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Solvent-assisted dispersive solid phase extraction

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In this research, a novel extraction technique termed solvent-assisted dispersive solid phase extraction (SADSPE) was developed for the first time. The new method was based on the dispersion of the sorbent into the sample to maximize the contact surface. In this method, the dispersion of the sorbent at a very low milligram level was achieved by injecting a solution of the sorbent into the aqueous sample. Thereby, a cloudy solution formed. The cloudy state resulted from the dispersion of the fine particles of the sorbent in the bulk aqueous sample. After extraction, phase separation was performed by centrifugation and the enriched analyte in the sedimented phase could be determined by instrumental methods. The performance of SADSPE was illustrated with the determination of the trace amounts of cobalt(II) as a test analyte in food and environmental water samples by using flame atomic absorption spectrometry detection. Some key parameters for SADSPE, such as sorbent selection and amount, type and volume of dispersive solvent, pH, chelating agent concentration, and salt concentration, were investigated. Under the most favorable conditions, good limit of detection (as low as 0.2 $\mu g\,L^{-1}$) and repeatability of extraction (RSD below 2.2%, $n=10$) was obtained. The accuracy of the method was tested with standard reference material (SRM-1643e and SRM-1640a) and spiked addition. The advantages of SADSPE method are simplicity of operation, rapidity, low cost, high recovery, and enrichment factor.

1. Introduction

Sample preparation is one of the most important and crucial steps in the whole analytical process, especially when trace determination is the purpose [1,2]. The main aims of this step are: (a) to transfer the analytes to a physical state that enables their analysis and final detection; (b) to enrich the analytes of interest; and (c) to purify the extracts prior to instrumental determination. Several procedures have been developed for these purposes such as liquid–liquid extraction (LLE) [3–5], co-precipitation [6–8], and solid phase extraction (SPE) [9–17]. However, some of these pretreatment methods need large amounts of sample and/or organic solvents, are time-consuming and expensive, and have unsatisfactory enrichment factors. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes.

SPE is more flexible and efficient than LLE in terms of simplicity, low consumption of the organic solvents, flexibility in choosing the adsorbent, and high enrichment factor. Recently, SPE has been increasingly used for the preconcentration and separation of ultra-trace amounts of inorganic and organic species from complex matrices [18,19]. Solid phase extraction techniques are surface-dependent processes since their efficiency directly depends on the particle size and the surface area of the sorbent [20]. Dispersive solid phase extraction (DSPE) has risen as an alternative to conventional solid phase extraction. It was, for the first time, proposed by Anastassiades et al. [21] and it can be considered as a quick, easy, cheap, effective, rugged, and safe (QuEChERS) sample treatment method. It is based on the SPE methodology, but the sorbent is added to the extract without conditioning, in small amounts (viz. 50 mg) and the dispersion is carried out assisted by an external energy (usually a vortex stirring). The phases are easily separated just by centrifugation. Sorbent dispersion leads to an increase of its active surface, and therefore to an improvement in the extraction kinetics. Moreover, this enhancement allows the use of a smaller amount of sorbent compared to the conventional extraction approaches resulting in the saving of material. In order to obtain analytical information, the sorbent is then recovered after the extraction. The analytes can be directly monitorized on the sorbent surface by using a spectroscopic technique [22,23] or can be conveniently eluted/desorbed for the subsequent analysis of the eluted fraction [24–27].

In the present report, for the first time, a novel extraction technique as a high performance and powerful preconcentration method named solvent-assisted dispersive solid phase extraction (SADSPE) is demonstrated. In this method, the appropriate mixture of sorbent and disperser solvent was rapidly injected into the aqueous sample by syringe. Thereby, a cloudy solution formed. The cloudy state resulted from the dispersion of the fine particles of

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the sorbent in the bulk aqueous sample. Then, this cloudy solution was centrifuged, following which the fine particles sediment at the bottom of the conical test tube. The determination of anlaytes in the sedimented phase was performed by instrumental analysis. In this extraction method, any component in the solution, directly or indirectly after previous derivatization reactions, interacts with the fine particles of the sorbent, and consequently, gets extracted from the initial solution. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery, and high enrichment factor are some advantages of SADSPE. For evaluating the performance of SADSPE, cobalt was selected as a test analyte and determined in food and water samples using flame atomic absorption spectrometry detection. The effects of various experimental parameters on the extraction were investigated.

