

Determination of Cobalt in Food, Environmental and Water Samples with Preconcentration by Dispersive Liquid-Liquid Microextraction

Catalina Bosch Ojeda, Fuensanta Sánchez Rojas, José Manuel Cano Pavón

Department of Analytical Chemistry, Faculty of Sciences, University of Málaga, Málaga, Spain

Email: fsanchezr@uma.es

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ABSTRACT

A new method for the determination of cobalt was developed by dispersive liquid-liquid microextraction preconcentration and flame atomic absorption spectrometry. In the proposed approach, 1,5-bis(di-2-pyridyl) methylene thiocarbohydrazide (DPTH) was used as a chelating agent, and chloroform and ethanol were selected as extraction and dispersive solvents. Some factors influencing the extraction efficiency of cobalt and its subsequent determination, including extraction and dispersive solvent type and volume, pH of sample solution, concentration of the chelating agent, and extraction time, were studied and optimized. Under the optimum conditions, a preconcentration factor of 8 was reached. The detection limit for cobalt was $12.4 \text{ ng}\cdot\text{mL}^{-1}$, and the relative standard deviation (RSD) was 3.42% ($n = 7$, $c = 100 \text{ ng}\cdot\text{mL}^{-1}$). The method was successfully applied to the determination of cobalt in food, environmental and water samples.

Keywords: Cobalt; Dispersive Liquid-Liquid Microextraction; Flame Atomic Absorption Spectrometry; Water; Environmental and Food Samples

1. Introduction

In general, heavy metal ions are toxic, non-biodegradable, and tend to be accumulated in vital human organs, where they can act progressively over a long period through food chains. The determination of trace heavy metal ions in environmental samples has received increasing attention. Some trace elements are essential to man, whose daily requirement is only a few milligrams. However, if ingested in high levels, this can be harmful to human health. Thus, the elemental composition is essential to ensure food quality [1]. Cobalt is an essential trace element that has an important role in many bodily functions. It is toxic in large amounts and chronic ingestion of Co in the daily diet can cause toxic effects [2]. Toxicological effects of cobalt include vasodilatation, flushing and cardiomyopathy in humans and animals [3]. There is great interest in the determination of trace levels of Co in environmental investigations because cobalt affects living species as complexed Vitamin B12.

The quantification of metal species in various matrices has been performed by different techniques, including flame atomic absorption spectrometry (FAAS) [4], graphite furnace atomic absorption spectrometry (GFAAS) [5] and inductively coupled plasma optical emission spectrometry (ICP-OES) [6], among others. However, these techniques do not have adequate sensitivity and selective-

ity for some analyses. Thus, procedures of separation or preconcentration may be required to purify the sample and remove matrix interference before the determination of trace elements. In recent decades the developments of preconcentration steps prior to analytical determinations of trace level compounds have been explored in considerable depth. In this way, a number of accurate and reliable methods have been developed for Co(II) determination [7-19].

Dispersive liquid-liquid microextraction (DLLME) is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced comparing with the other methods [20,21]. DLLME is a novel miniaturized sample pre-treatment technique, which was successfully used for the extraction of different analyte types, organic and inorganic compounds. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery and high enrichment factor are some advantages of DLLME.

In DLLME, the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes. DLLME employs a mixture of a high-density solvent (extractant) and a water miscible, polar solvent (disperser). Acetone, methanol and acetonitrile can be used as dispersers, whereas chlorinated solvents (e.g. chlorobenzene, carbon tetrachloride, tetra-

chloroethylene) are useful as extractants. In practice, the extractant represents only around 1% - 3% of the total volume of the extraction mixture. Thereby, cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent, which disperse in the sample solution. Then, this cloudy solution shall be centrifuged and the fine droplets sediment at the bottom of the conical test tube. The determination of analytes in sediment phase can be performed by instrumental analysis.

The aim of present work was to develop a DLLME procedure combined with FAAS for cobalt determination, using 1,5-bis (di-2-pyridylmethylene) thiocarbonohydrazide (DPTH) as chelating reagent.

2. Experimental

2.1. Instrumentation

Phase separation was achieved with a centrifuge Selecta Centromix in 10 mL calibrated conical tubes.

A thermostated bath Model Selecta Precistern, maintained at the desired temperature, was used for the evaporation of chloroform.

A Varian Model SpectrAA 50 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for the analysis with the appropriate nickel hollow cathode lamp. The operating parameters were set as recommended by the manufacturer. Atomic absorption measurements were carried out in an air-acetylene flame. The following conditions were used: absorption line Co: 240.7 nm; slit widths: 0.2 nm; and lamp currents: 7 mA.

