

Determination of trace cobalt (II) in spices samples by ultrasonic assisted cloud point extraction with spectrophotometry

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ABSTRACT

In this study, ultrasonic assisted cloud point extraction (UA-CPE) method was developed for the determination of Cobalt (II) (Co(II)) in spices. After extraction and preconcentration, the Co(II) contents of the samples were determined by UV-VIS. After complexing with Ponceau Xylydine (PX) and EDTA in the presence of cationic surfactant, CTAB at pH 4.0 with Britton-Robinson (BR) buffer, Co(II) ion was withdrawn the surfactant-rich phase of nonionic surfactant, Triton X-114 (TX-114). The concentrated surfactant-rich phase containing the analyte was diluted with ethanol to a volume of 1.0 mL and then analyzed by UV-VIS spectrophotometer. The various analytical parameters affecting the UA-CPE yield were investigated and optimized. Analytical data achieved after optimization: limits of detection (LOD) and: limits of quantification (LOQ) are 0.76 and 2.59 $\mu\text{g L}^{-1}$, respectively; The calibration curve is rectilinear for Co(II) with changed calibration sensitivity in the range of 1–10 and 10–210 $\mu\text{g L}^{-1}$. The precision (as RSD%) is 4.8. This optimized method was applied in the analysis of various spice samples.

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1. Introduction

Spices and herbs have always been of great importance in live nutrition and health sector from time immemorial to the present day. There are documents that these species were used not only for food but also for medical purposes in ancient times [1]. Plants, which are the main source of spices and herbs, are affected by the composition of the soil, climatic conditions, environmental factors and pesticides used. For this reason, toxic residues may be observed in the plant due to the above-mentioned factors, which are not normally in the plant's body [2–9].

Trace amounts of metals found in foods by direct addition or contamination may accumulate in the living body over time. This situation may endanger the life of the living in the future. It can also pose a biological and chemical threat when these polluted species are used directly as food ingredients or for medicinal purposes. While some of the metal species taken into the living body through plants are necessary for life in trace amounts, those above the determined limit put their life at risk [10]. Cobalt, one of these metals, has many important roles in living things such as red blood cell production and neurological systems, and is also the main component of vitamin B12 [11,12]. Cobalt, which is important for

human life when it is in trace amounts, causes some health problems when it is found in large amounts. These problems include serious diseases such as asthma, diarrhea, nausea, lung, heart and blood disorders [13–15]. Acceptable cobalt concentration in drinking water as determined by the World Health Organization (WHO) should be less than 1–2 mg L^{-1} [16]. Cobalt is often found in trace amounts in environmental and food samples; Therefore, it is necessary to develop analytical methods that are accurate, sensitive, precise, easy to apply and inexpensive to detect trace amounts of cobalt. Before starting the trace element analysis, it is of great importance to develop a sample preparation process that will affect the analysis method such as dissolution, separation and preconcentration [17]. Among the methods used for this purpose, several types of microextraction such as cloud point extraction (CPE) [18,19], liquid-liquid extraction (LLE) [20], dispersive liquid-liquid micro extraction (DLLME) [21], single-drop microextraction (SDME) [22], switchable solvent liquid phase microextraction (SS-LPME) [23] and magnetic solid-phase extraction (MSPE) [24] have been located.

According to literature data, cloud point extraction (CPE) methods have received intense attention in the field of analytical chemistry because it complies with the “Green Chemistry” principle [25–30]. CPE has advantages such as simplicity of application, high efficiency, use of chemicals with low toxicity, safety, low cost and results in a short time. In CPE technique, surfactant is one of the key reagents. CPE is based on the phase behavior of non-ionic sur-

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factants in aqueous solutions. Non-ionic surfactants undergo phase separation upon increasing the temperature or the addition of a salting-out agent [31–33]. Among many surfactants, TX-114 with its low cloud point temperature (30 °C) is often the preferred reagent in applications.

Several instrumental methods used in trace element analysis have been reported. Many metals determined by flame atomic absorption spectrometry (FAAS) [34,35], slotted quartz tube flame atomic absorption spectrometry (SQT-FAAS) [36], thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) [37], GF-AAS [38], inductively coupled plasma-optical emission spectrometry (ICP-OES) [39], inductively coupled plasma mass spectrometry (ICP-MS) [40], gas chromatography (GC) [41], electrothermal atomic absorption spectrometry (ET-AAS) [42,43], high-performance liquid chromatography (HPLC) [44,45], HPLC-inductively coupled plasma-mass spectrometry (HPLC - ICP - MS) [46] and UV-VIS [47].

