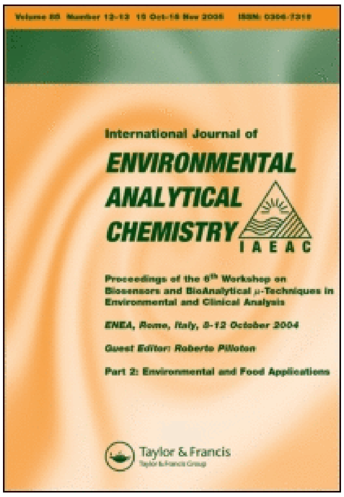

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# Preconcentration of cobalt using Amberlyst 36 as a solid-phase extractor and its determination in various environmental samples by flame atomic absorption spectrometry

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# Preconcentration of cobalt using Amberlyst 36 as a solid-phase extractor and its determination in various environmental samples by flame atomic absorption spectrometry

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A new and simple column-solid-phase extraction method has been developed to separate and preconcentrate trace cobalt in water and soil prior to its determination by flame atomic absorption spectrometry (FAAS). Different factors such as pH of sample solution, sample volume, amount of resin, flow rate of aqueous solution, volume and concentration of eluent, and matrix effects for preconcentration were optimized. Under optimized experimentally established conditions, an analytical detection limit of $0.44\,\mu g\,L^{-1}$, precision (RSD) of 1.9%, enrichment factor of 200, and capacity of resin of $82\,mg\,g^{-1}$ were obtained. The method was applied for cobalt determination by FAAS in tap water, natural drinking water, soil, and roadside dust samples. The accuracy of the method is confirmed by analysing standard reference material (Montana Soil, SRM 2711).

*Keywords:* Cobalt determination; Water analysis; Soil analysis; Roadside dust analysis; Preconcentration; Amberlyst 36

## 1. Introduction

The determination of trace amounts of cobalt in water samples and human environments is of great interest because cobalt is essential for living species as complexed vitamin $B_{12}$ (hydroxocobalamin), which catalyses reactions, such as the synthesis of methionine, the metabolism of purines and folates, and the formation of methylmalonic acid in succinic acid [1]. The deficiency of cobalt in humans and animals results in anaemia [2], while large amounts of cobalt lead to toxic effects (vasodilatation, flushing, and cardiomyopathy), usually after occupational exposure to cobalt dust (cobalturia, cobaltemia) [3, 4]. Since one of the routes of incorporation of cobalt into the human body is by ingestion, its determination in drinking water, food, and human environments such as soil and dust becomes very important [5]. Due to the high complexity of the matrixes and the low levels of metal ions in the aquatic samples, their separation and also the use of a preconcentration step prior to metal analysis

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are usually required. In this regard, many preconcentration procedures such as solid-phase extraction (SPE), coprecipitation [6], and liquid–liquid extraction [7] have been developed for the enrichment of trace cobalt in a diversity of matrices.

SPE involves the transfer of analytes from the aqueous phase to the active sites of the adjacent solid phase. SPE has come to the forefront compared with other preconcentration and/or separation techniques, as it offers several advantages such as higher enrichment factors, low cost (because of lower consumption of reagents), suitability for on-line procedures, speed and simplicity, safety with respect to hazardous samples and more importantly environmental friendliness [8, 9]. Consequently, in recent years, SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples [10].

Various sorbents, such as activated carbon [11], XAD-4 [12], silica-gel [13], and other sorbents [14–18] have been used to preconcentrate trace cobalt ions from various media. Cerutti and co-workers [5] developed a preconcentration-electrothermal atomic absorption spectrometry method for trace determination of cobalt in drinking water samples by sorption on a conical mini column packed with activated carbon at pH 9.5. Eskandari *et al.* [14] proposed an analytical method using $\alpha$-benzilmonoxime and microcrystalline naphthalene for sensitive and selective determination of cobalt. Taher [15] described an efficient method for the preconcentration of cobalt from a large volume of aqueous solutions of various alloys and biological samples with 1-nitroso-2-naphthol-3,6-disulphonate-tetradecyldimethylbenzyl-ammonium-naphthalene adsorbent.