2. Experimental

2.1. Apparatus

A PG-990 (PG instrument Ltd., United Kingdom) atomic absorption spectrometer, equipped with deuterium background correction, cobalt hollow cathode lamp and an air–acetylene flame was used for cobalt determination. All data acquisition was made according to peak height with the equipment software. The operating conditions were: wavelength 240.7 nm, spectral resolution 0.2 nm, applied lamp current 5.0 mA, air flow rate 10.0 L min^{-1}, and acetylene flow rate 1.3 L min^{-1}. A Hettich centrifuge (Model Universal 320 R, Germany) was used for centrifugation. The pH values were measured with a Metrohm pH-meter (model: 827) supplied with a glass-combined electrode. The particle size and the distribution of dispersed sorbent were both determined by dynamic light scattering (DLS) on a Zetasizer Nano ZS (Malvern Instruments Ltd., United Kingdom).

2.2. Reagents and solutions

All reagents used were of analytical reagent grade. Ultrapure distilled water was used throughout the experiment. A 1000.0 mg L^{-1} stock standard solution of Co(II) was prepared from pure $Co(NO_3)_2 \cdot 6H_2O$ (Merck, Darmstadt, Germany). Prior to the investigations, working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions.

The all standard solutions for FAAS instrument calibration were prepared in ethanol.

A 0.010 mol L^{-1} solution of 1-(2-Pyridylazo)-2-naphthol (PAN) (Merck, Darmstadt, Germany) was prepared in pure ethanol. Naphthalene, benzophenone, and 1,4-dichlorobenzene were purchased from Sigma-Aldrich (Louis, USA). All glass vessels used for trace analysis were cleaned before use by soaking them in 10% nitric acid solution for at least 24 h and then rinsed thoroughly with ultrapure water. A buffer solution (pH 6.0, 1.0 mol L^{-1}) was prepared by mixing an appropriate amount of acetic acid with sodium acetate solution. Water standard reference material SRM 1643e (trace elements in water) and SRM-1640a (trace elements in natural water) from National Institute of Standards and Technology (NIST) were both employed to test the proposed methodology.

2.3. Preparation of the real samples

Spinach and black tea samples were purchased at a local supermarket. Spinach sample was washed with ultrapure water and cut and oven-dried at 100 °C for 24 h. Next, it was ground in a household grinder. 500 mg of the sample was placed in a 100 mL beaker, and 10 mL of concentrated HNO_3 (65% w/w) was added to the beaker. The mixture was evaporated to near dryness on a hot plate at about 130 °C for 4 h. After cooling to room temperature, 3 mL of concentrated hydrogen peroxide (30%, w/w) was added. The mixture was again evaporated to near dryness. The resulting solution was diluted to 25 mL with distilled water. Further, the resulting solution was filtered and its pH was adjusted to 6.0 by adding NaOH and 2 mL of acetic acid/sodium acetate buffer solution (pH 6.0). Finally, the solution was diluted to 100 mL with double distilled deionized water. The same preparation procedure was used for the black tea sample. One blank test was performed for each sample. The samples were analyzed immediately after preparation.

All of the collected water samples (tap, mineral, river, and sea water) were filtered through a cellulose membrane filter (Millipore) with a pore size of 0.45 μm, and after their acidification to 1% with concentrated nitric acid, were stored in polyethylene bottles.

2.4. Solvent-assisted dispersive solid phase extraction (SADSPE) procedure

50 mL sample or standard solution containing Co(II), PAN (1.0×10^{-4} mol L^{-1}) and acetic acid/sodium acetate buffer (1 mL of 1.0 mol L^{-1}, pH 6.0) was poured into a glass screw-cap conical-bottom centrifuge tube. 0.5 mL of methanol solution (as disperser solvent) containing benzophenone (1.0%) (as sorbent) was rapidly injected into a sample solution by using 1.0 mL syringe, and then, the mixture was gently shaken. A cloudy solution was formed in the test tube (the cloudy state was stable for a long time). This cloudy state resulted from the dispersion of fine particles of benzophenone in the bulk aqueous sample. Then, the mixture was centrifuged at 4000 rpm for 5 min. Accordingly, the dispersed fine particles of benzophenone were sedimented in the bottom of the conical test tube. The aqueous phase was then separated completely by a syringe. Later, the sedimented phase was dissolved and made up to 1.0 mL by adding ethanol. The resultant solution was introduced into the flame by conventional aspiration. The extraction steps are illustrated in Fig. 1.

