined directly by ICP-OES.

Preconcentration is an effective means for extending the detection limits of ICP-OES methods. However, when practiced manually in the batch mode, the operations are usually too tedious to be compatible with the ICP-OES measurements. Stringent control of the laboratory environment is also required to avoid sample contamination if ultra-trace determinations in the ng $mL^{-1}$ range are to be attempted. This situation has been improved significantly by utilizing flow injection (FI) coupled with ICP-OES (12–14).

Activated carbon (AC) has been widely used for many purposes both in laboratory and industrial settings, due to its ability to adsorb organic and inorganic compounds. Since its introduction in analytical chemistry, enrichment of trace metals using AC has been favorably performed with very high concentration factors in different matrices (12–14).

The mechanism of sorption on AC is still under investigation. The most common model used for heavy metal adsorption is the classic empirical adsorption (e.g., Langmuir and Freundlich equations). The major advantage of this model is its simplicity; however, it fails to describe accurately the adsorption equilibrium under varying conditions, such as pH and ionic strength. Adsorption equilibrium studies have revealed that the pH

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is the dominant parameter controlling the adsorption (18).

Generally, sorption of dissolved metal ions on AC can be improved in the presence of chelating or precipitating agents (19–25). Trace levels of Co have been determined using complexing reagents such as ammonium pirrolidinedithiocarbamate (26), 8-hydroxyquinoline (27,28), potassium xanthogenate (29), potassium ethyl xanthate (30), pyrocatechol violet (31,32), 2-(5-Bromo-2-pyridylazo)-5-[N-propyl-N-(3-sulfopropyl)amino]phenol and 1-(2-Pyridylazo)-2-naphtol (33).

In this work, an on-line procedure for the preconcentration and determination of Co at low concentration levels by inductively coupled plasma using a conical mini column packed with AC is proposed. Cobalt was retained by sorption on activated carbon in the absence of a complexing reagent. The pH adjustment of the solution suffices to retain the cobalt ion.

## EXPERIMENTAL

### Instrumentation

The measurements were performed with a sequential ICP spectrometer (Baird, Bedford, MA, USA, Model ICP2070]. The 1-m Czerny-Turner monochromator had a holographic grating with 1800 grooves $mm^{-1}$.The ICP conditions are listed in Table I. The FI system used is shown in Figure 1. A Minipuls™ 3 peristaltic pump (Gilson, Villiers-le-Bel, France) was used. Sample injection was achieved using a Rheodyne® (Cotati, CA, USA) Model 50, four-way rotary valve. A home-made conical mini column (40 mm length, 4.5 mm internal upper diameter and 1.5 mm internal lower diameter) was used as the activated carbon holder. Tygon™ type pump tubes (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel the sample, reagent, and eluent. The 228.616-nm spectral line was used and FI system measurements were expressed as peak height emission, which was corrected against the reagent blank.

**TABLE I**
**ICP-OES Instrumental Parameters Used for Cobalt Determination**

| | |
|---|---|
| Forward Power | 1.0 kW |
| RF Generator | 40.68 MHz |
| Nebulizer | Glass, Meinhard |
| Plasma Gas Flow Rate | 8.5 L min-1 |
| Auxiliary Gas Flow Rate | 1.0 L $min^{-1}$ |
| Carrier Gas Flow Rate | 0.5 L $min^{-1}$ |
| Solution Uptake Rate | 1.5 mL $min^{-1}$ |
| Observation Height | 15 mm |
| Co Wavelength | 228.616 nm |

### Reagents and Standard Solutions

The activated carbon (Merck, Darmstadt, Germany, 50-70 mesh) was used after pretreatment with acid [activated carbon was heated to 60°C with 10% (v/v) hydrochloric acid for 30 minutes, then with 10% (v/v) nitric acid for 20 minutes, and finally washed with deionized water until neutral pH was reached]. The activated carbon can be used in several retention and elution runs without exhaustion.

Cobalt standard solution was prepared by appropriate dilutions of a 1000 mg $L^{-1}$ stock solution (Merck, Darmstadt, Germany) immediately before use.

Buffer solution was prepared by diluting a 0.05 mol $L^{-1}$ solution of borax adjusted to pH 9.5 with hydrochloric acid solution.

Ultrapure water (18 MΩ $cm^{-1}$) was obtained from an EASY pure RF (Barnstedt, Dubuque, IA, USA).

