DETERMINATION OF COBALT BY ICP-AES IN DRINKING WATER SAMPLES USING A KNOTTED REACTOR WITH FLOW-INJECTION ON-LINE

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Abstract

An on-line cobalt preconcentration and determination system using a knotted reactor (KR) implemented with inductively coupled plasma atomic emission spectrometry (ICP-AES) associated to flow injection (FI) with ultrasonic nebulization (USN) was studied. The cobalt was retained as the complex cobalt-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Co-(5-Br-PADAP)), at pH 8.2. The cobalt complex was removed from the KR with 30% v/v nitric acid. A total enhancement factor of 140 was obtained with respect to ICP-AES using pneumatic nebulization (14.8 for USN and 9.5 for KR). The value of detection limit for the preconcentration of 10 ml of aqueous solution was 0.03 $ng.ml^{-1}$. The precision for 10 replicate determinations at the 5 $\mu g.l^{-1}$ Co level was 2.3 % relative standard deviation (RSD), calculated with the peak heights obtained. The calibration graph using the preconcentration system for cobalt was linear with a correlation coefficient of 0.9993 at levels near the detection limits up to at least 100 $ngml^{-1}$. The method was successfully applied to the determination of cobalt in drinking water samples.

Resumen

En el presente trabajo se estudió un sistema de preconcentración y determinación de cobalto usando reactores anudados (KR) y espectrometría de emisión atómica con plasma acoplado inductivamente (ICP-AES) asociado a un sistema de inyección en flujo (FI) y nebulización ultrasónica (USN). El cobalto fue retenido bajo la forma del complejo Co-2-(5-bromo-2-piridilazo)-5-dietilaminofenol (Co-(5-Br-PADAP)), a pH 8,2. The complejo de cobalto fue removido desde el KR con ácido nítrico al 30% v/v. Se obtuvo un factor de refuerzo total de 140 con respecto a la utilización de ICP-AES con nebulización neumática (14,8 para USN y 9,5 para KR). El límite de detección alcanzado para la preconcentración de 10 ml de solución acuosa fue de 0,03 $ng.ml^{-1}$. La precisión para 10 réplicas a un nivel de concentración de Co de 5 $\mu g.l^{-1}$, fue de 2.3 % expresado como desviación estándar relativa, calculada con la altura de los picos obtenidos. La curva de calibrado para el sistema propuesto, presentó un coeficiente de correlación de 0.9993 y fue lineal desde valores cercanos al límite de detección y hasta al menos 100 $ng\ ml^{-1}$. El método fue aplicado con resultados satisfactorios a la determinación de cobalto en muestras de agua de bebida.

Introduction

The toxicity of cobalt is low. Nevertheless, ingestion or inhalation of large doses may lead to pathological disorders. In acute toxicity, the main clinical manifestations are pulmonary edema, allergy, nausea, vomiting, and hemorrhage. In chronic toxicity, the clinical manifestations are pulmonary syndrome, skin syndrome, allergy, gastrointestinal irritations, nausea, cardiomyopathy, hematological disorders, and thyroid lesion [1].

Two main routes of absorption have been described for cobalt: inhalation and ingestion [1], therefore, its determination in drinking water becomes very important. Since the concentration of Co is usually low in drinking water (0.1-5 µg/liter) [2], powerful techniques are required for its determination although only a few of the most widely used methods show sufficient sensitivity.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is one of the most used techniques for the determination of cobalt traces. The most sensitive line for Co is at 228,616 nm. However, the determination limit that can be reached (approximately 40 $\mu g.L^{-1}$) is not enough for Co determination in drinking water without performing preconcentration and separation.

Many preconcentration techniques [3-7] for the determination of Co have been proposed, including chelation and extraction, precipitation, coprecipitation, and ion-exchange resins. However, many of these methodologies are performed in batch, thus requiring great sample volumes in order to reach low detection limits. Besides, these systems present higher contamination risks.

When preconcentration techniques are applied in batch mode, the time of analysis increases and the operations are usually too tedious to be compatible with the ICP-AES measurements. Furthermore, these procedures are not practical for application in routine analysis. This situation has been significantly improved utilizing FI associated with ICP-AES [8-9], such that general drawbacks of batch preconcentration procedures have been largely eliminated, and currently the preconcentrations can be achieved almost as efficiently as by simple ICP-AES determination. Reagent consumption is reduced usually to a little percent of that in batch procedures, and sample contamination is reduced, which becomes important when trace concentrations are determined. In fact, to date the most dramatic improvements achieved in FI-ICP-AES have been in the field of on-line preconcentration.

