# Rapid preconcentration and determination of Co (II) ions in aqueous medium using ultrasound assisted cloud point extraction method

## Ultrason destekli bulutlanma noktası ekstraksiyonu yöntemiyle sulu ortamda bulunan Co (II) iyonlarının hızlı önderiştirilmesi ve tayini

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**Abstract**

A flame atomic absorption spectrophotometric technique was studied for the preconcentration and determination of $Co^{2+}$ ions in trace amounts after ultrasound enhanced enrichment of its 1-(2-pyridylazo)-2-naphthol (PAN) complexes by cloud point extraction. The $Co^{2+}$ ions were firstly complexed with PAN molecules at pH 4 and the complex transferred to a surfactant Tergitol NP-7 (TNP-7) rich phase with a very small volume under ultrasound waves. The surfactant rich phase was separated and dissolved by 1 mL, 1.0 M $HNO_3$ in ethanol prior to determination of $Co^{2+}$ concentration by flame atomic absorption spectrophotometry. The optimization steps of ultrasound interaction time, solution pH and surfactant volumes were achieved by response surface methodology (RSM) which is a combination of statistical approaches. PAN concentration and possible interfering ions were optimized conventionally. The $Co^{2+}$ ions were extracted only in 150 s at pH 4 quantitatively under optimum conditions (>95%). The accuracy and validity of developed ultrasound assisted cloud point extraction (UA-CPE) was granted by employing a certified reference material wastewater UME CRM 1204. The technique was applied to wastewater and natural water with satisfactory results.

**Keywords**: Non-heated cloud point extraction, Ultrasound, PAN, Response surface methodology, Flame atomic absorption spectroscopy

**Öz**

Eser miktardaki $Co^{2+}$ iyonlarının 1-(2-Piridilazo)-2-Naftol (PAN) komplekslerinin ultrason destekli bulutlanma noktası ekstraksiyonu ile zenginleştirilmesi ve alevli atomik absorpsiyon spektrofotometri yöntemi ile tayini için bir yöntem geliştirilmiştir. $Co^{2+}$ iyonları ilk olarak pH 4'te PAN molekülleri ile kompleksleştirildi ve oluşan kompleksultrasonik dalgalar ile küçük hacimli yüzey aktif madde Tergitol NP-7 (TNP-7) bakımından zengin faza aktarıldı. Yüzey aktif madde açısından zengin faz ayrıldıktan sonra 1 mL 1.0 M HNO3 etanolde çözülmüş ve ardından alevli atomik absorpsiyon spektrofotometrisi ile $Co^{2+}$ konsantrasyonu belirlenmiştir. Ultrason etkileşim süresi, çözelti pH'sı ve yüzey aktif madde hacimlerinin optimizasyon adımları istatistiksel yaklaşımların bir kombinasyonu olan yüzey yanıt yöntemi (RSM) ile gerçekleştirilmiştir. PAN konsantrasyonu ve olası girişim yapan iyonların etkisi geleneksel olarak optimize edilmiştir. $Co^{2+}$ iyonları sadece 150 saniye içerisinde pH 4'te optimum koşullar altında kantitatif olarak (>%95) ekstrakte edilmiştir. Geliştirilen ultrason destekli-bulutlanma noktası ekstraksiyonu (UA-CPE)'nin doğruluğu ve geçerliliği, sertifikalı referans malzeme atıksu UME CRM 1204 kullanılarak sağlanmıştır. Yöntem, atık su ve doğal sulara tatmin edici sonuçlarla uygulanmıştır.

**Anahtar kelimeler**: Isıtmadan bulutlanma noktası ekstraksiyonu, Ultrason, PAN, Yanıt yüzey yöntemi, Alevli atomik absorpsiyon spektroskopisi