In this study, analysis of trace Co(II) in spices samples by ultrasonic assisted cloud point extraction was carried out using the UV-VIS spectrophotometric determination method, since it is easy to apply, simple, fast, economical and has wide application ranges.

In the existing study, we describe a validated method for the determination of Co(II) ions in spices samples. The method is based on the selective ion-pairing complex formation of Co(II) with PX, using TX-114 in the presence of BR buffer at pH 4.0. A new ion-pairing CPE approach coupled with UV-VIS spectrophotometry at 335 nm has been reported for speciative analysis of Co species in spices samples.

2. Experimental

2.1. Instrumentation

The analytical signal values were measured through a UV-VIS Spectrophotometer (Shimadzu 1800, Japan). The pH meter (Jenway 3010 pH meter, Staffordshire, UK) was used to adjust the pH. To accelerate phase separation, a centrifuge (Hettich Universal-320, UK) was employed. A heat-regulated and frequency controlled ultrasonic bath (UCS-10 model, Seoul, Korea) was used for CPE.

2.2. Reagents and solutions

The solutions were prepared using analytically pure reagents and double distilled water. All solutions were prepared daily for freshness. Stock solution of Co(II) (250 mg L⁻¹) was prepared from cobalt (II) nitrate hexahydrate. The universal Britton-Robinson (BR) buffer solutions were prepared by mixing H₃BO₃, H₃PO₄ and CH₃COOH. A 0.1 mmol L⁻¹ PX solution as chelating agent was prepared. A 1.0 mmol L⁻¹ CTAB. The solutions (5.0%, v/v) of TX-114 (Sigma) as extractant was prepared with 100 mL of water. To prepare EDTA solution, an adequate amount of Na₂EDTA 2H₂O was dissolved in water to provide 0.02 mol L⁻¹ (Sigma-Aldrich Co., St. Lois MO, USA).

2.3. Sample preparation

We evaluated spices supplied by a supermarket in Sivas, Turkey for our experiment. The first step was to pre-treat 0.5 g of spices samples by (mixture 4.0 mol L⁻¹ HNO₃, 4.0 mol L⁻¹ HCl, 0.5 mol L⁻¹ H₂O₂, 3:2:1, v/v) for destruction of matrix [48,49]. Subsequently, the sample and other reagents were then vigorously mixed by vortexing at 1200 rpm for 15 s. This mixture was widely sonicated for 15 min in an ultrasonic bath at 55 °C. By centrifuging for 15 min at 3000 rpm, the extracted aqueous phase and solid phase were separated. Water was added to the 5 mL mixture to dilute it to 50 mL [50]. The process was then repeated to determine

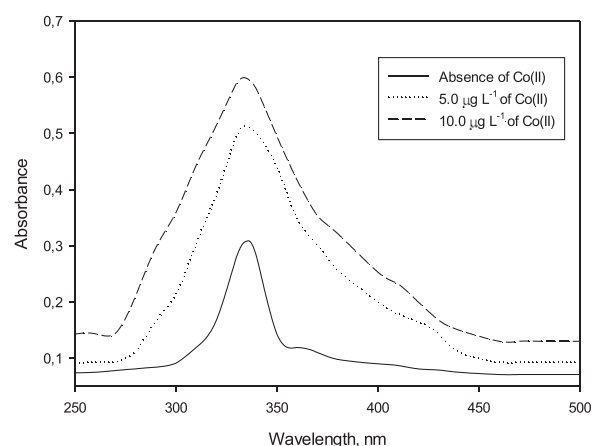


Fig. 1. The dependence of absorption spectra maximum to Co(II) concentration at levels of 5.0 and 10 µg L⁻¹ against analyte blank under optimum conditions.

Co(II) amount by using 3 mL of the spices samples under predetermined optimal conditions.

2.4. Procedure for UA-CPE

In the study, an appropriate volume (3.0 mL) of sample solution and a Co(II) standard solution in a linear range of 1–10 µg L⁻¹, 0.4 mmol L⁻¹ of BR buffer solution at pH 4.0, 7.0 µmol L⁻¹ of PX, 0.05 mmol L⁻¹ CTAB, 0.25% (v/v) TX-114 and 1.0 mmol L⁻¹ EDTA were consecutively poured to a test tube. After, the solution volume was made up to 50 mL using distilled water. Thereafter, the obtained solution was sonicated in an ultrasonic bath at 50 °C for 7 min. The final solution, which has the aqueous phase and the surfactant rich phase, was centrifuged at 3000 rpm for 5 min to perform phase separation. Following centrifugation, it was kept in an ice bath for 15 min for easy phase separation and the phase mixture was separated. 2.0 mL of ethanol was mixed to reduce the viscosity of the surfactant rich phase, which was taken into another tube. All the experimental procedures described above were applied to the blank solution. Finally, the amount of Co(II) in all pretreated and extracted spices samples was determined spectrophotometrically at 335 nm. The absorbance change of sample spiked with two concentration levels against sample blank under optimized reagents can clearly be seen in Fig. 1, in terms of linear relationship of absorbance with increasing Co(II) concentration at peak maximum at 335 nm.