In many separation/preconcentration procedures, such as those described above, either a known amount of chelating agent is added to the solution to form the metal chelate or a chelating agent is immobilized on a support of column prior to enrichment procedures. However, in this study, no agent was used as a chelating material or immobilized material. Cobalt(II) ions were retained on the resin without a chelating agent. In this SPE method, cobalt was adsorbed quantitatively onto Amberlys 36 without a chelating agent and then recovered using 5 mL of 4 mol $L^{-1}$ nitric acid. In this work, Amberlyst 36 was used first for the preconcentration of trace cobalt as a solid-phase extractor. It has been used before for the preconcentration of copper in our previous study [19]. This resin has also been used by Yadav and Joshi for different purposes [20]. They used it as a catalyst in the reactions of several organic components.

In the present study, a simple, selective, economical, and sensitive preconcentration/separation solid-phase extraction method for the determination of Co(II) has been established. The column-SPE method developed was applied to tap water, natural drinking water, soil, and roadside dust samples for determination of cobalt.

## 2. Experimental

### 2.1 *Apparatus*

A Philips PU 9285 model atomic absorption spectrometer, equipped with a deuterium-lamp background corrector, a cobalt hollow cathode lamp (Philips), and an air-acetylene flame as the atomizer was used for the determination of cobalt. The wavelength, lamp current, slit width, and acetylene flow rate were 240.7 nm, 11.0 mA, 0.5 nm, and 1.1 L min$^{-1}$, respectively. pH measurements were made with a Jenway 3010 model pH meter and a combination glass electrode.

### 2.2 *Reagents and solutions*

Triple-distilled water was used to prepare all solutions. All reagents were of analytical grade, unless stated otherwise. Laboratory glassware was kept overnight in a 5% nitric acid solution. A stock solution of cobalt (1000 mg L$^{-1}$) was prepared by dissolving 0.4933 g $Co(NO_3)_2 \cdot 6H_2O$ (Merck) in 100 mL of water. A working aqueous solution of cobalt (10 mg L$^{-1}$) was also prepared from cobalt stock solution. Sodium fluoride, hydrochloric acid (37%), and nitric acid (65%) were from Merck. Amberlyst 36 (Aldrich) was used after washing with methanol, 1 mol L$^{-1}$ HCl solution, and water, respectively, and dried for 4 h at 60°C.

### 2.3 *Collection and preparation of samples*

A tap-water sample was collected from our laboratory, and commercial natural drinking water was collected from a local market in Ankara, Turkey. These water samples were filtered through a Millipore cellulose nitrate membrane with a pore size of 0.45 µm. The samples were stored in polythene bottles and then acidified with 1.0 mL of concentrated hydrochloric acid per litre of sample. Soil samples were collected from Kılıçözü Industrial Estate, which includes mainly automotive services (from seven different sample points), Kırşehir, Turkey, and roadside dust samples were collected (from six different sample points) from both sides of the Ankara-Kayseri Main Road in the city of Kırşehir, Turkey. Samples were collected from the top of the soil and roadside, and stored in plastic bags. In the laboratory, pieces of wood, grass, etc. were manually removed from the samples. Equal amounts of samples collected from different sample points have been mixed manually. Samples were dried in an oven at 100°C for 24 h. Dried samples were ground in a ball mill (steel balls). These ground samples were sieved through a 0.5 mm stainless steel sieve in order to obtain a homogenous sample and for easy dissolution. The soil sample, roadside dust sample and certified reference material were dissolved by the aqua regia extraction procedure recommended by the International Organization for Standardization (ISO) [21]. Samples were digested at room temperature with 37% HCl/70% $HNO_3$ (3 : 1) mixture (10 mL per 200 mg of sample) for 16 h. After this, the suspension was evaporated to dryness. The residue was treated with 10 mL 2 mol L$^{-1}$ $HNO_3$ instead of 0.5 mol L$^{-1}$ $HNO_3$ recommended by ISO 11466. The suspension was filtered through a fine-porosity filter paper, and the insoluble part was washed with distilled water. The resulting solution was diluted with distilled water to 100 mL in a volumetric flask.