## 1 Introduction

Cobalt is a unique element that is the only metal ion consisting in the chemical structure of a vitamin. This metal ion centrally located in the vitamin B12 molecular structure as a complex of a corrin ring [1]. Among the heavy metals, cobalt ions are essential for human metabolism at low concentrations and also play an effective role in regulating of the pro-oxidants in blood [2]. Besides all these useful features, exposure to cobalt may cause symptoms for example failure of the nervous system, lowering the blood pressure, vomiting and paralysis. Inflammation of the lungs, lung toxicity and asthma and chest tightness are other disorders at higher concentrations of cobalt. Also, cobalt has

defined as a potential carcinogen by The International Agency for Research on Cancer (IARC) [3]. Total $Co^{2+}$ concentration in freshwater should not exceed 4 μg/L and 110 μg/L respectivelyto protect from chronic toxic effects and acute toxic effects [4]. Cobalt is generally used to produce corrosion-resistant, heat-resistant and other specific alloys and steels in many industries such as electronic manufacturing, nuclear power plants, pigments, electroplating, metallurgical industry and mining, etc. Tons of wastewater containing $Co^{2+}$ ions are released from these industries. Directly discharged wastewaters without any treatment method contaminates the environment nature and relatively harms the living organisms [5]. Therefore,

determination of cobalt pollutions in waters may be considered as a key point to avoid such serious problems. Pre-treatment of samples in which the analytes are in low concentrations such as preconcentrationmethods are of prime importance for their separations and determinations. The common treatment methods for enrichment, separation and removal of metal ions in aqueous samples are adsorption, ion exchange, membrane separation, ultrafiltration, chemical precipitation, coagulation, nanofiltration and flocculation [6]. In last few decades, analytical chemists focused on more reliable, faster and greener methods in separation science. A surfactant-based new and alternative technique for extraction and preconcentration of analytes called "the cloud point extraction" (CPE), which involves a micelle mediated phase separation [7].

The CPE namely, cloud point extraction is a simple, efficient, low cost and environmentally friendly extraction method with high enrichment factor and receiving attention for only requires a very small amount of chemicals. CPE is based on separation of two phases involving the micelle phase whom aggregation of the surfactant rich micelles in a very small volume and aqueous phase including the matrix and aqua, above a temperature and surfactant concentration. This allows the preconcentration of the organic substances and/or heavy metal ions from aqueous samples into the surfactant rich phase [8].

In recent researches, using of ultrasound in analytical separation methods resulted with developing some ultrasound-assisted extraction techniques. The ultrasound energy can accelerate some of the reactions and some extraction processes by increasing the interaction rate between the species involved in extraction media.

Ultrasound assisted cloud point extraction (UA-CPE) is also one of improved CPE techniques. In this improved method, basic principles of cloud point extraction (CPE) combined with the benefits of ultrasound especially in the clouding phenomena of the CPE process occurred under ultrasonic waves to accelerate the reactions of micelle forming. Ultrasonic waves also improve dispersion of surfactant rich phase and aqueous phase in CPE while reducing the process duration. Consequently, the target analytes can be separated and preconcentrated more precise and faster [9,10].

The UA-CPE method performed with ultrasound support and without heating, was used for the first time in this research for the determination of Co with PAN ligand and TNP-7 surfactant. Using ultrasound waves in CPE is a new approach for this preconcentration technique [11,12].

## 2 Material and methods

### 2.1 Apparatus

The metal concentrations were measured by a double beam flame atomic absorption spectrophotometer(Shimadzu UV-160 A, Kyoto, Japan). Ultra-sonication was applied by an AXUY-06LAB model ultrasonic bath (Alex Machine, İstanbul, Türkiye) and the phase separation experiments were conducted by a NUVE brandcentrifuge (NF 400,Nuve,

Ankara, Turkey). The acetylene-air flow rates were adjusted to obtain the highest$Co^{2+}$ absorbance.

### 2.2 Reagents and solutions

All the chemicals used in UA-CPE experiments were obtained from Sigma–Aldrich (Missouri, USA) and Merck (Darmstadt, Germany) brands. The chemicals were in analytical grade and used without additionally purification. The pH arrangements were made by using buffer solutions containing appropriate couples of citric acid, ammonia, sodium dihydrogen phosphate/phosphoric acid/ disodium monohydrogen phosphate solutions. The complexing agent PAN was prepared as $1 \times 10^{-3}$mol $L^{-1}$aqueous solution by dissolving the pure solid in 5mL of ethyl alcohol. The surfactant source was a non-ionic nonylphenolethoxylate (2% (w/v) TNP-7), its cloud point temperature is 20°C, and the density is 1.044 g $cm^{-3}$ (DOW, Midland, USA). $Co^{2+}$ stock solution (1000 mg $L^{-1}$) was prepared from pure $Co(NO_3)_2$ solid. The metal solutions used in the experiments were prepared by dilution of 1000 mg $L^{-1}$ stock cobalt solution.

