

## A simple and efficient approach for preconcentration of some heavy metals in cosmetic products before their determinations by flame atomic absorption spectrometry

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**Abstract:** In the current study, a simple and efficient analytical method for preconcentration and determination of Cd(II), Pb(II), and Sn(II) in some cosmetic samples, using ultrasonic assisted-cloud point extraction and flame atomic absorption spectrometry, was developed. The method is based on the ternary complex formations of Sn(II), Pb(II), and Cd(II), which are available in the form of neutral and/or anionic hydroxo complexes ( $\text{Sn}(\text{OH})_3^-$ ,  $\text{Pb}(\text{OH})_3^-$ ,  $\text{Cd}(\text{OH})_2$ , and/or  $\text{Cd}(\text{OH})_3^-$ ), with Victoria Pure Blue BO ( $\text{VPB}^+$ ) in the presence of cetylpyridinium chloride at pH 8.5, and then extraction of the formed ternary complexes into the micellar phase of polyoxyethylene sorbitan monostearate (Tween 60). Using the optimized conditions, a linear relationship was observed in the ranges of 12–330  $\mu\text{g L}^{-1}$  for Cd(II), 4–200  $\mu\text{g L}^{-1}$  for Pb(II), and 1–275  $\mu\text{g L}^{-1}$  for Sn(II). The detection limits for Cd(II), Pb(II), and Sn(II), respectively, were 3.70, 1.35, and 0.45  $\mu\text{g L}^{-1}$ , with a preconcentration factor of 50, and the precision as relative standard deviations was lower than 4.2% for each analyte. The validity was verified by analysis of two certified reference materials. Finally, the method was successfully applied to the determination of these metals in various cosmetic samples.

**Key words:** Extraction, green chemistry, heavy metals, pollution, spectroscopy, surfactants

### 1. Introduction

As is known, cosmetic samples have been commonly used to change the appearance of the skin, hair, and nails by people worldwide for centuries. Cosmetic samples include face and body care preparations (creams, lotions, soaps, etc.), color cosmetics (lipsticks, mascaras, eye shadows, etc.), and hair products (shampoos, colors, gels, etc.).<sup>1</sup> Unfortunately, some harmful chemicals are known to occur during the preparation of cosmetic samples.<sup>2</sup> Some harmful chemical species in cosmetic samples are toxic elements such as lead (Pb), cadmium (Cd), arsenic (As), mercury (Hg), and tin (Sn). Compounds of the elements are water-soluble, and sweat can support the percutaneous absorption of elements.<sup>3</sup> Heavy metals (Pb, Cd, and Sn) in cosmetics can be also accumulated in living tissues, particularly in human bodies, causing vital health problems such as to central nervous function, lungs, kidneys, livers, and other vital organs.<sup>4</sup> Therefore, the directive 76/768/EEC and further revisions banned the use of Cd, Co, Cr, Ni, and Pb as metallic ions or salts in the preparation of cosmetic formulations.<sup>1</sup> Hence, the accurate and reliable determination of heavy metal levels in cosmetic samples is one of the main research subjects of analytical chemistry.

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Numerous atomic spectroscopic and electroanalytical techniques such as flame atomic absorption spectrometry (FAAS),<sup>5–7</sup> atomic fluorescence spectrometry (AFS),<sup>8</sup> electrothermal atomic absorption spectrometry (ETAAS),<sup>9,10</sup> anodic and cathodic stripping voltammetry (ASV and CSV),<sup>11,12</sup> inductively coupled plasma optical emission spectrometry (ICP-OES),<sup>13–15</sup> differential pulse stripping voltammetry (DPSV),<sup>16</sup> and inductively coupled plasma mass spectrometry (ICP-MS)<sup>17–19</sup> have been used for determination of Cd, Pb, and Sn in foods, cosmetics, and solid environmental samples. Among these techniques, FAAS is widely used for determination of heavy metals in various matrices due to its good precision and accuracy, low cost, and simple instrument.<sup>20</sup> It also has special features such as high selectivity and low susceptibility to matrix interferences. However, the sensitivity of FAAS is not sufficient for determination of Cd, Pb, and Sn in many real samples because they are found in very low concentrations in those samples. Thus, an analytical step such as extraction, hydride generation, or preconcentration is required before FAAS detection. For alleviation of this problem, ultrasonic assisted-cloud point extraction (UA-CPE) was recently developed as an alternative to conventional liquid–liquid extraction (LLE) and co-precipitation. This extraction procedure shows some advantages such as simplicity, quickness, lower toxicity, high recoveries, and high concentration factors.<sup>21</sup> It is usually insufficient due to matrix interferences and trace amounts of metal ions. Initially, UA-CPE was employed for the separation and preconcentration of chemical species from various sample matrices. It is important to mention that, when the UA-CPE is applied for extraction of chemical species in different samples, it is necessary to add a suitable chelating agent, which results in a complex formation with affinity to extraction solvent, which can easily be extracted to surfactant-rich phase.<sup>22</sup>