### 2.4 *Column preparation*

The glass column, with a stopcock, was 15 cm in length and 0.8 cm in internal diameter. A small amount of glass wool was placed at one end of the column to hold a certain amount (0.5 mg) of resin. Then, another small glass-wool plug was inserted onto the tap of the resin. The bed height of the resin in the column was approximately 1.5 cm. The resin was then washed successively with water, methanol, and 1 mol $L^{-1}$ of hydrochloric acid, respectively. After each use, the resin in the column was washed with 2 mL of 4 mol $L^{-1}$ nitric acid solution and triply distilled water, and stored in water for the next experiment.

### 2.5 *Preconcentration and determination procedure*

In order to test the proposed preconcentration procedure, prior to the determination of trace cobalt in real samples, an aliquot of a model solution (50 mL) containing 10 µg of the cobalt was used. This was placed in a beaker, and the pH of the solution was adjusted to 1.5 by using a dilute HCl solution. The column was preconditioned by passing the aqueous solution (pH 1.5) through the column, and then the model solution was passed through the column at a flow rate of 4 mL $min^{-1}$. The adsorbed cobalt(II) ions on the resin were eluted into a 5 mL calibrated flask by using 5 mL of 4 mol $L^{-1}$ nitric acid solution. The cobalt concentration in the eluent was determined by FAAS. The Amberlyst 36 column has been used repeatedly (up to 50 times) after washing with 2 mL of 4 mol $L^{-1}$ nitric acid solution and triply distilled water, respectively. Using the procedure described above, the recovery of the cobalt was calculated from the ratio of the concentration found by FAAS and the concentration calculated theoretically.

## 3. Results and discussion

In order to obtain the maximum recoveries, a large number of parameters such as the pH of the sample solution, type and concentration of the elution solution, and flow rates of the sample solution have been optimized. Interfering effects have also been studied.

### 3.1 *Effect of pH of sample solution*

Because pH is one of the most important environmental factors influencing site dissociation, the solution chemistry of the heavy metals, and the sorption availability of the heavy metals, pH was the first optimized parameter. The recovery was determined by applying the general procedure (section 2.5) by changing the pH of the model solution in the range of 1–8. The model solutions were adjusted to the desired pH with dilute hydrochloric acid and/or a dilute ammonia solution. The results for the recovery of cobalt as the mean of three measurements are shown in figure 1. Quantitative recoveries (>95%) were obtained in a pH range of 1.5–8.0. Therefore, pH 1.5 was selected for subsequent studies. Lower pH values are generally preferred for analysing real samples, because real samples (geological, biological, etc.) are generally dissolved with acids, and there is no precipitation risk of sample components.

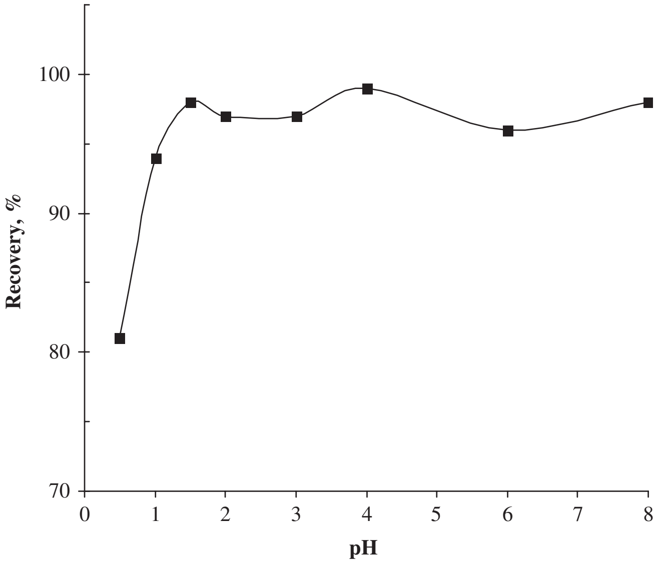

Figure 1. Effect of pH on the recovery of cobalt on a column of Amberlyst 36 (sample volume, 50 mL; amount of the cobalt, 10 µg; eluent, 5 mL of 4 mol $L^{-1}$ nitric acid; flow rate of sample, 4 mL $min^{-1}$).