3. Results and discussion

There are different factors that affect the SADSPE extraction process namely selection of suitable sorbent, selection of suitable disperser solvent, amount of sorbent, volume of disperser solvent, and extraction time. It is very important to optimize them in order to obtain good recovery, high EF, and low limit of detection.

3.1. Selection of sorbent and its amount

Careful attention should be paid in the selection of the sorbent. It should have extraction capability of the concerning compounds, high solubility in disperser solvent and low solubility in water. Naphthalene, benzophenone, and 1,4-dichlorobenzene were compared in the extraction of cobalt(II). A series of sample solutions were studied using 500 μL methanol containing 1.0% of the sorbent. As Fig. 2 shows the highest extraction recovery was obtained with benzophenone. The similarity of the structure of benzophenone and Co(II)–PAN complex and their proper interaction could thus explain the higher extraction recovery of benzophenone. Therefore, benzophenone was selected as the sorbent.

To examine the effect of the sorbent amount, a series of sample solutions were studied using 500 μL methanol containing different amounts (0.2–10.0%) of benzophenone. As Fig. 3 shows, the extraction recovery increased as the amount of benzophenone increased from 0.2 to 1.0%, as was expected. Further increase of the amount of benzophenone to 10.0% did not have any effect on extraction recovery. Therefore, 1.0% of the benzophenone was

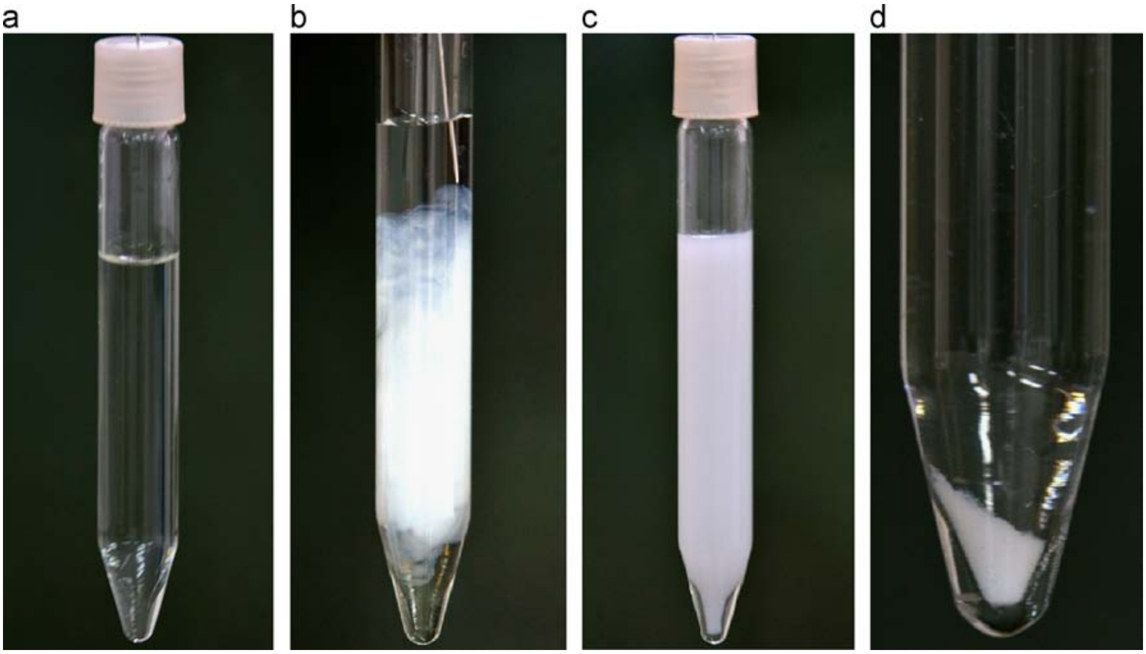

Fig. 1. Photography of different steps in SADSPE: (a) sample solution (ultrapure distilled water), (b) starting injection of mixture of disperser solvent (methanol, 500 μL) and sorbent (benzophenone, 10.0%), (c) end of injection, and (d) enlarged view of sedimented phase after centrifuging.