### 2.3 UA-CPE procedure

1.0 mL of 5 μg/mL $Co^{2+}$analyte solution was added on to centrifuge tube containing 5.0 mL citrate buffer (pH 4) and 0.25 mL (from $1 \times 10^{-3}$mol $L^{-1}$ in ethanol) complexing agent PAN was added to this mixture and shaken for 30 seconds for complexation. Finally, 1.0 mL of non-ionic surfactant TNP-7 was added to this mixture up to 50 mL of total volume by distilled water. The ultrasonic waves (420 W, 32 kHz) were applied to resultant mixture at 25°C for 2 min. After clouding, phases were separated by centrifugation(4 min) at 4000 rpm. Than the supernatant was removed by decantation. The surfactant-rich phase was dissolved by 0.5 mL of 1.0 M $HNO_3$ in ethanol. Dissolved solution was diluted to 2 mL by 1.0 M aqueous $HNO_3$ solution and absorbance of $Co^{2+}$metal ions wereobtained by flame atomic absorption spectrometer measurements (FAAS). All experiments were conducted as triplicate.

## 3 Results and discussions

The UA-CPE method was optimized by response surface methodology (RSM) which is a combination of statistical approaches to optimize the analytical processes in which the response is analysed by significant variables.

### 3.1 Response surface methodology of UA-CPE

In the RSM method, the optimum conditions of selected variables can simultaneously be determined by using the least number of analysis. The Box-Behnken Design (BBD) is a one of the most effective method in multivariate optimization. BBD is a quadratic design in which the experimental points are located in the centre and the middle of the edges of a cube [13]. For this purpose, BBD was adopted for the main optimization steps of our UA-CPE experiments. Multi-variable quadratic regression fitting analysis was performed for $Co^{2+}$ recovery (%) by UA-CPE using analysis of variance (ANOVA) and RSM was performed by using a statistical software. The mathematical relationship of the $Co^{2+}$ recovery (%) against solution pH,

surfactant volume and ultrasound time is shown by Equation (1).

$$Co^{2+} \text{ recovery (\%)}$$
$$= +95{,}60 + 20{,}13A + 23{,}63B$$
$$+ 16{,}50C + 20{,}25AB + 19{,}00AC \quad (1)$$
$$+ 18{,}00BC - 30{,}68A^2 - 32{,}68B^2$$
$$- 26{,}93C^2$$

As a sum of Figure 1, the solution pH is a critical factor in UA-CPE method especially if the method involves chelating metal chelation or metal-ligand complexation in which pH strongly affect the extraction efficiency. Figure 1a and Figure 1b approve this phenomenon. The effect of pH on the UA-CPE technique was studied for pH 2.0–8.0. Figure1-a and b represents that the recovery of cobalt ions raised to a quantitative value (98 %) at pH. The recovery values slightly changed after pH 4. Above pH 5, $Co^{2+}$ recoveries were over 90 %. Lower recovery values of $Co^{2+}$ ions are observed between pH 2.0 and pH 4. On the other hand, when the solution pH values were 4.0 and higher, quantitative recovery values were obtained. This allows the technique to applicate real samples up to pH 8.