Flow injection on-line preconcentration based on the sorption of metallic complexes on the inner walls of a PTFE knotted reactor has been successfully applied [10-13]. ICP-AES thus appears to be an interesting alternative for coupling with KR in order to perform preconcentrations and determinations of metal traces, since besides exhibiting sensitivity similar to that of ETAAS, it has the advantage of coupling to systems working on-line.

Additionally, KR has the advantage of presenting low hydrodynamic impedance, permitting high load sample rates and elevated throughput sample.

2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) has been used as a reagent in the spectrophotometric determination of numerous metallic ions [14-16], although precautions such as the addition of surfactant agent have to be taken in order to

avoid the precipitation of the corresponding chelate. This suggested to us that, in absence of a surfactant, 5-Br-PADAP could be a suitable reagent for preconcentration of cobalt on KR.

In the present work, a method for preconcentration and determination of cobalt using a KR is proposed. Cobalt was retained under the form of Co-(5-Br-PADAP) complex. The determination was performed using ICP-AES associated with an FI methodology with ultrasonic nebulization.

Experimental
Reagents
A solution of 5-Br-PADAP (Aldrich, Milwaukee, WI, USA) 10^{-2} mol.L^{-1} was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution.

Working standard solutions were prepared by stepwise dilution from 1000 mg.L^{-1} Co stock standard solution (Merck) immediately before use.

A buffer solution was prepared by diluting a 0.05 M solution of borax adjusted to pH 8.2 with a hydrochloric acid solution.

Ultrapure water (18 MΩ.cm^{-1}) was obtained from a "EASYpure RF" (Barnstedt, Iowa, USA).

All the reagents were of analytical – reagent grade, and the presence of cobalt was not detected within the working range.
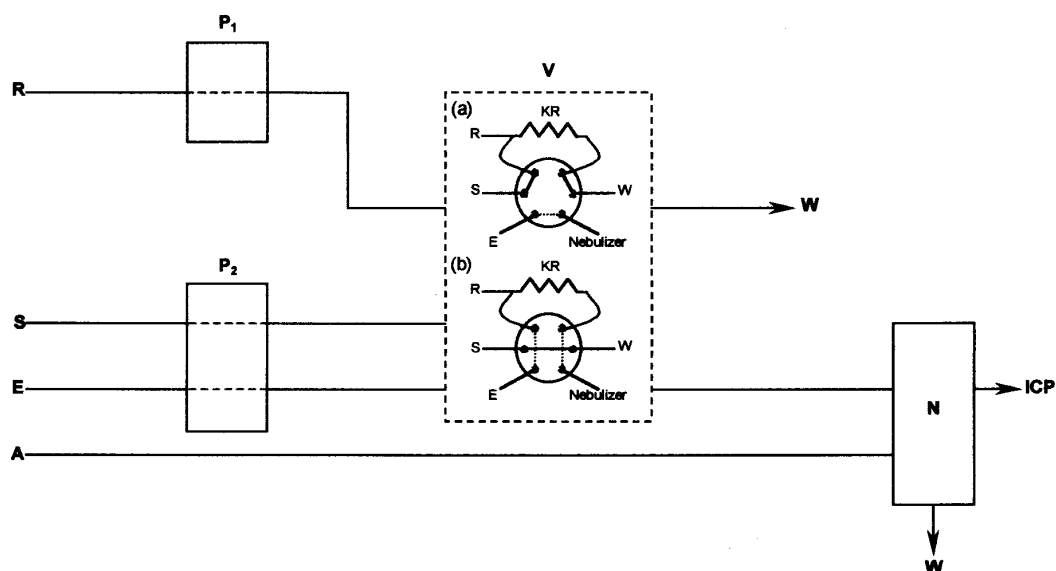

Figure 1: *Schematic diagram of the instrumental setup. R: 5 x 10^{-5} mol/L 5-Br-PADAP solution (2.5 mL/min) S: sample (flow rate: 5.0 mL/min), E: eluent (flow rate: 1.5 mL/min), A: Ar (flow rate: 0.8 L/min), W: waste, P₁, P₂: peristaltic pumps, V: injection valve, KR: Knotted Reactor, N: ultrasonic nebulizer. Valve positions: (a) sample loading; (b) injection.*

Instrumentation

The measurements were performed with a sequential ICP spectrometer [Baird (Bedford, MA, USA) ICP 2070]. The 1m Czerny-Turner monochromator had a holographic grating with 1800 grooves mm^{-1}. The ICP operating conditions are listed in Table 1. The FI system used is shown in Figure 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bell, France) was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. For sorption of the complex, a KR was made from a 2 m length of PTFE tubing of 0.5 mm internal diameter by tying interlaced knots of approximately 5 mm diameter loops. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was 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. An ultrasonic nebulizer (U-5000 AT [CETAC Technologies (Omaha, Nebraska, USA)]) with a desolvation system was used.