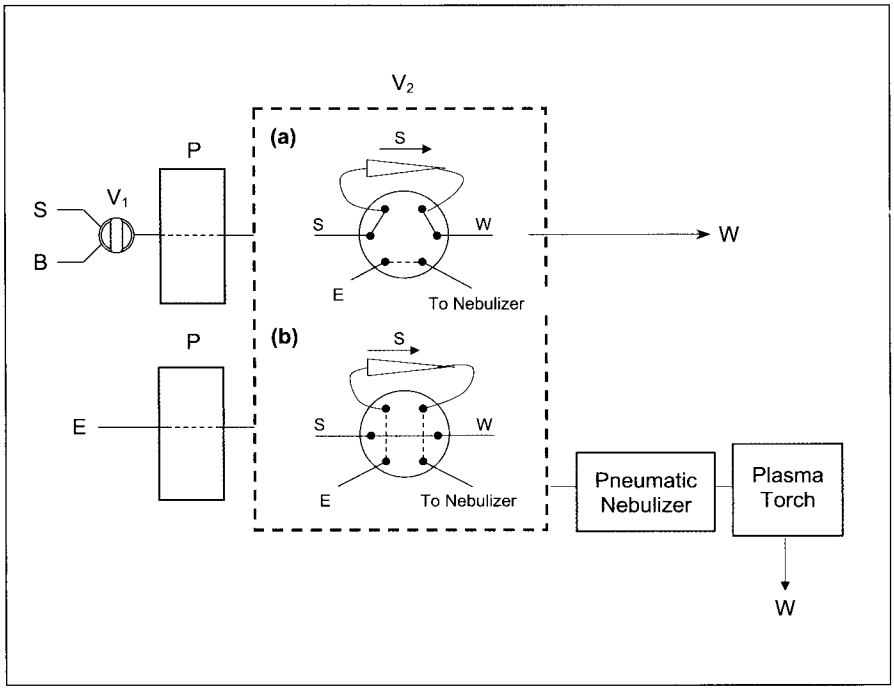


*Fig. 1. Schematic of instrumental setup.*
*S = sample (flow rate: 17 mL $min^{-1}$); E = eluent (flow rate: 1.5 mL $min^{-1}$); Ar flow rate of 0.7 L $min^{-1}$; W = waste; P = peristaltic pump; V2 = injection valve. Valve positions: (a) sample loading; (b) injection.*

All other solvents and reagents were of analytical reagent grade or better, and the presence of cobalt was not detected in the working range.

### Column Preparation

The conical mini column was prepared by placing 100 mg of activated carbon into an empty column using the dry packing method. To avoid loss of activated carbon when the sample solution passes through the conical mini column, a small amount of quartz wool was placed at both ends of the conical mini column. The column was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system.

### Sample Preparation

The natural water samples were filtered through 0.45-mm pore size membrane filters immediately after sampling, adjusted to pH 9.5 with borax solution, and stored at 4°C in Nalgene® bottles (Nalge Nunc International, Rochester, NY, USA).

All the instruments used were previously washed with a 10% (v/v) $HNO_3$ water solution and then with ultrapure water.

### Preconcentration Step

Before loading, the conical mini column was conditioned for preconcentration at the correct pH level (9.5) with 0.05 mol $L^{-1}$ borax buffer solution, valve V1 in position B (Figure 1).

The cobalt solution was then loaded on the activated carbon at a flow rate of 17 mL $min^{-1}$ with valve V1 in position S and valve V2 in load position (a).

After the loading time, the sample still present in the lines and the conical mini column was removed with a further washing with buffer-diluted solution, with valve V1 again on position B. Finally, peristaltic pump P was stopped and the injection valve V2 was switched on to the injection position (b) and the retained metal was eluted with 20% (v/v) nitric acid at a flow rate of 1.5 mL $min^{-1}$ directly in the glass nebulizer at the plasma. The operating system measurements were expressed as peak height emission, which was corrected against the reagent blank.

### Validation

In order to demonstrate the validity of this method, 1000 mL of water sample was collected and divided into 10 portions of 100 mL each. The proposed method was applied to six portions and the average quantity of cobalt obtained was taken as a base value. Then, increasing quantities of cobalt were added to the other aliquots of the sample, and cobalt was determined by the same method (Table II).

## RESULTS AND DISCUSSION

The analytical parameters, such as pH, activated carbon conditions, column design, size of activated carbon particles, sample loading rate, selection of eluent, interferents, and preconcentration system performance, were optimized.