The ANOVA table of $Co^{2+}$ recovery (%) (Table 1), the adjusted $R^2$ of 09994 and predicted $R^2$ of 0.9968 were in reasonable agreement. The precision measures the signal to noise ratio and when this value is bigger than 4, it is desirable. Our ratio of 117.12 indicates an adequate signal. Consequently, this model can be used to navigate the design space.
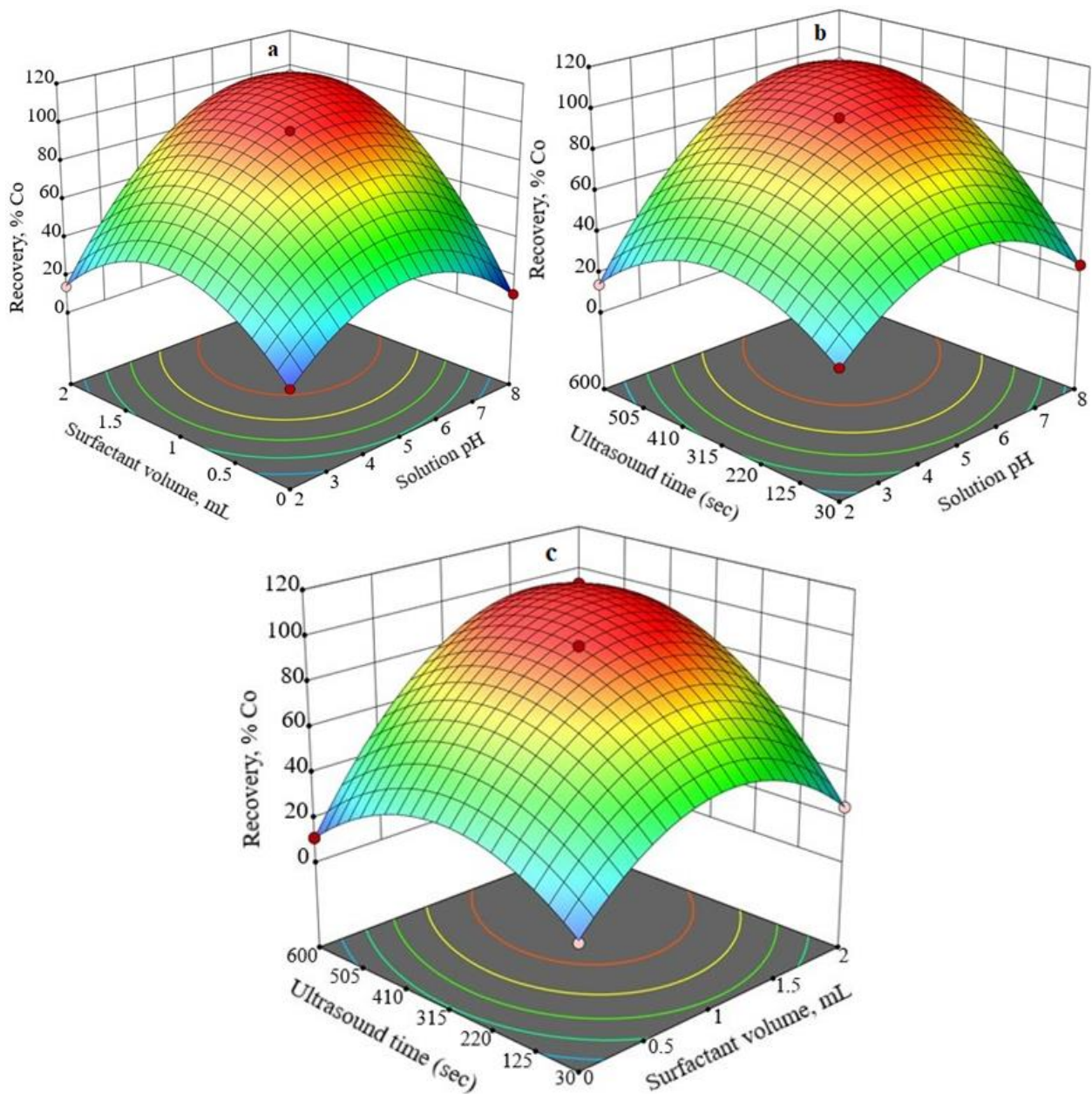


**Figure 1.** Three-dimensional surface response diagram of $Co^{2+}$ recovery in terms of solution pH (a,b), ultrasound time (b,c), and surfactant volume (a,c)