2.2. Reagents and Samples

High purity water (resistivity 18.2 M Ω cm) obtained by a Milli-Q® water purification system (Millipore, Bedford, MA, USA) was used throughout this work. 1000 mg·L⁻¹ stock solutions of cobalt (E. Merck, Darmstadt, Germany). Working standard solution was obtained daily by stepwise dilution of the standard stock solution. DPTH solution in DMF was prepared by dissolving solid reagent samples prepared and purified by the authors [22].

The accuracy of the method for determination of cobalt content was checked by analyzing two reference standard materials: TMDA-54.4 "Lake Ontario water"; for this sample the certified cobalt content was 309 ± 14 μ g·L⁻¹ and BCR 176 "City waste incineration ash"; for this sample the certified cobalt content was 30.9 ± 1.3 mg·kg⁻¹. BCR 176 was first prepared in accordance with the instructions on the analysis certificate, after which an accurately weighed amount (50.04 mg) was subjected to microwave digestion. The solution obtained was then adjusted to the optimum pH and, finally, the sample was diluted to 100 mL with de-ionized water in a calibrated flask.

Food and drinking water are the largest sources of ex-

posure to cobalt for the general population. In this sense, the proposed method was also evaluated by analysis of cobalt in several spiked samples. The cobalt concentrations in all the original samples were below the detection limit. For this purpose, standard solutions containing cobalt were added to 1 g of diverse food, soil and plants, and the resulting materials were mineralized by microwave digestion, adjusted pH and diluted at convenient volume.

Natural waters were collected in polypropylene bottles previously cleaned by soaking for 24 h in 10% (v/v) nitric acid and finally rinsed thoroughly with ultra-pure water before use.

2.3. Dispersive Liquid-Liquid Microextraction Procedure

For DLLME under optimum conditions, 10 mL analyte solution containing cobalt, 2 mL acetate buffer solution pH 5.2, 0.5 mL of 0.05% DPTH solution as chelating agent was placed in a 10 mL screw cap glass test tube. Then, 0.5 mL of ethanol (as disperser solvent) and 200 μ L of chloroform (as extraction solvent) were rapidly injected into a sample solution by using a microsyringe. A cloudy solution was formed in the test tube and separation of the phases was achieved by centrifugation at 3800 rpm for 5 min. After this process, a small droplet of organic phase was sedimented in the bottom of conical test tube. After removal of the whole aqueous solution, the extraction phase was evaporated in a water bath and the residue was dissolved into 0.5 mL of 0.1 M HNO₃ and the cobalt concentration was determined by FAAS. All experiments were performed in triplicate and the mean of results was used in plotting curves or preparation of tables for optimization.

3. Results and Discussion

In this work, we combined DLLME method with FAAS to evaluate the concentration of Co²⁺ in different real samples at trace levels. For this purpose, the effect of several experimental parameters influencing the extraction (DLLME) were investigated and optimized. These parameters comprise pH, amount of acetate buffer solution, amount of the chelating agent, selection of the type and volume of extraction and disperser solvents and ultrasound. One-variable-at-a-time optimization method was used to obtain optimum conditions for DLLME procedure. All analyses were carried out in triplicate.

3.1. Effect of pH

The extraction of cobalt ions by proposed DLLME procedure involves the formation of a complex with DPTH and extraction of this complex into small volume of extraction phase. Extraction yield depends on the pH at

which complex formation is carried out. The effect of pH on the complex formation and extraction of cobalt from water samples was studied within the range of 2.2 - 6.0 by using different buffers. From the results illustrated in **Figure 1**, a pH = 5.2 was chosen.

Also, the influence of acetate buffer solution amount was investigated for variation of volume added from 1 to 3 mL. The extraction efficiency was stable in all studied range. A volume of 2 mL was selected as optimum value for subsequent work.

3.2. Effect of DPTH Concentration

Concentration of chelating agent is an important variable to be optimized in a pre-concentration method. It is highly important to establish the minimal reagent concentration that leads to total complex formation while achieving the highest extraction [23]. The variation of the analytical signal as a function of the concentration of DPTH in the range of $2.5 \times 10^{-3}\%$ - $7.5 \times 10^{-3}\%$ (w/v) was studied, and the results showed that the change of DPTH concentration in the studied range has little effect on analytical signals. A $2.5 \times 10^{-3}\%$ (w/v) DPTH was selected for further research.