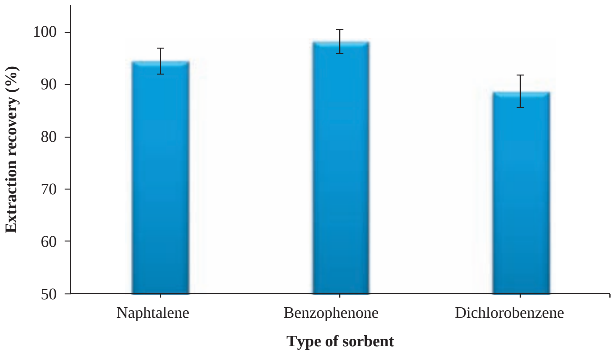

Fig. 2. Effect of type of sorbent on the extraction recovery of cobalt. Conditions: sample volume: 50 mL, cobalt concentration: 50.0 μg L^{-1}, PAN concentration: 1.0×10^{-4} mol L^{-1}, disperser solvent: methanol, 500 μL, pH: 6.0.

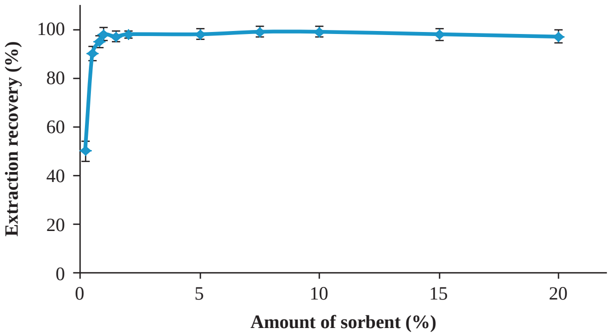

Fig. 3. Effect of amount of sorbent. Conditions: sample volume: 50 mL, cobalt concentration: 50.0 μg L^{-1}, PAN concentration: 1.0×10^{-4} mol L^{-1}, sorbent: benzophenone, disperser solvent: methanol, 500 μL, pH: 6.0.

selected as the optimum amount of the sorbent for further studies. Also, the effect of the sorbent amount on the size of the dispersed particles was investigated. The particle size distributions were measured by DSL, and the results showed that the average size of the particles changed and increased from 500 to 1500 μm by increasing the amount of sorbent.

3.2. *The effect of the type and volume of the disperser solvent*

The disperser solvent plays a key role in the extraction procedure since it permits the appropriate dispersing of the sorbent into the sample, generating a cloud of fine particles. Essentially, this solvent must fulfill the following requirements: (a) it should be miscible with the sample matrix in order to easily release the sorbent; (b) it should be able to dissolve the sorbent; and (c) it should not interfere in the extraction of the target analytes. Therefore, different solvents (acetone, tetrahydrofuran, methanol, and ethanol) were evaluated. A series of sample solutions were studied using 500 μL of each disperser solvent containing 1.0% of benzophenone. The extraction recovery obtained for acetone, tetrahydrofuran, methanol, and ethanol were 98.2 ± 1.3, 98.0 ± 1.1, 98.4 ± 1.4, and 98.1 ± 1.3, respectively. The results showed no statistically significant differences between the disperser solvents. However, methanol was selected as the disperser solvent for subsequent experiments.

The effect of the volume of methanol on the extraction recovery was also studied. The experimental conditions were fixed and included the use of different volumes of methanol 250, 500, 750, 1000, 1250, and 1500 μL containing 5 mg of benzophenone. As shown in Fig. 4, there was no significant variation in extraction efficiency between 250 and 750 μL of methanol and the extraction recovery was quantitative. The extraction efficiency slightly decreased when the volume of methanol exceeded 1000 μL. It is clear that an increase in the volume of methanol results in an increase in the solubility of the complex. Therefore, the extraction recovery decreases. Thus, 500 μL of methanol was selected as the optimum volume in order to achieve a better cloudy solution.