3. Results and discussion

3.1. Effects of pH and buffer concentration

During extraction in the UA-CPE, the amount of complexation of metal ions and the extraction yield are mostly connected to the pH of the solution [25]. Generally, in the extraction step, it is aimed to form both a binary complex and a hydrophobic ternary complex based on proton and charge transfer. To this end the effect of pH in the range of 2–8 on extraction yield was researched. From the obtained results in Fig. 2(a), it was observed that the extraction efficiency was the best at pH 4. It is thought that there is a decrease in analytical signal due to metal hydroxide formation at high pH. Additionally, the influence of buffer solution amount of 0.04 mol L⁻¹ on absorbance value at pH 4.0 was analyzed in range of 0.1–3.0 mL in Fig. 2(b) and a buffer volume of 0.5 mL was determined to be sufficient for highest sensitivity. At volumes below or above 0.5 mL, absorbance value more and more was declined.

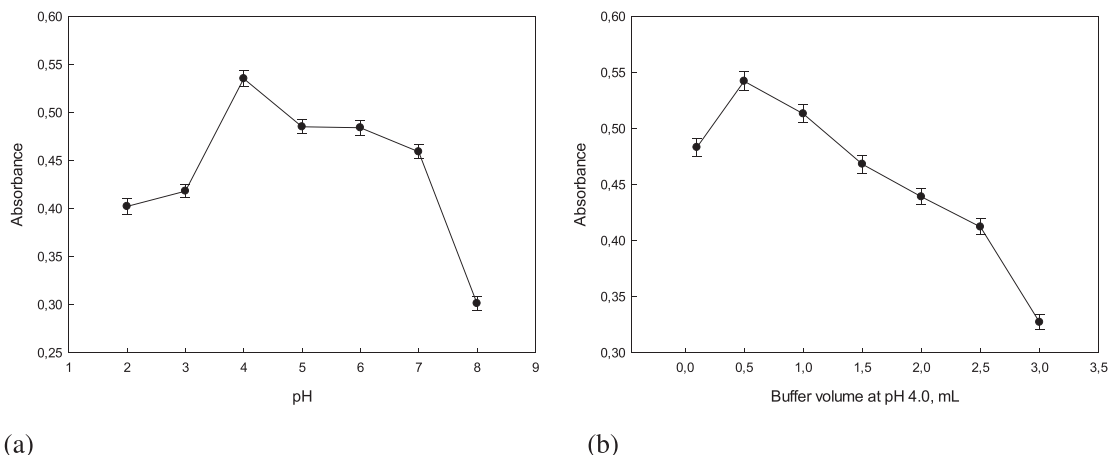


Fig. 2. The effect of (a) pH and (b) 0.04 mol L⁻¹ pH 4.0 BR buffer volume to analytical signal.

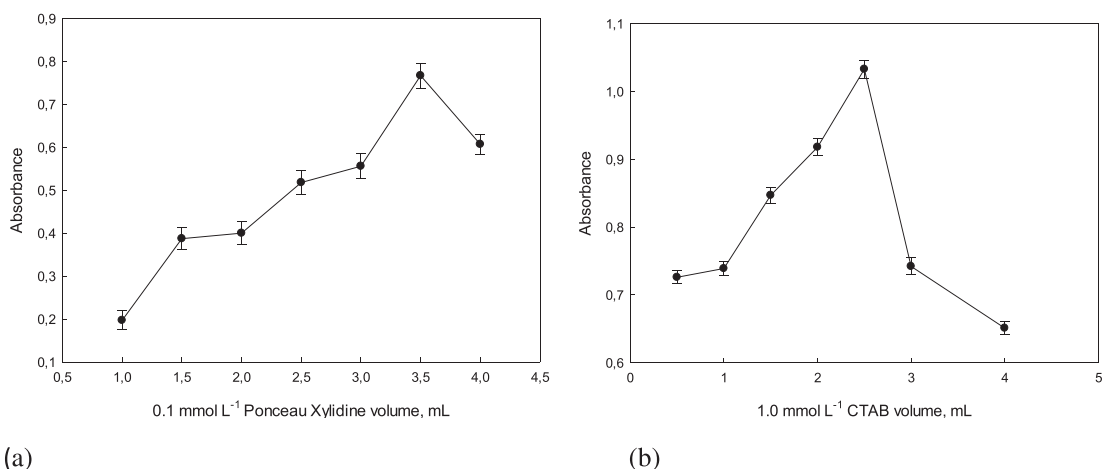


Fig. 3. The effect of (a) 0.1 mmol L⁻¹ PX volume and (b) 1.0 mmol L⁻¹ CTAB volume to analytical signal.