3.3. Effect of Disperser Solvent and Its Volume

The choice of dispersive solvent in DLLME depends on the miscibility in the organic extraction solvent and in the aqueous sample, with the purpose to disperse the extraction solvent into very fine droplets in to the aqueous sample. To study this effect, two different solvents and its volume, methanol and ethanol, were tested. As can be seen in **Figure 2**, results showed that there were no significant difference among absorbances obtained by the disperser solvent and the volume studied (0.5 to 1.5 mL), specially for ethanol. So, in further experiments, 0.5 mL of ethanol volume was selected.

3.4. Effect of Extraction Solvent Volume

Volume of extraction solvent is another important parameter for obtaining higher preconcentration factor and better extraction efficiency. To examine the effect of the extracting solvent volume, 0.5 mL ethanol solutions with different chloroform volumes, in the range of 200 - 400 μL , were subjected to the same DLLME procedure. The results showed that there were no significant differences among absorbances obtained. For this reason, 200 μL was selected because this volume required minor evaporation time.

3.5. Ultrasound Energy Effect

In DLLME, the ultrasound-assisted process was applied to accelerate the formation of fine cloudy solution with

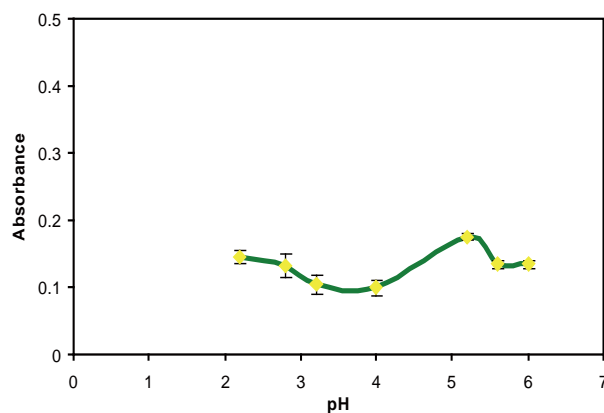


Figure 1. Influence of pH.

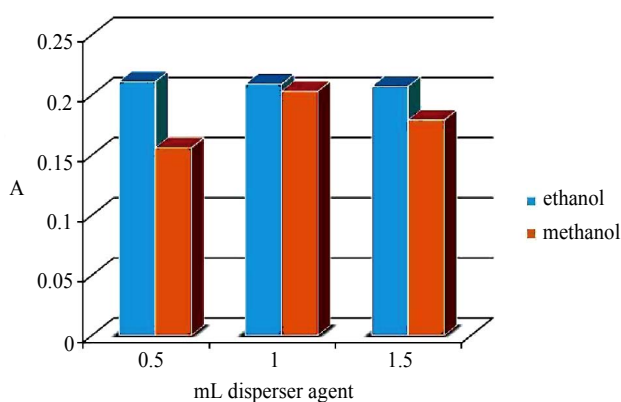


Figure 2. Effect of disperser solvent and its volume.

less disperser solvent, which is increased the extraction efficiency and reduced the equilibrium time. The use of ultrasound energy to disrupt the extractant phase reduces the consumption of organic solvent because even the disperser solvent is not needed, being ultrasound-assisted dispersive liquid-liquid microextraction a more environmentally friendly technique. However, no significant differences were obtained.

3.6. Analytical Figures of Merit

Under the optimal experimental conditions, a series of experiments were designed for obtaining linear range, precision, detection limit, preconcentration factor and other characteristics of the proposed DLLME method. Three replicate extractions were performed for each concentration level. The calibration curves were observed as linear in the concentration range of 50 - 500 $\text{ng}\cdot\text{mL}^{-1}$ Co by using 10 mL of the solution. The correlation coefficient of the calibration curve equation was above of 0.999, which indicates that a good linear regression was established between the absorbance and the concentrations. The detection limit was defined as the concentration of analyte giving signals equivalent to three times the standard devia-

tion of the blank plus the net blank signal. The precision for seven replicate determinations at $100 \text{ ng}\cdot\text{mL}^{-1}$ of cobalt was expressed as a relative standard deviation (RSD). Finally, the preconcentration factor was calculated by the ratio of the slopes of the lineal section of the calibration graphs before and after preconcentration. The results were given in **Table 1**.

3.7. Study of Interferences

In order to demonstrate the selectivity of the developed microextraction system, the effect of coexisting ions in samples on the recovery of cobalt were also evaluated. In these experiments, different amounts of ions were added to the test solutions containing $100 \text{ ng}\cdot\text{mL}^{-1}$ of cobalt and then followed according to general procedure. The tolerance level was defined as the maximum concentration of the foreign ion causing a change in the analytical signal no higher than 5%, when compared with the signal of $100 \text{ ng}\cdot\text{mL}^{-1}$ of cobalt alone. The results are given in **Table 2**.