**Table 1.** Analysis of variance for the fitted quadratic model for optimization parameters of UA-CPE

| Source | Sum of squares | DF | Mean square | F-Value | p-value | |
|---|---|---|---|---|---|---|
| Model | 26564.49 | 9 | 2951.61 | 3203.30 | < 0.0001 | significant |
| A-Solution pH | 3240.13 | 1 | 3240.13 | 3516.41 | < 0.0001 | |
| B-Surfactant conc. | 4140.50 | 1 | 4140.50 | 4493.57 | < 0.0001 | |
| C-Ultrasound time | 1953.13 | 1 | 1953.13 | 2119.67 | < 0.0001 | |
| AB | 1640.25 | 1 | 1640.25 | 1780.12 | < 0.0001 | |
| AC | 1444.00 | 1 | 1444.00 | 1567.13 | < 0.0001 | |
| BC | 1260.25 | 1 | 1260.25 | 1367.71 | < 0.0001 | |
| $A^2$ | 3929.69 | 1 | 3929.69 | 4264.78 | < 0.0001 | |
| $B^2$ | 4529.85 | 1 | 4529.85 | 4916.12 | < 0.0001 | |
| $C^2$ | 3080.85 | 1 | 3080.85 | 3343.56 | < 0.0001 | |
| Residual | 6.45 | 7 | 0.9214 | | | |
| Lack of Fit | 5.25 | 3 | 1.75 | 5.83 | 0.0607 | not significant |
| Pure Error | 1.20 | 4 | 0.3000 | | | |
| Cor Total | 26570.94 | 16 | | | | |

| | |
|---|---|
| $R^2$ | 0.9998 |
| Adj $R^2$ | 0.9994 |
| Pred $R^2$ | 0.9968 |
| Adeq Precision | 117.12 |

According to Table 1, the F-value of the model was 3203.3 that implies the model is significant. The P-values in Table 1 are less than 0.0500 that indicate model terms are also significant. These results make the model terms A, B, C, AB, AC, BC, $A^2$, $B^2$, $C^2$ significant. The lack of fit F-value of 5.83 which is not significant and implies there is a 6.07% chance that a lack of fit.

The graphical relationship between recovery of $Co^{2+}$ versus surfactant volume/solution pH, ultrasound time/solution pH and ultrasound time/surfactant volume was evaluated using response surface methodology (RSM). The three dimensional graphics were given in Figure 1 based on the proposed model's equation (Equation 1).

The CPE and UA-CPE procedures are similar with each other but ultrasonic waves are in UA-CPE are used to enhance and reduce the time in the process involving reactions and clouding phenomena. The enhancement effect of sonication process between 30 to 600 s on the UA-CPE technique was shown in Figure 1b and Figure 1c. The recovery values of $Co^{2+}$ dramatically raised by ultrasound at 150 s application time. Recoveries were quantitative and stable at higher sonication times. This means the ultrasound waves enhance 1- the complex formation between $Co^{2+}$ and PAN molecules, 2- micelle formation of TNP-7 monomers and 3- phase transfer of the $Co^{2+}$-PAN complexes from aqueous phase to surfactant rich phase [14].

Formation of micelles and becoming 'cloudy' of a surfactant solution is simply based on the surfactant concentration. When the concentration of a surfactant is raised in an aqueous solution, the non-ionic surfactant monomers starts to become insoluble and this aggregation is called as micelles. In the micelle formation the dielectric constant of water decreases and water acts as a weak solvent for the hydrophilic parts of the non-ionic surfactants. This behaviour leads to aggregation of monomers asmicelles and

a certain phase separation between the micellar and aqueous phases [15]. The non-ionic surfactant TNP-7 has a low critical micelle concentration (CMC) about 20 °C and chosen as micelle source for our UA-CPE experiments. The effect of TNP-7 concentration on the recovery of $Co^{2+}$ was analysed between 0–2.0 mL (from 2% w/v stock solution) and the recovery results were given in Figure 1a and Figure 1c. The recovery values increased up to 97 % $Co^{2+}$ at 1.0 mL surfactant volume and slightly decreased with the increase of surfactant volume. The low recovery values before 1.0 mL of surfactant volume can be related to inadequate micelle formation.

Consequently, 1.0 mL of surfactant volume, 150 s of sonication time and pH 4 values were chosen as optimum conditions for UA-CPE method.