Table 1. Effect of type, concentration, and volume of elution solution on the recovery of cobalt (pH, 1.5; flow rate of sample, 4 mL $min^{-1}$; sample volume, 50 mL; amount of the cobalt, 10 µg).

| Type, concentration and volume of eluent | $R^a$ (%) |
|---|---|
| 10 mL 1 mol $L^{-1}$ $HNO_3$ | 55 |
| 10 mL 2 mol $L^{-1}$ $HNO_3$ | 81 |
| 5 mL 3 mol $L^{-1}$ $HNO_3$ | 93 |
| 5 mL 4 mol $L^{-1}$ $HNO_3$ | 101 |
| 10 mL 2 mol $L^{-1}$ HCl | 69 |
| 5 mL 4 mol $L^{-1}$ HCl | 94 |
| 5 mL 2 mol $L^{-1}$ $HClO_4$ | 64 |
| 0.4 mol $L^{-1}$ KCN | 98 |
| 10 mL methanol | 4 |
| 10 mL ethanol | 3 |
| 10 mL acetone | 28 |

[a] Mean of three replicates.

### 3.2 *Effect of eluent type and concentration*

In order to choose a proper eluent for the elution of the retained cobalt ions, cobalt ions were stripped with varying concentrations of different eluting agents, such as, $HNO_3$, HCl, $HClO_4$, KCN, ethanol and acetone. As can be seen in table 1, the performance of the inorganic acids was much better than that observed with organic eluents. Quantitative recovery (>95%) was also obtained when 5 mL of 4 mol $L^{-1}$ nitric acid solution was used as eluent. Therefore, in subsequent experiments, 5 mL of 4 mol $L^{-1}$ nitric acid solution was chosen as eluent to desorb the cobalt on the column.

### 3.3 *Effect of amount of resin*

The amount of resin is another important parameter that affects the recovery. A quantitative recovery is not obtained when there is less resin. On the other hand, an excess amount of resin prevents the elution of the retained analyte by a small volume of eluent quantitatively. In order to optimize the amount of resin, different amounts of Amberlyst 36 (50–800 mg) were examined. Quantitative recoveries of the cobalt were obtained above 300 mg of resin. Therefore, 500 mg of resin has been used for subsequent experiments.

### 3.4 *Effect of flow rate of sample solution*

The retention of the analyte depends also upon the flow rate of the sample solution. Therefore, the effect of flow rate was examined by applying the recommended procedure (section 2.5). The model solution (50 mL, 0.2 μg L$^{-1}$ Co, pH 1.5) was passed through the column with the flow rate adjusted by gravity action in the range of 1–7.5 mL min$^{-1}$. As can be seen in figure 2, at flow rates greater than 3 mL min$^{-1}$, the recovery of cobalt decreases slightly but not below 95%, which is generally accepted as a quantitative recovery for this purpose. Therefore, in order to decrease the time required for the procedure, 4 mL min$^{-1}$ was selected as the optimum flow rate of the sample solution and was used for further studies. Because the eluent volume is very low, the effect of eluent volume has not been studied.

### 3.5 *Effect of sample volume (analyte concentration)*

In order to determine the maximum applicable sample solution (or minimum analyte concentration), the effect of the volume of sample solution on the recovery of cobalt was investigated by using the model solution and by applying the general procedure mentioned above. For this purpose, cobalt was preconcentrated from volumes of 50, 100, 250, 500, 750, and 1000 mL model sample solutions containing 10 μg of cobalt with cobalt concentrations of 0.2, 0.1, 0.04, 0.02, 0.0133, and 0.01 μg mL$^{-1}$, respectively.

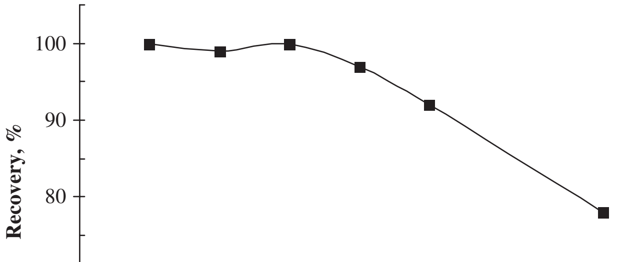

Figure 2. Effect of the flow rate of the sample solution on the recoveries of cobalt.

The recovery of cobalt was quantitative (>95%) for all sample volumes tested. By analysing 5 mL of the eluent after the preconcentration of 1000 mL of sample solution, the preconcentration factor was found to be 200. The preconcentration factor could have been improved further by using a larger sample volume and/or a smaller eluent volume. It can be concluded that cobalt can be determined at the concentrations of about 10 μg $L^{-1}$, which cannot be determined directly by FAAS with sufficient accuracy.