Sample preparation

The drinking water samples were filtered through 0.45 μm pore size membrane filters immediately after sampling, and were acidified to pH 2 with nitric acid and stored at 4ºC in bottles (Nalgene; Nalge, Rochester, NY, USA).

All laboratory ware was previously washed with a 10% v/v HNO_3 water solution and then with ultrapure water.

Procedure
Dependence of signal with sample loading rate

A known amount of cobalt and 5-Br-PADAP 5×10^{-5} mol.l^{-1} buffered a pH 8.2 were mixed to form the metal complex. This mixture was then loaded on the KR at variable-flow rate between 1 and 10 ml.min^{-1} during 120 s. Finally, the retained metal complex was eluted with 30% v/v nitric acid at 1.5 ml.min^{-1}.

Preconcentration step

The aqueous sample solution (0.01 mol.L^{-1} nitric acid) containing cobalt, at a flow rate of 5.0 ml.min^{-1}, and 5-Br-PADAP 5×10^{-5} mol.L^{-1}, at a flow rate of 2.5 ml.min^{-1} buffered to pH 8.2, were mixed on-line to form the metal complex. This mixture was then loaded on the KR for 120 s, valve V in load position (a) (Figure 1). Finally, peristaltic pump P_1 was stopped and the injection valve V was switched on to the injection position (b) and the retained metal complex was eluted with nitric acid 30% v/v at a flow rate of 1.5 ml.min^{-1}, directly in the ultrasonic nebulizer and ICP-AES.

Since the metal complex Co-5-Br-PADAP is not totally retained on the KR the standard solution must be also passed through the KR. The operating conditions were established and the determination was carried out.

Results and discussion

The preconcentration of cobalt from drinking water samples was necessary because its concentration is too low to be compatible with ICP-AES detection limits, even when an ultrasonic nebulization system is employed.

The preconcentration system using KR allowed the lowering of the ICP-AES detection limits to values compatible with the Co content in drinking water.

The cobalt signal was monitored by measuring it with ICP-AES while changing the pH of the solution that passes through of KR, in order to optimize the sorption conditions for the retention of the metal complexes. Figure 2 shows that the optimal pH values were in the 7.5 – 8.8 range. This phenomenon is understandable, since a better complexation occurs within this range. According to these results, the selected pH was 8.2.
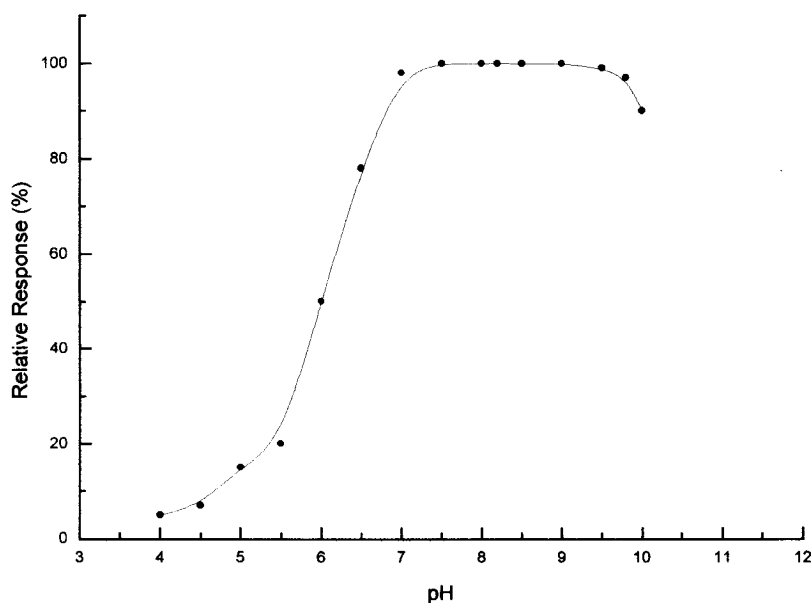

Figure 2: *Dependence of retention of complex Co-5-Br-PADAP on pH of loading solutions. Sample loading flow rate was 5 mL/min; the elution flow rate was 1.5 mL/min; Co concentration was 50 μg/L; 5-Br-PADAP concentration was 5 x 10^{-5} mol/L.*

The flow rate sample through the KR is a very important parameter, since it is a step, among others, that controls the time of analysis. We could verify that the optimum sample loading flow-rate was achieved at 5 ml.min^{-1}, which in optimum conditions allows reaching a total enhancement factor value of 140. A sample loading time of 120 s was used for preconcentration.