### 3.2 Effect of PAN concentration

The effect of PAN concentration on the separation efficiency of UA-CPE method and preconcentration of $Co^{2+}$ ions were analysed in detail. The complete formation of $Co^{2+}$-PAN complex strongly depends on the PAN sufficient concentration in the extraction medium. For this purpose, the PAN volume was studied between 0 to 0.50 mL (from $1 \times 10^{-3}$ M stock solution) and the recovery values were given in Figure 2.

Figure 2 claims that the UA-CPE recovery of $Co^{2+}$ ions were raised up to 96% when the PAN volume was 0.25 mL (in 50 mL test tube), and remained stable after this value. Accordingly, 0.25 mL of PAN volume was selected as optimum for studied UA-CPE experiments.

### 3.3 InterferingIons

Some of the ions rather than the analyte-$Co^{2+}$ for our experiments- in real aqueous sample solutions are the matrix or interfering ions. These ions especially the metal ions may affect the $Co^{2+}$-PAN, complexation reaction resulting with

performance losses in proposed UA-CPE process. The tolerable levels of matrix ions on the enrichment and determination of cobalt ions defined as having a lower error of 10%. Table 2 shows the effect of interfering ions on the recovery of $Co^{2+}$ by proposed UA-CPE.
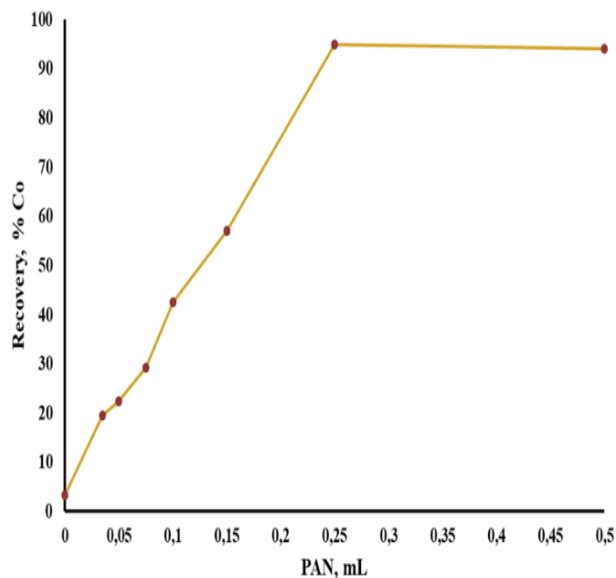


**Figure 2.** Effect of PAN volume on the recovery of $Co^{2+}$ by UA-CPE

**Table2.** Effects of possible interfering ions on the UA-CPE of $Co^{2+}$

| MatrixIons | TolerableConc. (mg/L) | $Co^{2+}$Recovery (%) |
|---|---|---|
| $Na^+$ | 500 | 98 ± 3 |
| $K^+$ | 500 | 97 ± 2 |
| $Ca^{2+}$ | 100 | 96 ± 2 |
| $Mg^{2+}$ | 25 | 95 ± 3 |
| $Fe^{2+}$ | 25 | 95 ± 4 |
| $Fe^{3+}$ | 25 | 95 ± 4 |
| $Al^{3+}$ | 25 | 95 ± 2 |
| $Mn^{2+}$ | 25 | 96 ± 2 |
| $Cu^{2+}$ | 50 | 95 ± 4 |
| $Cd^{2+}$ | 50 | 96 ± 2 |
| $Ag^+$ | 50 | 98 ± 3 |
| $Cl^-$ | 500 | 98 ± 3 |
| $NO_3^-$ | 500 | 98 ± 3 |
| $SO_4^{2-}$ | 500 | 97 ± 2 |

According to Table 2, common anions and cations have no significant interfering effect on the proposed UA-CPE method.

### 3.4 Analytical figures of merit

Analytical characteristics of the proposed UA-CPE technique were evaluated for LOD (limit of detection), LOQ (limit of quantitation) and PF (preconcentration factor). The LOD and LOQ values were calculated according to the utility of $3 \times s_{blank}/m$ and $10 \times s_{blank}/m$ equations, respectively, where m is the slope of the calibration curve. The linear calibration graph $Co^{2+}$ was obtained according to the optimized UA-CPE technique.