3.2. Effect of Ponceau xylidine concentrations

PX, with the chemical name 1-(2,4-xylyazo)-2-naphthol-3,6-disulphonic acid disodium salt, a textile azo-group indicator dye is known as Acid Red 26, Ponceau 2 R and Xylidine ponceau 2R. It is a *o*-hydroxy azo dye with the ability to act as chelating ligand with the tendency to make complexes with "hard" metals such as Co(II) and Co(III). The effect of 1.0×10^{-4} mol L⁻¹ of dye in the range of 1.0–4.0 mL in Fig. 3(a), on extraction yield was studied. In range of 1.0–3.5 mL, absorbance value distinctly increased with increasing PX amount. At volumes greater than 3.5 mL the analytical signal is reduced as excess of the ligand dissolves the hydrophobic metal-chelates. Therefore, a volume of dye 3.5 mL was determined as optimal for next all process.

3.3. Effect of amount of CTAB

To examine efficiency of the amount of cationic surfactant, CTAB, on the extraction yield, the ranges of CTAB 0.5–4.0 mL was investigated. For demonstrate of the enhancing effect of CTAB for determination of analytes, the definition of the Co-PX-CTAB is given in Fig. 3(b). The studies made clearly show that, absorbance value distinctly increased with increasing CTAB volume. Another important role of CTAB is to act as an anti-sticking agent. Based

on these results, a volume of 2.5 mL was determined as optimum next all process.

3.4. Effect of amount of TX-114

The influence of the amount of TX-114 on extraction yield was tested in the concentration range of 0.05–0.5% in Fig. 4(a). In range of 0.5–2.5 mL, absorbance value increased with increasing TX-114 vol. According to the data obtained, when more of TX-114 is added, analytical signal gradually was decreased. Based on these results, the volume value of 2.5 mL was taken as optimum volume for further experiments.

3.5. Effect of EDTA concentration

In this proposed method, EDTA was used to form cobalt chelate. Since the maximum analytical signal was observed at 2.5 mL in Fig. 4(b), increased distinctly with increasing EDTA amount in 0.08–1.0 mmol L⁻¹, and decreased in concentrations above 1.0 mmol L⁻¹.

3.6. Effects of equilibrium temperature and incubation time

The cloud point of the 5% (v/v) TX-114 aqueous solution was observed to increase significantly (50 °C) in existence of a little

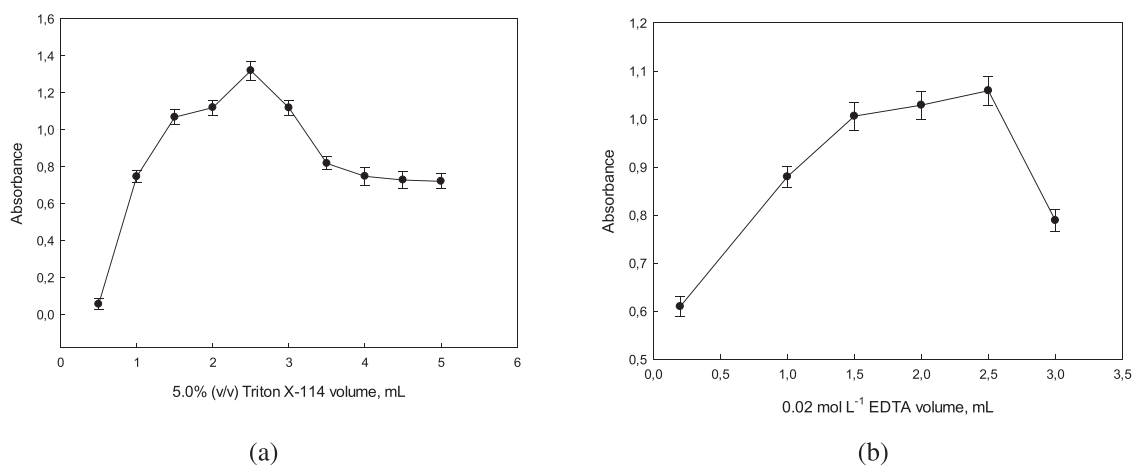


Fig. 4. The effect of (a) 5.0% (v/v) Triton X-114 vol and (b) EDTA volume to analytical signal.