3.3. *The effect of the extraction time*

In SADSPE, the extraction time is defined as the time interval between the injection of the mixture of disperser solvent and sorbent in the sample and the beginning of centrifugation. This parameter was evaluated in the range of 5 s–5 min, while all the experimental conditions were kept constant. The negligible effect of the extraction time on the extraction recovery of cobalt(II) was

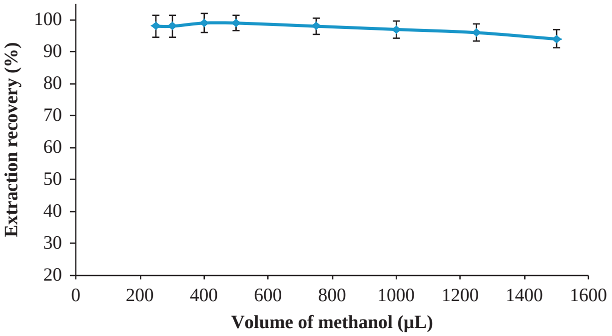

Fig. 4. Effect of amount of disperser solvent. Conditions: sample volume: 50 mL, cobalt concentration: 50.0 μg L^{-1}, PAN concentration: 1.0 × 10^{-4} mol L^{-1}, sorbent: benzophenone, 1.0%, disperser solvent: methanol.

observed. This fact indicates that the transfer of cobalt(II) chelate from the sample to the sorbent is very fast, which is one of the main characteristics of dispersion procedures.

3.4. *The effect of pH*

The separation of metal ions by solvent-assisted dispersive solid phase extraction involves prior formation of a complex with sufficient hydrophobicity interacting and adsorbing with the fine particles of the sorbent. pH plays a unique role in metal–PAN chelate formation and its subsequent extraction because the existing form of metal ions and PAN is pH dependent. The effect of pH on the extraction efficiency of Co(II) was evaluated in the pH range of 1–10. The results shown in Fig. 5 indicate that the complex of Co–PAN had a relatively wide range of solution acidity. When the pH of the solution increased, the extraction recovery increased in the pH range of 1–4 correspondingly. In the range of pH 4–9, extraction recovery remained constant and the stronger alkalescency induced a decrease in extraction recovery. Competition between protons and metal species could thus explain the weak extraction recovery in acid medium. On further increase in pH, extraction recovery decreased probably due to the formation of cobalt hydroxide. Hereby, a pH range from 4 to 9 could be selected as the optimal condition in further experiments. A pH value of 6.0 was chosen for further experiments and acetate/acetic acid buffer was chosen for pH adjustment.

3.5. *The effect of PAN concentration*

As the principle reagent in this work, PAN was selected to form Co–PAN complex. The effect of chelating reagent concentrations on the extraction recovery was investigated in the range of 1.0 × 10^{-6}–2.0 × 10^{-4} mol L^{-1}, as shown in Fig. 6. It was noticed that the extraction recovery increased with the increase of PAN concentrations in the range of 1.0 × 10^{-6}–2.0 × 10^{-5} mol L^{-1}, and at higher PAN concentrations, the extraction recovery remained constant. Because of some other ions that could be present in real samples and probably react with PAN, a concentration of 1.0 × 10^{-4} mol L^{-1} was used in the experiments.

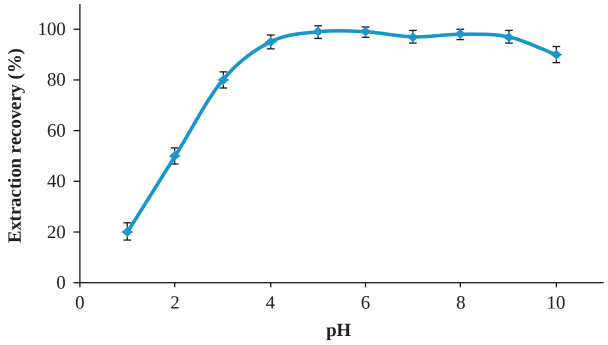

Fig. 5. Effect of pH on the extraction recovery. Conditions: sample volume: 50 mL, cobalt concentration: 50.0 μg L^{-1}, PAN concentration: 1.0 × 10^{-4} mol L^{-1}, sorbent: benzophenone, 1.0%, disperser solvent: methanol, 500 μL.