### 3.6 *Influence of foreign ions on the preconcentration of the cobalt*

The effects of foreign ions usually coexisting in drinking water and soil samples on the determination of cobalt were examined. The ions were added to 50 mL of model solution containing 10 μg of cobalt as their nitrate or chloride salts, and the general preconcentration procedure (section 2.5) was applied. The experimental results are given in table 2. The results show that the most serious interference arises from iron(III). Interference from this ion arises probably because it is retained more strongly on the resin than cobalt. In order to eliminate the iron interference, sodium fluoride was added to the model solution. Because the concentration of iron in the standard reference material (Montana Soil SRM 2711) is higher than 5 mg $L^{-1}$, prior to the preconcentration procedure, sodium fluoride was added to the solution of soil, roadside dust, and standard reference material samples in order to prevent the iron interference. However, sodium fluoride was not added to tap water and natural drinking water sample because the concentration of iron in drinking water is normally lower than

Table 2. Effect of some ions on the recovery of cobalt (pH, 1.5; eluent, 5 mL of 4 mol $L^{-1}$ nitric acid; flow rate of sample, 4 mL $min^{-1}$; sample volume, 50 mL; amount of cobalt, 10 μg).

| Interfering ions | Concentration (mg $L^{-1}$) | $R^a$ (%) | Interfering ions | Concentration (mg $L^{-1}$) | $R^a$ (%) |
|---|---|---|---|---|---|
| $Na^+$ | 1 | 96 ± 1 | $K^+$ | 1 | 100 ± 1 |
| | 5 | 97 ± 1 | | 5 | 100 ± 1 |
| | 25 | 98 ± 2 | | 25 | 97 ± 2 |
| | 100 | 97 ± 1 | | 100 | 96 ± 2 |
| $Mg^{2+}$ | 1 | 97 ± 2 | $Ca^{2+}$ | 1 | 101 ± 2 |
| | 5 | 97 ± 1 | | 5 | 97 ± 1 |
| | 25 | 95 ± 3 | | 25 | 98 ± 1 |
| | 100 | 96 ± 2 | | 100 | 99 ± 2 |
| $Al^{3+}$ | 1 | 101 ± 2 | $Fe^{3+}$ | 1 | 96 ± 1 |
| | 5 | 96 ± 3 | | 5 | 98 ± 2 |
| | 25 | 99 ± 1 | | 25 | 97 ± 2 |
| $Zn^{2+}$ | 1 | 97 ± 2 | $Fe^{3+b}$ | 1 | 98 ± 2 |
| | 5 | 99 ± 2 | | 5 | 85 ± 4 |
| | 25 | 97 ± 1 | | 25 | 42 ± 4 |
| $Cu^{2+}$ | 1 | 98 ± 2 | $Cd^{2+}$ | 1 | 100 ± 2 |
| | 5 | 102 ± 2 | | 5 | 99 ± 2 |
| | 25 | 96 ± 1 | | 25 | 100 ± 1 |
| $Mn^{2+}$ | 1 | 99 ± 1 | $Ni^{2+}$ | 1 | 98 ± 2 |
| | 5 | 98 ± 2 | | 5 | 99 ± 1 |
| | 25 | 95 ± 3 | | 25 | 95 ± 2 |

[a] Mean ± standard deviation for three determinations. [b] Without masking agent (NaF).

$5\,\mathrm{mg\,L^{-1}}$ [22], and there is no interference from iron at below tenfold of the concentration of cobalt. As can be seen in the table 2, among the other tested cations, none had any serious interfering effect.

### 3.7 *Adsorption isotherm and adsorption capacity*

The adsorption capacity of the resin for cobalt was determined by the batch technique described in Kendüzler and Türker [19] by employing the following experimental conditions: amount of resin, 100 mg; pH of the solution, 1.5; volume of sample solution, 50 mL; cobalt concentration, 10–400 $\mathrm{mg\,L^{-1}}$. The data obtained from the adsorption of cobalt on the solution showed that a contact time of 75 min was sufficient to achieve equilibrium, and the adsorption did not change with further increases in contact time.