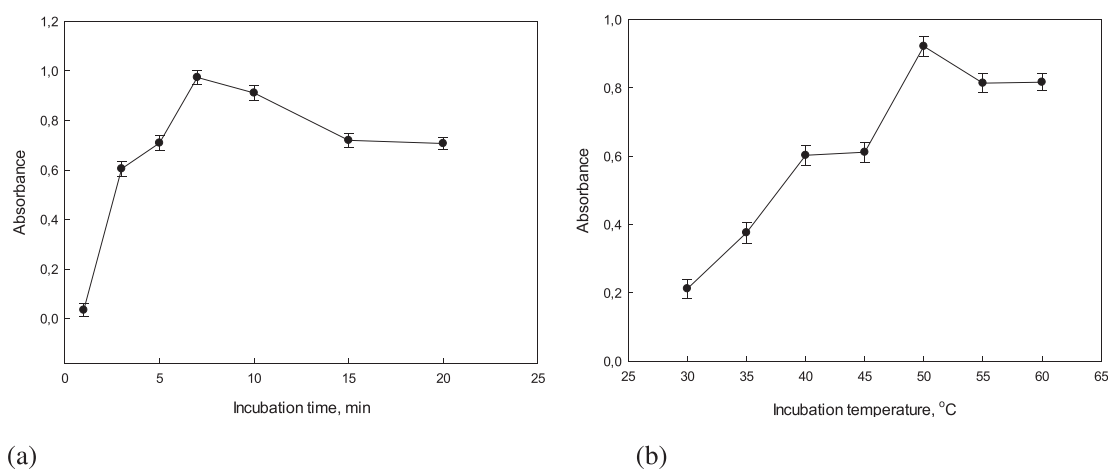


Fig. 5. The effect of (a) Incubation time, min (b) Incubation temperature, °C.

amount of ionic surfactant (CTAB). Through observing the occurrence of cloud point phenomenon in different temperatures. As a result of the optimization experiments carried out, it was observed that an equilibration temperature of 50 °C and a time of 7 min for Co(II), was sufficient for efficient extraction. The obtained results were shown in Fig. 5(a, b).

A centrifuge device was used to increase the efficiency of ultrasound assisted extraction and facilitate phase separation. After this process, the initially cloudy solution became transparent. Looking at the obtained results, the best condition for phase separation was obtained at 3000 rpm for 5 min. The obtained results were shown in Fig. 6(a, b).

3.7. Effect of diluent type

Because of the small volume of obtained organic phase after extraction, it must be diluted prior to UV-VIS measurement. The traditional dispersive solvents as methanol, ethanol, acetone, acetonitrile, tetrahydrofuran (THF) were researched and compared. Ethanol was optimal diluent for the quantitative recovery of Co(II). The obtained results were shown in Fig. 7. There is an optimal volume (diluted to 1.0 mL with ethanol) for the quantitative recovery of Co(II). The smaller volumes of ethanol were not tested because in this case it was not possible to quantitatively transfer the surfactant-rich phase from test tubes to the graduated tubes and

Table 1

The analytical figures of merit.

Analytical parameters	Co(II) at 335 nm
Linear working range, $\mu\text{g L}^{-1}$ (n: 10)	1–10
Intercept, b	0.0856
Slope, m	0.0048
Regression coefficient, R ²	0.993
Limit of detection, LOD $\mu\text{g L}^{-1}$	0.76
Limit of quantification, LOQ, $\mu\text{g L}^{-1}$	2.59
RSD% (5, 25 and 100 $\mu\text{g L}^{-1}$, n: 5)	4.80

measuring the absorbance. Larger volumes of the diluted solution with ethanol lead to a gradual decrease in absorbance.

3.8. Analytical figures of merit

The analytical characteristic values obtained after determining the optimal extraction conditions of the proposed UA-CPE are given in Table 1. The correlation coefficient (R²) is 0.993, which indicates that the calibration curve is close to linearity. It was determined that the factor sensitivity of Co(II) increased after UA-CPE application. The LOD and LOQ was calculated as $3 \times S_{\text{blank}}/m$ and $10 \times S_{\text{blank}}/m$, respectively, where S_{blank} was the standard deviation of ten replicate measurements of blank samples and m was