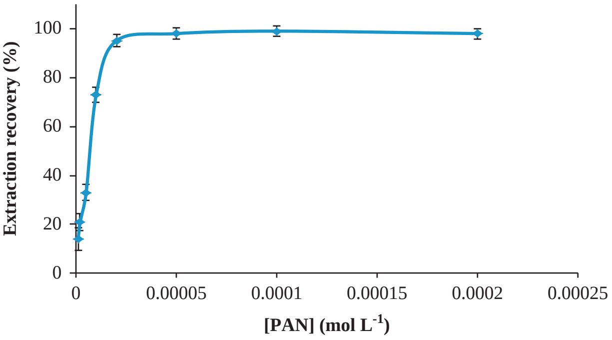

Fig. 6. Effect of PAN concentration on the extraction recovery. Conditions: sample volume: 50 mL, cobalt concentration: 50.0 μg L^{-1}, sorbent: benzophenone, 1.0%, disperser solvent: methanol, 500 μL, pH: 6.0.

3.6. *The effect of Ionic strength*

In order to investigate the effect of ionic strength on the extraction of cobalt(II), several experiments were performed with different $NaNO_3$ concentrations (0–20%) while keeping other experimental parameters constant. The results confirmed that salt addition had no significant effect on the extraction process and the recovery of cobalt(II) was quantitative. The negligible influence of the salt could be ascribed to the rapidity of cobalt(II) chelate distribution between the involved phases and can be seen as the likely result of the dispersion process. These observations suggest the possibility of the application of the method for the separation of Co(II) from saline solutions.

3.7. *The effect of coexisting ions*

The effects of common coexisting ions in real samples on the recovery of cobalt were also studied. In these experiments, 50 mL of solutions containing 50.0 μg L^{-1} of cobalt and various amounts of interfering ions were treated according to the recommended procedure. Given species were considered to interfere if it resulted in a ±5% variation of the AAS signal. Table 1 shows the maximum tolerance of the cations and anions (Ion/Co (II) ratio (w/w)) investigated. According to the results, the major ions in the real samples have no obvious influence on the Co(II) extraction under the selected conditions.

3.8. *Figures of merit*

Table 2 summarizes the analytical characteristics of the optimized method, such as limit of detection, reproducibility, and preconcentration factor. Under the optimum conditions, the solvent-assisted dispersive solid phase extraction procedure was applied for the extraction and preconcentration of various standard solutions of cobalt(II) and the calibration graph was linear in the range of 2–100 μg L^{-1}. The LOD, defined as $3S_b/m$ (where S_b and m are the standard deviation of the blank and the slope of the calibration graph, respectively), was found to be 0.2 μg L^{-1}. The preconcentration factor that was calculated by dividing the aqueous phase volume into the final volume of the diluted phase was 50. Repeatability was carried out by spiking blank samples at the

Table 1
Effect of foreign ions on the recovery of cobalt(II).

Ion	Ion/Co (II) ratio (w/w)	Recovery (%)
F^-	10,000	101
Cl^-	10,000	98
Br^-	10,000	102
I^-	10,000	98
ClO_4^-	10,000	100
HCO_3^-	10,000	97
SO_4^{2-}	10,000	100
PO_4^{3-}	10,000	98
Li^+	10,000	97
K^+	10,000	99
Ba^{2+}	10,000	98
Mg^{2+}	10,000	97
Ca^{2+}	10,000	97
Mn^{2+}	10,00	98
Cd^{2+}	1000	99
Cr^{3+}	1000	97
Ag^+	500	99
Pb^{2+}	500	97
Al^{3+}	500	97
Ni^{2+}	250	99
Zn^{2+}	100	98
Cu^{2+}	50	97
Fe^{2+}	50	99
Fe^{3+}	50	98

Table 2
Analytical characteristics of the proposed method.

Parameter	**Analytical feature**
Linear range, $\mu g\ L^{-1}$	2–100
Limit of detection, $\mu g\ L^{-1}$ ($n=10$)	0.2
RSD, % ($C=50.0\ \mu g\ L^{-1}$, $n=10$)	2.2
Preconcentration factor	50

Table 3
Determination of cobalt(II) in water samples.

Sample	**Co (II) amount ($\mu g\ L^{-1}$)**		**Recovery (%)**
	Added	**Found**[a]	
Tap water	0.0	n.d.[b]	–
(Drinking water system of Behshahr, Iran)	20.0	19.5 ± 0.5	97.5
	50.0	49.1 ± 1.5	98.2
Mineral water	0.0	n.d.	–
(Persam mineral water, Iran)	20.0	20.1 ± 0.6	100.5
	50.0	50.6 ± 1.6	101.2
River water	0.0	7.2 ± 0.3	–
(Babol river, Babol, Iran)	20.0	27.4 ± 0.7	101.0
	50.0	56.5 ± 1.2	98.6
Sea water	0.0	10.2 ± 0.5	–
(Caspian sea water, Behshahr, Iran)	20.0	30.6 ± 1.1	102.0
	50.0	59.8 ± 2.3	99.2

[a] Mean ± standard deviation ($n=3$).
[b] Not detected.

concentration of $50.0\ \mu g\ L^{-1}$, and the relative standard deviation (RSD) for ten replicate experiments was 2.2%.