The correlation coefficient ($R^2$) for $Co^{2+}$ was 0.9996, and this value is considered to be the evidence of high sensitivity of the optimized procedure. The LOD and LOQ of the UA-CPE method were determined as 2.9 and 9.7µg/L of $Co^{2+}$. The ratio of sample volume before and after preconcentration is described as PF was calculated as 25.

### 3.5 Analytical eco-scale (Greenness)

The evaluation of proposed UA-CPE technique in the context of green chemistry was achieved by AGREE (Analytical GREEnness Metric calculator) [16] and the obtained results were given in Figure 3.
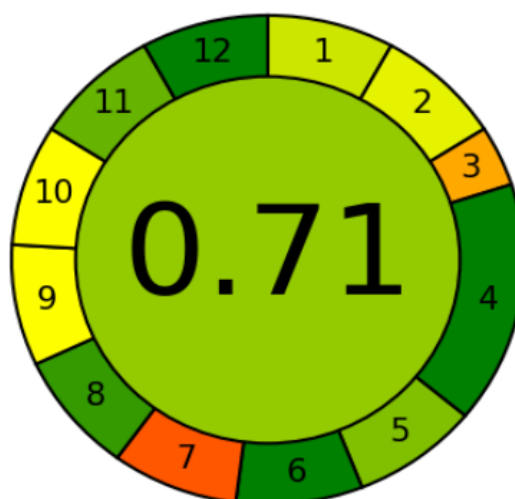


**Figure3.** Pictogram of the AGREE metric for the proposed UA-CPE technique

According to AGREE pictogram, green, yellow, and red colours indicate the 12 different parameters of the method by scoring from 0 to 1. Final colour and score of the proposed technique is given in the middle [17]. The AGREE score of the UA-CPE technique was 0.71 and the colour was close to green. The number three was about the positioning of the measurement device and the number seven was concerning the amount of waste. According to these results the method can be accepted as a green technique.

### 3.6 Analysis of certified reference material and real samples

Theaccuracy of the studied UA-CPE technique was evaluated by the analysis of a certified standard reference material (UME-CRM 1204, "Elements in wastewater"). Applicability of the UA-CPE technique was tested on natural water, wastewater and tap water samples. Measurements were given in Table 3 and Table 4 respectively.

**Table 3.** Determination of $Co^{2+}$ in certified reference material

| Certified reference materials | Certified value (mg/L) | Co Found (mg/L) | Recovery, % |
|---|---|---|---|
| UME CRM 1204 | 0.419 | 0.40±0.01[a] | 95.4±2 |

[a]Mean ± standard deviation

**Table 4.** Determination of $Co^{2+}$ in real water samples

| Samples | Added (µg) | Found (µg) | Recovery, % |
|---|---|---|---|
| Tap water | - | BDL | - |
| | 2.0 | 1.92±0.05[a] | 96±2.8 |
| | 4.0 | 3.85±0.18 | 96±4.6 |
| Natural spring water | - | BDL | - |
| | 2.0 | 1.94±0.06 | 97±3 |
| | 4.0 | 3.92±0.07 | 98±4 |
| Factory wastewater | - | 1.41±0.04 | - |

[a]Mean ± standard deviation      BDL: Below detection limit

Table 3 proves that the precision and accuracy of the proposed UA-CPE method is valid. On the other hand, the applicability of the UA-CPE technique was tested by using different real water samples and the recovery values were quantitative according to Table 4. The $Co^{2+}$ concentration of the wastewater sample was found as1.41±0.04 µg (in 45 mL of sample) according to proposed UA-CPE method.

## 4 Conclusions

A fast and simple ultrasound assisted cloud point extraction technique (UA-CPE) was optimized for the preconcentration and determination of $Co^{2+}$ ions as its PAN complex in aqueous solutions. Experimental studies revealed that using a 1.0 mL of surfactant under 150 s of sonication allowed to recovery of 97 % of $Co^{2+}$ ions at pH 4. The $Co^{2+}$ metal ions were successfully separated and determined in different matrix. The UA-CPE technique procedure showed its effectiveness in the determination of cobalt ions from certified reference material and real water samples.

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In the articles accepted for publication after the evaluation, if any, the institution, project, person, etc. information should be specified in this section.

### Conflict of interest

The authors declare that there is no conflict of interest.

**Similarity rate (iThenticate):** 16%

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