A preconcentration time of 120 s allows obtaining an acceptable enhancement factor as well as elevated throughput sample.

An important parameter to be optimized was KR length. Good results are obtained for a length of 200 cm, and further increases in length did not show any improvement in the enhancement factors. All other conditions were as in Table 1.

In order to avoid the precipitation of reagent 5-Br-PADAP in aqueous medium the solution of the complexing reagent was prepared in the presence of ethanol. It was observed that with 10% v/v of ethanol, 5-Br-PADAP remained in solution up to concentrations in the order of 10^{-4} mol.L^{-1}. Subsequently, the influence of ethanol concentration on the preconcentration of complex Co-5-Br-PADAP was assessed. From these results it can be seen that preconcentration decreases when ethanol concentrations above 25% v/v are used in the 5-Br-PADAP solutions. This behavior was to be expected since increasing solvent concentrations leads to higher solubility of the Co-5-Br-PADAP complex, which hinders its precipitation and adsorption on the KR walls.

Ethanol concentration was set at 10% v/v, which enabled to achieve both stability of the complexation reagent solution and efficiency of the system for preconcentration of the Co-5-Br-PADAP complex.

Concentration and flow rate 5-Br-PADAP solution

The 5-Br-PADAP solution concentration and loading flow rate were optimized. The minimum reagent-metal ratio necessary to achieve optimum preconcentration was 5:1. However, the maximum possible concentration of 5-Br-PADAP was 10^{-4} mol.L^{-1}, since at higher values the preconcentration capacity of the system is decreased, which could be attributed to the fact that the complexating reagent and the Co-5-Br-PADAP complex compete for adsorption on the KR inert walls. The 5-Br-PADAP concentration selected for the present work was 5×10^{-5} mol.L^{-1}.

The optimum load rate of the 5-Br-PADAP solution was 2.5 ml.min^{-1}. All other conditions are as indicated in Table 1.

-ICP conditions-	
RF generator power	0.8 kW
Frequency of RF generator	40.68 MHz
Plasma gas flow rate	8.5 L/min
Auxiliary gas flow rate	1 L/min
Carrier gas flow rate	0.8 L/min
Observation height (above load coil)	15 mm
Analytical line: Co	228,616 nm
-Preconcentration conditions-	
pH of loading solution	8.2
5-Br-PADAP concentration	5×10^{-5} mol/L
Loading flow rate 5-Br-PADAP	2.5 mL/min
Loading flow rate sample	5 mL/min
Loading time	120 s
KR length	200 cm
Ethanol concentration	10% (v/v)
Eluent concentration (HNO_3)	30% (v/v)
Eluent flow rate	1.5 mL/min

Table 1. *ICP instrumental parameters[a] and operating conditions. [a]A ultrasonic nebulizer was used*

Optimization of the elution conditions

The selection of eluent for the complex was critical. In most of the reported work, determination is done using ETAAS and therefore the use of an organic solvent does not cause any difficulties. This was not possible in this case, however, since organic solvents generate strong turbulence in the ICP, which can eventually lead to its extinction. Nitric acid turned out to be a good eluent for the Co-5-Br-PADAP complex with 25% v/v as the minimum concentration necessary to obtain the best response. A concentration of 30% v/v nitric acid was adopted for the remainder of this work.

The effect of the flow rate of eluent was also investigated, with the best response achieved at 1.5 ml.min^{-1}.

The typical elution profile for Co after complete optimization of the FI system is shown in Figure 3.
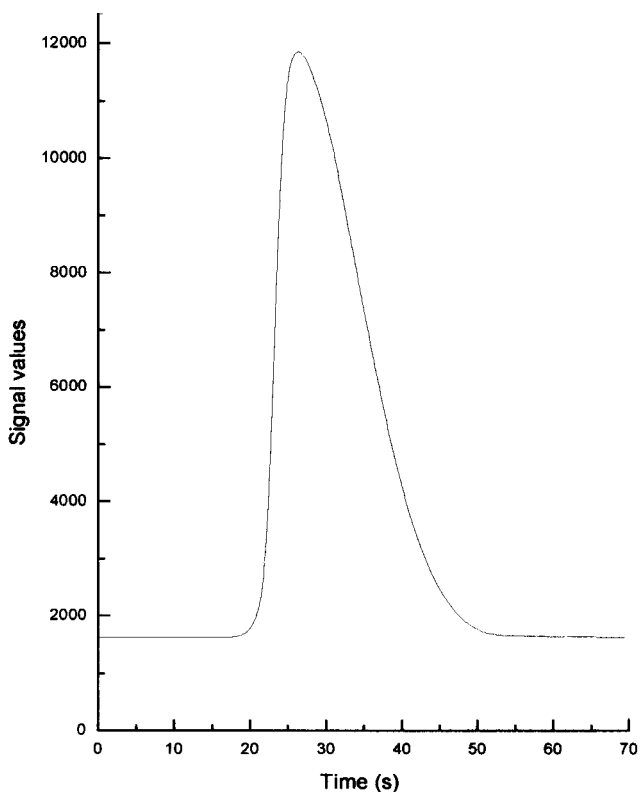