3.9. *Analysis of natural water and food samples*

Real water samples (tap water, mineral water, river water, and sea water) and food samples (spinach and black tea) were subjected to the proposed method to evaluate the concentration of cobalt. The obtained results are shown in Tables 3 and 4. Recovery studies were also carried out after known cobalt concentrations were spiked to samples at levels of 20 and 50 $\mu g\ L^{-1}$. The recovery values calculated for the added standards ranged from 97 to 102%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Furthermore, the accuracy of the developed method was evaluated by recovery experiments for the determination of cobalt in water CRMs. The following standard reference materials were used to verify the accuracy of the proposed method: NIST SRM-1643e and SRM-1640a. The results listed in Table 5 reveal that there is a good agreement between obtained results and certified values, and indicate that the proposed procedure was helpful for the determination of cobalt in real samples with complicated matrices.

3.10. *Comparison with other methods*

A comparison of the presented method with other reported preconcentration methods for cobalt determination is given in Table 6. The presented method has low LOD, high-enrichment factor, and good RSD and these characteristics are comparable or even better than most of the other methods named in Table 6.

Table 4
Determination of cobalt(II) in spinach and black tea.

Sample	**Added ($\mu g\ g^{-1}$)**	**Found ($\mu g\ g^{-1}$)**[a]	**Recovery (%)**
Spinach	–	8.2 ± 0.2	–
	2.0	10.2 ± 0.3	100.0
	5.0	13.3 ± 0.3	102.0
Black tea	–	12.2 ± 0.4	–
	2.0	14.1 ± 0.5	95.0
	5.0	17.1 ± 0.4	98.0

[a] Mean ± standard deviation ($n=3$).

Table 5
Determination of cobalt(II) in standard reference materials.

Certified reference material	**Certified ($\mu g\ L^{-1}$)**	**Found ($\mu g\ L^{-1}$)**[a]	**Recovery (%)**
SRM-1643e	27.06 ± 0.32	26.41 ± 0.62	97.6
SRM-1640a	20.24 ± 0.24	19.94 ± 0.56	98.5

[a] Mean ± standard deviation ($n=3$).

Table 6
Comparison of SADSPE with other methods for determination of cobalt(II) in water samples.

Method	LOD[a] ($\mu g\ L^{-1}$)	RSD[b] (%)	Sample volume (mL)	PF[c]	Reference
SPE-FAAS	3.9	2.0	250	25	[28]
SPE-FAAS	12.3	1.3	1000	200	[29]
CPE-UV–vis	7.5	2.7	10	10	[30]
CPE-FAAS	1.0	3.6	50	25	[31]
CPE-FAAS	2.1	1.5	15	30	[32]
DLLME-FAAS	0.9	5.8	5	16	[33]
US-DLLME-FAAS	0.8	3.3	5	10	[34]
CPE-FAAS	0.5	3.2	25	50	[35]
SADSPE-FAAS	0.2	2.2	50	50	Present work

[a] Limit of detection.
[b] Relative standard deviation.
[c] Preconcentration factor.

All these results indicate that solvent-assisted dispersive solid phase extraction is a reproducible, simple, and low cost technique that can be used for the preconcentration of metal ions, like cobalt, from real samples.

4. Conclusions

The analytical potential of solvent-assisted dispersive solid phase extraction is presented and critically evaluated in this article. The SADSPE allows the rapid extraction of cobalt(II), which was selected as model analyte, using a low amount of sorbent material (5 mg). This method is environment friendly and robust against very high contents of salt. The other benefits of the method are its simplicity, ease of operation, good accuracy and precision, short extraction time, low cost, and a good enrichment factor. Although the obtained results in this work are related to cobalt determination, the system could be readily applied for the determination of other metals using various ligands. Future work will be directed toward extending the method for the separation and preconcentration of different inorganic and organic species.

Acknowledgments

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