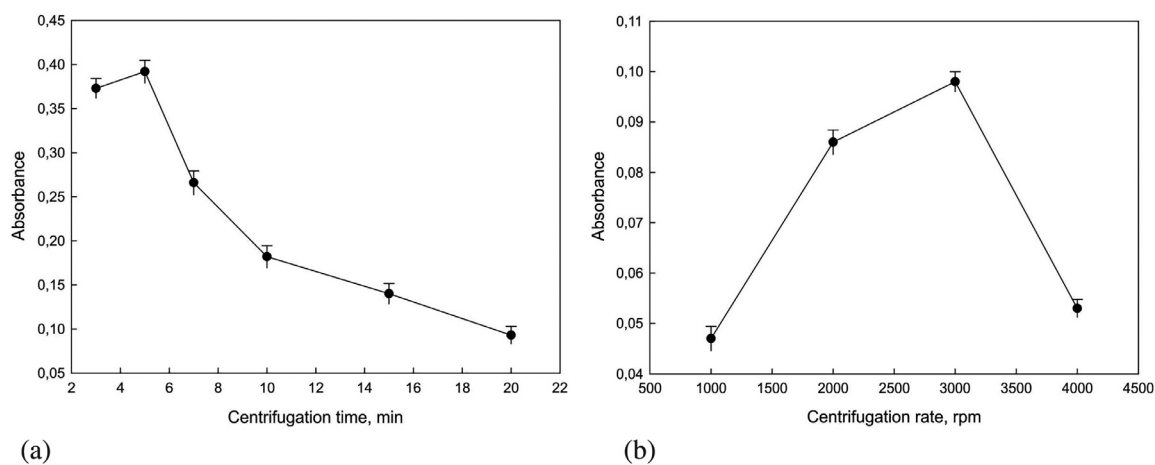


Fig. 6. The effect of (a) centrifugation time, min (b) centrifugation rate, rpm.

Table 2

The intra-day and inter-day accuracy and precision studies for the measurements of Co(II) in two quality control samples spiked with 5 and 10 $\mu\text{g L}^{-1}$.

Samples	Spiking level, $\mu\text{g L}^{-1}$	Repeatability, n: 5 in same day			Reproducibility, n: 5 in three succeed days		
		Found, $\mu\text{g L}^{-1}$	RSDr%	Recovery%	Found, $\mu\text{g L}^{-1}$	RSDr%	Recovery%
Black pepper	–	0.258 \pm 0.013	5.0	–	0.254 \pm 0.013	5.11	–
	5	4.77 \pm 0.2	4.20	90.2	4.80 \pm 0.2	4.21	90.0
	10	10.06 \pm 0.4	3.97	98.0	10.10 \pm 0.4	4.00	97.5
Green tea	–	0.217 \pm 0.01	4.60	–	0.220 \pm 0.01	4.67	–
	5	4.89 \pm 0.2	4.09	93.5	4.90 \pm 0.2	4.10	93.12
	10	10.09 \pm 0.3	2.97	98.7	10.05 \pm 0.3	2.98	98.3

*All values represent a mean plus standard deviation for five replicate measurements for Co(II).

**The recovery was calculated by determining the Co(II) amount ($\mu\text{g L}^{-1}$) in a pre-treated sample and in another one to which a known amount of Co(II) was added ($\mu\text{g L}^{-1}$). The difference between these two quantities represents the recovered Co(II). The ratio between recovered Co(II) to the added one gives the recovery degree.

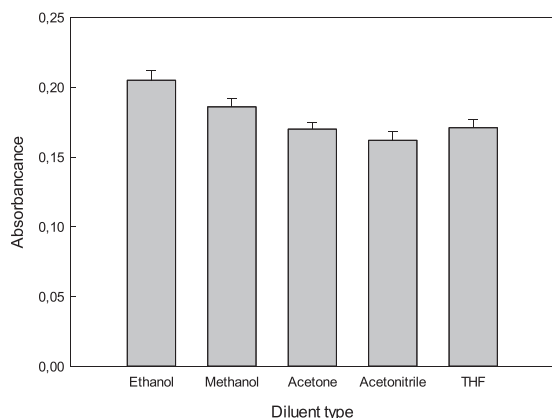


Fig. 7. The effect of diluent type to analytical sensitivity.

the slope of the linear sections of the calibration curves. The LOD and LOQ were obtained 0.76 and 2.59 $\mu\text{g L}^{-1}$ respectively. Precision of the analytical method were determined as 4.80% by repeating the method five times. According to ATSDR, the minimal risk level for Hazardous Co through oral route and has acute effect is 0.01 $\text{mg kg}^{-1}\text{day}^{-1}$ [51]. The values of metal concentrations were compared with the maximum permissible concentration of 0.2 mg kg^{-1} for Co as recommended by Codex Alimentarius Commission and Turkish Food Codex [52,53]. The accuracy of the method was tested by the intra-day/inter-day accuracy and precision studies