Preconcentration of cobalt in natural water samples was necessary because its concentration is too low to be compatible with ICP-OES detection limits. The analytical results thus obtained were accuarate and precise.

The retention conditions of the metal were optimized and the cobalt signal was monitored by measuring it with ICP-OES while changing the pH of the solution that passes through the sorption conical mini column. Figure 2 shows that the optimal pH values were in the range of 8.0–12.0. Based on these results, the pH selected was 9.5.

The flow rate of the sample through the conical mini column is a very important parameter, since this is one of the steps that controls the analysis time. It could be verified that with flow rates up to 17 mL $min^{-1}$ there is no effect on analyte recovery, which in optimum conditions is approximately 95%. Figure 3 shows that at higher flow rates the recovery decreases. In comparison with adsorption resins type XAD and complexing reagents, optimum recovery was reached only up to 12 mL $min^{-1}$ (34–37).

The column design strongly influences the performance of preconcentration systems (38). The proposed method was applied to a classical column (3.0 mm i.d.) and a conical mini column (4.5 mm internal upper diameter and 1.5 mm internal lower diameter), both columns packed with the same activated carbon mass.

From our studies, we could verify that the conical mini column performance was much better than that of the classical column, the

**TABLE II**
**Recovery Study (Tap Water) (95% Confidence Interval; n=6)**

| Aliquots | Base Value (μg $L^{-1}$) | Quantity of Co Added (μg $L^{-1}$) | Quantity of Co Found (μg $L^{-1}$) | Recovery (%)[a] |
|---|---|---|---|---|
| 1 | – | 0.00 | 0.50 ± 0.03 | – |
| 2 | 0.50 | 0.50 | 0.98 ± 0.03 | 96.0 |
| 3 | 0.50 | 1.00 | 1.49 ± 0.05 | 99.0 |
| 4 | 0.50 | 2.00 | 2.50 ± 0.04 | 100.0 |
| 5 | 0.50 | 5.00 | 5.49 ± 0.04 | 99.8 |

[a] 100 x [(Found-Base)/Added].

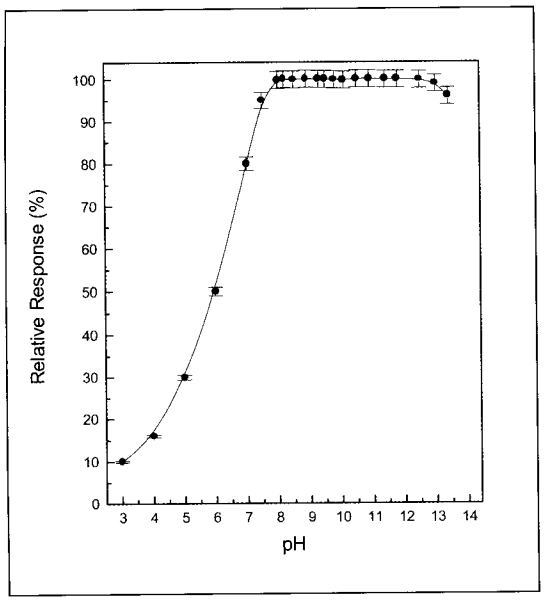


*Fig. 2. Dependence of Co preconcentration on pH of loading solutions. Sample loading volume was 50 mL; loaded flow rate was 17 mL min$^{-1}$; elution flow rate was 1.5 mL min$^{-1}$; and Co concentration was 5 µg L$^{-1}$.*