Figure 3: *Peak profile obtained by preconcentration of 10 mL of Co solution using the system depicted in Figure 1. Sample loading flow rate was 5 mL/min; the elution flow rate was 1.5 mL/min; Co concentration was 50 μg/L; 5-Br-PADAP concentration was 5 x 10^{-5} mol/L; pH: 8.2*

Interferences

The effects of representative potential interfering species (at the concentration levels at which they may occur in the sample concerned) were tested. Thus, $Cu^{+2}, Zn^{+2},$

Cd^{+2}, Ni^{+2}, Ca^{+2}, Mn^{+2} and Fe^{+3} could be tolerated up to at least 2,500 $\mu g.L^{-1}$. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not retained on the KR. The cobalt concentration used in this study was 1.0 $\mu g.L^{-1}$.

Performance of the preconcentration system with KR

The overall time required for preconcentration of 10 ml of sample (2 min, at flow rate of 5 ml.min^{-1}), elution (approx. 0.5 min, at flow rate of 1.5 ml.min^{-1}) and washing (0.2 min, at flow rate of 1.5 ml.min^{-1}) was about 2.7 min; the throughput was about 22 samples per hour.

An enhancement factor of 140 was obtained with respect to ICP-AES using pneumatic nebulization (14.8 for USN and 9.5 for KR).

Aliquots	Base Value ($\mu g/L$)	Quantity of Co Added ($\mu g/L$)	Quantity of Co found ($\mu g/L$)	Recovery (%)[a]
1	---	0.00	1.52 ± 0.03	---
2	1.52	0.20	1.71	95.0
3	1.52	0.40	1.92	100.0
4	1.52	0.80	2.31	98.8
5	1.52	1.20	2.71	99.2

Table 2. *Method validation.* [a]*100 x [(found-base)/added]*

The reproducibility of the preconcentration method was evaluated passing 10 ml of standard solution of cobalt (5 $\mu g.L^{-1}$) through the KR and repeating this procedure 10 times. The relative standard deviation (RSD) was 2.3%, calculated with the peak heights obtained. The calibration equation was: peak height = 190 + 2950 x C ($\mu g/L$). The calibration graph using the preconcentration system for cobalt was linear, with a correlation coefficient of 0.9997 at levels near the detection limit up to at least 100 $\mu g/L$. The detection limit (DL) was calculated as the amount of cobalt required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ). The value of DL obtained for the preconcentration of 10 mL of aqueous solution was 0.09 $\mu g/L$.

Sample	Co concentration ($\mu g/L$)
1	0.35 ± 0.15
2	0.40 ± 0.20
3	1.52 ± 0.14
4	0.98 ± 0.10
5	2.00 ± 0.10
6	1.90 ± 0.14
7	3.00 ± 0.10

Table 3. *Concentrations of cobalt in drinking water samples (95% confidence interval; n = 6)*

Method validation

In order to demonstrate the validity of this method, 1 liter of drinking water 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 sample and cobalt was determined by the same method (Table 2).

Determination of cobalt in drinking water

The results of the application of the method to cobalt determination in drinking water samples are shown in Table 3. The concentration was in the range 0.35-3.00 μg/L. The results obtained are in good agreement with those of Thunus and Lejeune [17], who reported cobalt concentration range of 0.1-5 μg/L.

Conclusions

The connection of an on-line preconcentration using a KR system with a FI-ICP-AES increases the speed of the preconcentration and analysis process and reduces sample consumption and contamination risks. The manifold presented provided an enhancement factor of 140 with respect to ICP-AES using pneumatic nebulization. This system of preconcentration associated with ultrasonic nebulization allowed cobalt determination in drinking-water samples in which its concentration is of the order of the $\mu g.L^{-1}$. The determination shows good reproducibility and accuracy.

Acknowledgements

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