based on the measurements of Co(II) in two quality control samples with and without spiking at levels of 5 and 10 $\mu\text{g L}^{-1}$, due to the lack of a certified sample compatible with the sample matrix. The results are given in Table 2. When considered analysis of the quality control sample containing Co(II) around detection limit, the accuracy was good with a recovery ranging from 93.1% to 98.7%. This result seems to be acceptable for quantitative analysis of Co(II) at trace levels. The precision (as RSD%) was ranging from 2.97% to 4.67% for replicate measurement of 5 and 10 $\mu\text{g L}^{-1}$ Co(II) (n: 5 and 3 \times 5 in the same day and three consecutive days, respectively). The Co levels from Tokaloğlu were reported in one brand of red pepper (powdered) (1.44 $\mu\text{g g}^{-1}$) followed by one brand of red pepper (flakes) (1.19 $\mu\text{g g}^{-1}$), and in blackcurrant (0.01 $\mu\text{g g}^{-1}$), respectively [54]. Co concentrations in basil, peppermint, cumin, and black pepper samples were not detected by Abou-Arab and Donia from Egypt [55]. The Co levels from India were reported to be 0.84 $\mu\text{g g}^{-1}$ in nigella seeds, 0.48 $\mu\text{g g}^{-1}$ in cumin samples, 0.21 $\mu\text{g g}^{-1}$ in black pepper, and 4.12 $\mu\text{g g}^{-1}$ in fenugreek [56]. It has been determined that the proposed analytical process can be used for the determination of Co(II) quickly and simply, with low cost and by reducing the use of chemicals.

3.9. The matrix effect

In the UA-CPE process, the presence of other metal ions other than the analyte will pose a threat to Co(II) forming a complex with PX and EDTA. The complexation efficiency of Co(II) decreases when matrix species attempt to complex formation of Co(II). A triplicate measurement of 100 $\mu\text{g L}^{-1}$ of all possible ions was investigated to evaluate the selectivity and possible inhibitory ef-

Table 3

The effect of the possible matrix components on the determination of Co(II) at level of 100 µg L⁻¹ (n: 3).

Coexisting ions	Tolerance limit, [Interfering species]/[Co(II)]	Mean recovery%
Na ⁺	100	103.0
NO ₂ ⁻	100	102.0
F ⁻	25	97.8
Cl ⁻	100	95.0
NH ₄ ⁺	50	94.5
Fe ³⁺	75	101.0
Cd ²⁺	100	102.0
SO ₄ ²⁻	100	103.0
Cr ³⁺	25	100.0

Table 4

The analysis results of Co(II) in spices samples by UA-CPE method (n: 5).

Determination of Co(II) in Spices Samples				
	Co(II), µg/L		RSD%	Recovery%
	Added	Found		
Red pepper 1	0	8.82±0.13	1.47	–
	2.5	150±1.87	1.20	94.12
	5	300±2.43	0.9	97.1
	10	600±3.78	0.63	98.5
Cocoa	0	12±0.40	3.30	–
	2.5	147.6 ± 1.52	1.1	90.4
	5	300±2.84	0.94	96.0
	10	595.8 ± 3.63	0.61	97.3
Chicken spice	0	3.84±0.10	2.6	–
	2.5	130.2 ± 1.43	1.1	84.2
	5	330.6 ± 2.50	0.7	108.0
	10	592.2 ± 3.32	0.5	98.1
Red pepper 2	0	9.72±0.30	3.0	–
	2.5	131.4 ± 1.40	1.10	81.1
	5	326.4 ± 2.52	0.7	105.0
	10	589.8 ± 3.24	0.5	96.7
Turmeric	0	9.00±0.33	3.66	–
	2.5	153±1.87	1.2	96.0
	5	293.4 ± 2.24	0.77	94.8
	10	600±3.21	0.55	98.5
Red powdered pepper	0	13.80±0.24	1.70	–
	2.5	150±1.18	0.79	90.8
	5	300±2.12	0.71	95.4
	10	600±3.14	0.52	97.7
Black pepper	0	15.48±0.27	1.74	–
	2.5	158.4 ± 1.84	1.16	95.3
	5	286.2 ± 2.75	0.96	90.2
	10	603.6 ± 3.78	0.62	98.0
Thyme	0	9.42±0.18	1.91	–
	2.5	145.2 ± 1.47	1.01	90.5
	5	309±2.35	0.76	99.9
	10	600±3.55	0.59	98.4
Green tea	0	36.6 ± 0.74	2.10	–
	2.5	172.8 ± 1.11	0.64	98.9
	5	298.2 ± 2.74	1.03	93.5
	10	610.8 ± 3.12	0.51	98.7

ffects of the matrix components. The tolerance level was defined as the maximum amount of foreign species producing an error of ± 10.0% in Co(II) determination. The obtained results were shown in Table 3. It does not show a serious interference effect of foreign ions other than the analyte in the sample matrix since the recovery is quantitative in range of 94.5–103.0%. No serious interference was observed at the tolerable concentration level.