3.8. Applications

3.8.1. Analysis of Standard Reference Material

In order to assess the accuracy and validity of the presented procedure, the method was applied to the determination of cobalt in certified reference materials (TMDA-54.4 "Lake Ontario water" and BCR-176 "City Waste Incineration Ash"), which were analyzed according to the proposed method. It was found that analytical results were in good agreement with the certified values (**Table 3**).

3.8.2. Determination of Cobalt in Food, Plant and Water Samples

In view of the application of the method to the determination of cobalt in food and plant samples, the ability to recover cobalt from different samples spiked with cobalt was investigated. All food samples were arbitrarily selected and acquired from a local superstore. For this purpose, standard solutions containing different quantities of cobalt were added to samples and the resulting material was prepared as described under Experimental. Standard additions method was used in all instances and the results were obtained by extrapolation. The results of these analyses are summarised in **Table 3**, and indicated excellent recoveries in all instances.

In the laboratory, before the preconcentration procedure, all the water samples were filtered through a $0.45 \mu\text{m}$ pore-size membrane filter to remove suspended particulate matter and were stored at 4°C . The optimized methodology was applied for the determination of cobalt in different water samples and the analytical results along with the recovery are given in **Table 3**. As can be seen, good recoveries were obtained in the spiked real samples analysis.

Table 1. Analytical features of the proposed method.

Dynamic range	50 - 500 $\text{ng}\cdot\text{mL}^{-1}$ Co(II)
Regression equation	$y = 0.0008 [\text{Co}^{2+}] + 0.0449$
Correlation coefficient (R)	0.999
Detection limit	$12.4 \text{ ng}\cdot\text{mL}^{-1}$
Determination limit	$48.0 \text{ ng}\cdot\text{mL}^{-1}$
R.S.D. (%) (n = 7)	3.42 ($100 \text{ ng}\cdot\text{mL}^{-1}$)
Preconcentration factor	50 (Volume ratio) 8 (Slope ratio)

Table 2. Interference of foreign ions.

Species	Tolerance (m/m)
F^- , Pb^{2+} , K^+ , I^- , Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , Fe^{3+} , Cr^{3+}	>500
Mn^{2+} , Cd^{2+} , Sn^{2+} , Zn^{2+} , Ba^{2+}	>100
Ni^{2+} , Cu^{2+}	>10

Table 3. Determination of cobalt in real samples.

Sample	[Co(II)] added ($\mu\text{g}\cdot\text{g}^{-1}$)	[Co(II)] Found* ($\mu\text{g}\cdot\text{g}^{-1}$)	Recovery (%)
TMDA-54.4	309 ± 14^b	312 ± 12^b	101.0
BCR 176	30.9 ± 1.3^a	30.2 ± 1.0^a	97.7
Tap water (I)	20^b	20.4 ± 0.5^b	102.0
Well water	20^b	19.9 ± 1.9^b	99.5
Tap water (II)	20^b	20.2 ± 1.8^b	100.5
Lentil	3.75	3.73 ± 0.02	99.5
Liver	2.95	2.93 ± 0.03	99.3
Rice	3.71	3.66 ± 0.11	98.7
Fish	4.57	4.58 ± 0.10	100.2
Chick-pea	2.95	2.90 ± 0.04	98.3
Lettuce	4.54	4.68 ± 0.10	103.1
<i>Bignonia</i> leaves	4.15	4.15 ± 0.03	100.0
<i>Pino</i> leaves	4.16	4.32 ± 0.25	103.8
Soil	2.41	2.37 ± 0.07	98.3

*mean \pm standard deviation; n = 3; ^acertified and found value ($\text{mg}\cdot\text{kg}^{-1}$); ^bvalue in $\text{ng}\cdot\text{mL}^{-1}$.

4. Conclusions

DLLME is a procedure of samples preparation inside "Green Chemistry" because of the small volumes of dissolvent employed. All variables that influence in the formation of the complex Co-DPTH have been optimized by this procedure. FAAS has been used as detection technique and detection limit is in the order of $\text{ng}\cdot\text{mL}^{-1}$.

The accuracy of the method has been studied by means of the analysis of certified samples. To study the applicability of the method diverse spiked samples with cobalt have been analyzed by using standard additions method. Good recoveries were obtained in all cases.

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