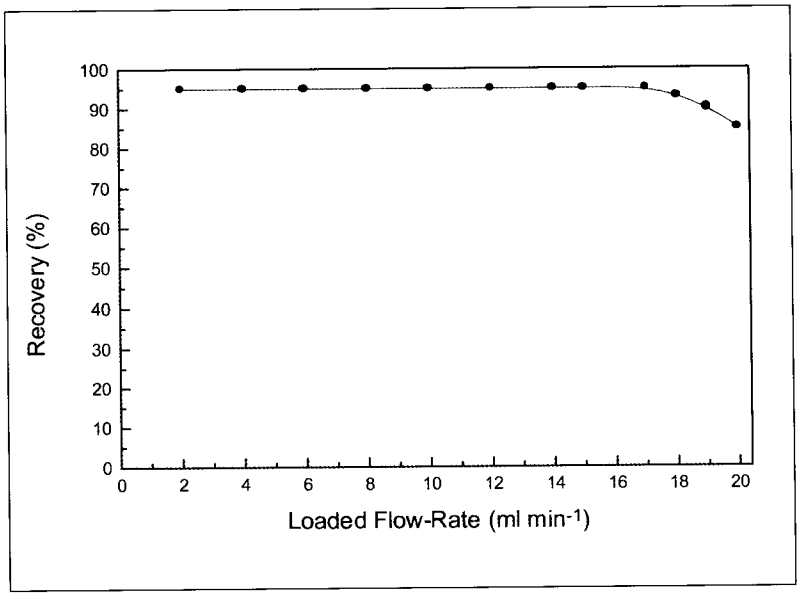


*Fig. 3. Dependence of metal recovery on loading sample flow rate. Preconcentration of 50 mL of Co; the elution flow rate was 1.5 mL min$^{-1}$; Co concentration was 5 µg L$^{-1}$.*

improvement being 120% with respect to the enrichment factor.

In the present work, an activated carbon of 50–70 mesh was considered adequate for the preconcentration procedure in the conical mini column. Smaller activated carbon particles could have improved the retention capacity, but this would have increased the backpressure of the mini column, requiring the flow rate to be reduced, with a subsequent increase in preconcentration time.

In order to elute cobalt adsorbed on the activated carbon, nitric acid was adopted as the eluent. Cobalt was completely eluted with 20% (v/v) $HNO_3$. The optimum eluent flow rate was 1.5 mL min$^{-1}$.

The effects of representative potentially interfering species (at the concentration levels at which they may occur in the sample studied) were also tested. Thus $Cu^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Mn^{2+}$, and $Fe^{3+}$ could be tolerated up to at least 2500 µg L$^{-1}$.

Commonly encountered matrix components such as alkali and alkaline earth elements are not retained on the activated carbon.

The overall time required for the preconcentration of 50 mL of sample (2.94 min, at a flow rate of 17 mL min$^{-1}$), washing (0.2 min), elution (0.5 min, at a flow rate of 1.5 mL min$^{-1}$) and conditioning (0.2 min) was about 3.84 min; hence, the throughput was approximately 15.62 samples per hour.

A total enrichment factor of 95-fold for a sample volume of 50 mL was obtained in the determination of Co by ICP-OES without preconcentration.

The relative standard deviation (RSD) for 10 replicates containing 5 µg L$^{-1}$ of Co was 2.7%. The calibration curve was linear with a correlation coefficient of 0.9994 up to at least 100 mg L$^{-1}$. The detection limit (DL), calculated as the amount of Co required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ), was 20 ng L$^{-1}$.

The accuracy of the method was evaluated by analyzing a standard reference material, NIST SRM 1640 Trace Elements in Natural Water, with a Co content of 20.28 ± 0.31 µg kg$^{-1}$, and a density of 1.0015 ± 0.0005 g mL$^{-1}$ at 22°C. Using the proposed method, the Co concentration determined in this SRM was 20.12 ± 0.11 µg kg$^{-1}$.

The results of the method obtained in the determination of Co in tap water and river water samples are given in Table III. The Co concentrations in tap water were in the range of 0.50–0.80 µg L$^{-1}$, and the Co concentrations in river water were in the range of 0.17–0.28 µg L$^{-1}$.

## CONCLUSION

The main difficulty in the determination of Co in natural waters is due to its low concentration levels. The procedure developed using an on-line preconcentration system with a FI-ICP-OES method shows adequate sensitivity, is simple and economical, since only activated

**TABLE III**
**Cobalt Concentrations in Tap Water and River Water Samples (95% Confidence Interval, n=6)**
**The tap water samples were collected in different places of San Luis City and the river water samples were collected in the Carolina River, Province of San Luis, Argentina.**

| Sample (Tap Water) | Co Conc ($\mu g\ L^{-1}$) |
|---|---|
| A | 0.50 ± 0.03 |
| B | 0.75 ± 0.04 |
| C | 0.40± 0.04 |
| D | 0.80 ± 0.03 |
| **Sample (River Water)** | **Co Conc ($\mu g\ L^{-1}$)** |
| A | 0.20 ± 0.03 |
| B | 0.28 ± 0.05 |
| C | 0.17 ± 0.03 |
| D | 0.23 ± 0.04 |

carbon is used for the preconcentration of Co without complexation.

The nearly instantaneous release of adsorbed metal during the elution phase and the dimensional stability of the activated carbon are ideal properties for its exploitation in on-line FI-ICP-OES systems.

The recovery studies using the standard addition method showed that the proposed method can be used for the determination of cobalt in natural water samples.

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