The adsorption behaviour of Amberlyst 36 was determined by studying the amount of adsorbed cobalt as a function of cobalt concentration at pH 1.5. The profile of the adsorption isotherm of the resin for cobalt is shown in figure 3, representing the amounts of adsorbed cobalt *versus* the cobalt concentration of the supernatant under equilibrium conditions. In figure 3, the graph shows an excellent fit to the data in the concentration interval studied in all cases for the Langmuir model. The capacity value was calculated from the slope of the graph derived from the plot of the ratio of cobalt concentration in solution ($C_E$, $\mathrm{mg\,L^{-1}}$) to the concentration of cobalt in solid ($Q_E$, $\mathrm{mg\,g^{-1}}$) at equilibrium *versus* the concentration of cobalt in solution (figure 4). The value of adsorption capacity of Amberlyst 36 is found to be $82\,\mathrm{mg\,g^{-1}}$ for cobalt. The adsorption capacity of this adsorbent for cobalt is much higher than the adsorbents already reported in the literature. Table 3 compares the adsorption capacities obtained in the present work with those reported so far using chelate functionalized commercial solid phases for cobalt.

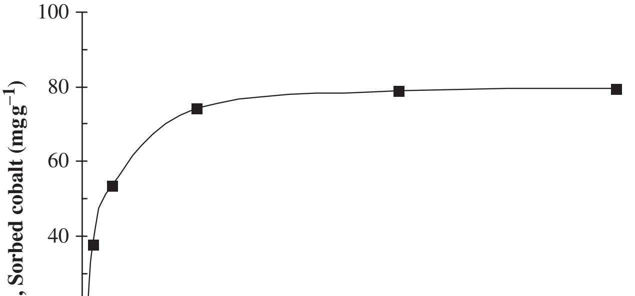

Figure 3. Adsorption isotherm of Amberlyst 36 for cobalt in a batch procedure.

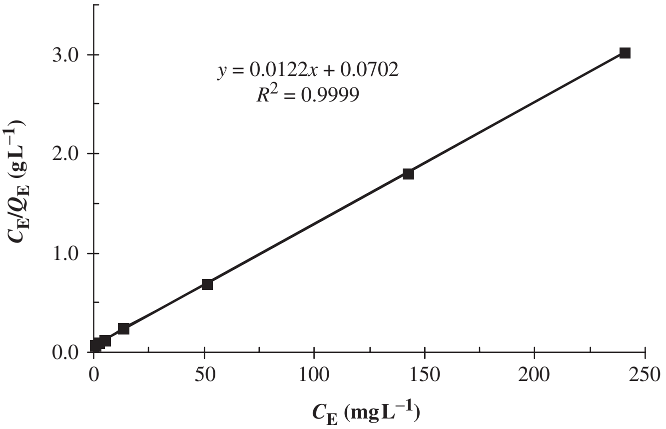

Figure 4. Linearized Langmuir isotherm obtained from the cobalt adsorption on Amberlyst 36.

Table 3. Comparison of adsorption capacities and enrichment factors.

| Support | Immobilized ligand or micro-organism | Adsorption capacity (mg $g^{-1}$) | Enrichment factor | References |
|---|---|---|---|---|
| Amberlite XAD-4 | *S. carlsbergensis* | 1.41 | 25 | 17 |
| Styrene-EGDMA | 5,7-Dichloroquinoline-8-ol | 11.46 | 200 | 23 |
| Styrene-DVB | 5,7-Dichloroquinoline-8-ol | 12.35 | 200 | 24 |
| Amberlite XAD-2 | Pyrogallol | 6.71 | 65 | 24 |
| Silica gel | Salicyldoxime | 3.54 | 40 | 25 |
| Silica gel | Acid red | 0.89 | – | 26 |
| Amberlyst 36 | – | 82 | 200 | Present work |

### 3.8 *Analytical performance of the method*

The dynamic linear range of the calibration graph was 0.2–6.0 μg $mL^{-1}$ by applying direct aspiration without the preconcentration step. The calibration equation of cobalt was $A = 0.0128 + 0.0761C$, where $C$ is the cobalt concentration (μg $mL^{-1}$), and $A$ is the absorbance. Calibration equation calculations are based on the average of triplicate readings for each standard solution.