3.10. Analysis of real samples

After verification of the accuracy and precision of the method, the applicability of the method was investigated for determination of Co(II) in spices samples by Spectrophotometry. The sample was spiked Co(II) at three concentration levels. According to

the results contained in Table 4, the recoveries of Co(II) for spiked samples in spices samples were in the range of 81.1–98.9%, 90.2–108.0% and 96.7–98.7%, respectively. Consequently, the Ultrasonic Assisted Cloud Point Extraction with Spectrophotometric method can be successfully applied for the preconcentration

3.11. Comparison with literature studies

Table 5 shows the comparison of the experimental results obtained as a result of the application of the proposed study for the extraction and determination of Co(II) to real samples with other studies in the literature. Looking at other studies, it is seen that more comprehensive devices and chemicals with higher toxicity are used. In addition, it can be suggested that the recommended

Table 5
Comparison of UA-CPE/spectrophotometry with other preconcentration methods for determination of trace cobalt (Co(II)) in different sample matrices.

Sample matrix	Preconcentration method	Detection tool	Linear dynamic range	LOD	RSD%	Refs.
Spices	MSPE ^a	FAAS	10.8 $\mu\text{g L}^{-1}$	1.6 $\mu\text{g L}^{-1}$	6.0	[24]
Medicinal plants	DES-RS-CPE ^b	Spectrophotometry	100 $\mu\text{g L}^{-1}$	0.08 $\mu\text{g L}^{-1}$	1.90	[25]
Saline Samples	ISFME ^c	AAS	0.2 and 1000.0 ng mL^{-1}	0.06 ng mL^{-1}	1.8	[57]
Water samples	DLLME ^d	FAAS	3.0–200.0 ng mL^{-1}	0.44 ng mL^{-1}	2.3	[58]
Water and food samples	DLLME	Spectrophotometry	2.0–20.0 ng mL^{-1}	0.65 ng mL^{-1}	0.4032	[59]
River and lake water	IL-UADLLME ^e	Chromatography	0.5–100.0 $\mu\text{g L}^{-1}$	0.03 $\mu\text{g L}^{-1}$	5.0	[60]
Water and fruit juice samples	DLLME	FAAS	0.50–50 $\mu\text{g L}^{-1}$	0.22 $\mu\text{g L}^{-1}$	3.4	[61]
Spices	UA-CPE	Spectrophotometry	1–10 and 10–210 $\mu\text{g L}^{-1}$	0.76 $\mu\text{g L}^{-1}$	4.80	The present study

^a Magnetic solid phase extraction.

^b Green deep eutectic solvent - rapidly synergistic cloud point extraction.

^c Ionic liquids, solvent formation microextraction.

^d Dispersive liquid–liquid microextraction.

^e Ionic liquid ultrasound-assisted dispersive liquid–liquid microextraction.

method can be reliably used for to determine of trace amounts of Co(II) with high sensitivity, from the results such as the working range and either a lower or comparable LOD values at the $\mu\text{g L}^{-1}$ level.

4. Conclusions

In this experimental research, a novel enrichment process was suggested for the detection of trace level of Co(II) in spice species by ultrasound assisted UV–VIS. The proposed process is associated with complexation of Co(II) ions with PX and EDTA at pH 4.0 and afterwards extraction of the created metal chelates into the micellar phase of TX-114 in existence of CTAB. In this study, UV–VIS spectrophotometer device was used for analytical signal measurement and extraction could be completed by using less reagents. The proposed method in this work has low LOD and LOQ sensitivity. A detection limit of $3.84 \mu\text{g kg}^{-1}$ obtained for the spiked sample matrix was much lower than the legal limit allowed for Co in products (0.2 mg kg^{-1}), where the Co(II) levels of samples are in range of $3.84\text{--}36.6 \mu\text{g kg}^{-1}$. As a result, a low limit of detection and good intra-day/inter-day precisions (low RSD%) were obtained. The method was also applied to the analysis of real samples with satisfactory results. Moreover, the proposed process has many benefits such as easy processing, cost-effective, good yield and harmless to the environment and reliable determination of Co(II) that can be easily implemented to spice types.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Nuket Kartal Temel: Conceptualization, Supervision, Methodology, Investigation, Writing – review & editing. **Mehtap Çöpür:** Conceptualization, Methodology, Investigation, Visualization, Writing – original draft.

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