The precision of the column-SPE method evaluated as the standard deviation of recovery obtained from seven replicates under the optimum experimental conditions (amount of cobalt, 10 μg; volume of solution, 50 mL; pH, 1.5; elution solution, 5 mL of 4 mol $L^{-1}$ nitric acid solution; flow rate, 4 mL $min^{-1}$) was 1.9%. The mean recovery of seven replicates was $98 \pm 2\%$ at a 95% confidence level.

The accuracy of the results was verified by analysing the standard reference material of soil (Montana Soil, SRM 2711). It was found that there was no significant difference between the result found by the proposed method ($9.4 \pm 1.2$ μg $g^{-1}$) as the mean of five determinations at 95% confidence level and the given value (10 μg $g^{-1}$, non-certified value) according to the *t*-test. It can be concluded that there is no systematic error in the determination at 95% confidence level (the relative error was −6.4%). The accuracy of the method was also checked by measuring the recovery of spiked samples. Good agreement was obtained between the added and found content (table 4).

Table 4. Determination of cobalt in various samples (volume of water samples: 1000 mL, amount of soil and roadside dust: 0.2 g).

| Sample | Added | Found[a] $\bar{x} \pm ts/\sqrt{N}$ | Relative error (%) |
|---|---|---|---|
| Tap water | – | nd | – |
| | $5.0\,\mu g\,L^{-1}$ | $4.8 \pm 0.4\,\mu g\,L^{-1}$ | −4.2 |
| Natural drinking water | – | nd | – |
| | $5.0\,\mu g\,L^{-1}$ | $4.7 \pm 0.3\,\mu g\,L^{-1}$ | −6.4 |
| Soil | – | $18.4 \pm 1.0\,\mu g\,L^{-1}$ | – |
| | $20\,\mu g\,g^{-1}$ | $36.3 \pm 1.4\,\mu g\,g^{-1}$ | −5.8 |
| Roadside dust | – | $12.1 \pm 0.6\,\mu g\,g^{-1}$ | – |
| | $20\,\mu g\,g^{-1}$ | $31.7 \pm 1.1\,\mu g\,g^{-1}$ | −1.3 |

[a] Mean of seven determinations at 95% confidence level. nd: not detected.

The errors calculated for the spiked samples were always lower than 10% (with recovery being higher than 95%). This result also confirms the accuracy of the procedure and absence of matrix effects.

The limit of detection (LOD) of the proposed method for Co has been studied under the optimized conditions. In order to determine the instrumental detection limit, 50 mL of blank solution was adjusted to pH 1.5, and then this solution was passed through the column. Blank solution was prepared by adding a minimum amount of cobalt to the tap water in order to obtain a readable cobalt signal. The column was washed by 50 mL of $4\,mol\,L^{-1}$ nitric acid solution (there was no preconcentration). The instrumental detection limit based on mean of blank values plus three times the standard deviation of the blank values was found to be $88\,\mu g\,L^{-1}$ for cobalt ($N = 20$). The analytical detection limit calculated by dividing the instrumental detection limit by the preconcentration factor (200) was $0.44\,\mu g\,L^{-1}$ [27].

### 3.9 *Application of the proposed method*

The proposed preconcentration method was applied for the determination of cobalt in tap water, natural drinking waters, soil and roadside dust samples, under optimal experimental conditions. The results calculated by assuming 100% recovery of cobalt are given in table 4. Relative errors, below 7%, demonstrate the applicability of the method and indicate that the proposed method is essentially free from interferences when applied to the analysis of drinking waters, soil, and roadside dust samples.

## 4. Conclusion

Cobalt could be determined by the proposed method from a large volume of samples with a high accuracy and precision. The method is simple, selective, and sensitive. This method permits a wide range of pHs to be used. Therefore, in this method, no buffer is needed to control the pH values precisely. This method does not require a chelating agent to increase the recovery. The enrichment factor (200) and the adsorption capacity of this resin ($82\,mg\,g^{-1}$) for cobalt are higher than the adsorbent previously reported in the literature [17, 23]. The detection limit is satisfactory for the samples studied and can be improved by using more sensitive detectors such as ICP-AES and ICP-MS. An improvement could also be obtained if an on-line system were used with the proposed solid-phase extractor.

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