In the current study, before analysis by FAAS, we proposed the UA-CPE procedure for separation/preconcentration of Cd(II), Pb(II), and Sn(II) ions from cosmetic samples by using a Victoria Pure Blue BO, a cationic triphenylmethane group dye, as a chelating agent in the presence of cetylpyridinium chloride (CPC) and polyoxyethylene sorbitan monostearate (Tween 60) at pH 8.5. Analytical variables such as pH, the ionic and nonionic surfactant amounts, the complexing agent amount, the sample volume, ultrasonic time, temperature, and matrix effect were exhaustively investigated. The method was validated by analysis of two certified reference materials (CRMs) by standard addition method, and then applied to the determination of the analytes in various cosmetic samples with satisfactory results.

## 2. Results and discussion

### 2.1. Sample preparation

In current study, for digestion of the cosmetic samples and CRMs, complete acid digestion with heating was used. The experimental steps of the process were as follows. All cosmetic samples (2.5 g) were accurately weighed into beakers of 100 mL. Then an aliquot of 20.0 mL of a mixture of 65% (v/v) HNO<sub>3</sub>, 35% (v/v) H<sub>2</sub>O<sub>2</sub>, and 3 mol L<sup>-1</sup> HClO<sub>4</sub> (2:1:1, v/v) was added to the beakers using a graduated pipette, and was completed to 100 mL with water. The resulting mixtures were allowed to decompose on heating plates at 125 °C for about 1 h in a hood. At the end of 1 h digestion, the resulting mixtures were transferred into centrifugation tubes and centrifuged for 10 min at 4000 rpm.<sup>23</sup> Then the solutions were filtered through a 0.45-μm membrane filter into volumetric flasks of 50 mL. The pH of the solutions was adjusted to 7.0 using dilute NaOH (1.0 mol L<sup>-1</sup>) and diluted to 50 mL with water. The above-mentioned sample preparation procedure was similarly applied to CRMs (Clay CRM051-050 metals on soil and SRM 1548a typical diet). In the same way, the reagent blanks were also prepared for the correction of the analytical signals of each metal. In the sample preparation step,

all sample preparations were repeated five times. For the determination of Cd(II), Pb(II), and Sn(II) in the cosmetic samples by FAAS, an aliquot of 2.0 mL of the pretreated cosmetic samples and CRMs was submitted to the proposed UA-CPE procedure.

## 2.2. The UA-CPE procedure

The UA-CPE procedure was carried out as follows. An aliquot of 10 mL of the standard solution containing analytes (Cd, Pb, and Sn) was placed into a 50-mL centrifuge tube and the pH was adjusted to 8.5 using tris-acetate buffer solution. Sequentially, 0.7% (w/v) of CPC, 0.25% (v/v) of Tween 60, and  $1.5 \times 10^{-5}$  mol L<sup>-1</sup> of VPB<sup>+</sup> were added. Then the tubes were sonicated for 10 min at 60 °C. In this stage, the solution became cloudy and the formed ternary complexes were extracted into the micellar phase of Tween 60. After that, for phase separation, the tubes were centrifuged for 5 min at 4000 rpm and the surfactant-rich phase was obtained at the bottom of the centrifuge tubes. Because the resulting micellar phase was very viscous, it was diluted to 1.0 mL using acidic methanol (containing 0.1 mol L<sup>-1</sup> HNO<sub>3</sub>). By only varying the burner and the radiant source, the contents of Cd, Pb, and Sn in samples were monitored and determined by FAAS. To determine the effects that may result from the reagents used, a blank solution was also subjected to a similar process and determined in parallel to the sample solutions and CRMs.

Data processing and all statistical calculations (ANOVA) were performed using Excel 2010 (Microsoft Office). The results obtained by three replicated measurements of samples and each CRM sample were expressed as mean  $\pm$  SDs. In terms of accuracy and precision, Student's t-test and variance ratio F-test were used to assess whether there was a significant difference between certified and experimentally found values. A significance level of 95% was adopted for all comparisons.

## 2.3. Optimization of UA-CPE conditions

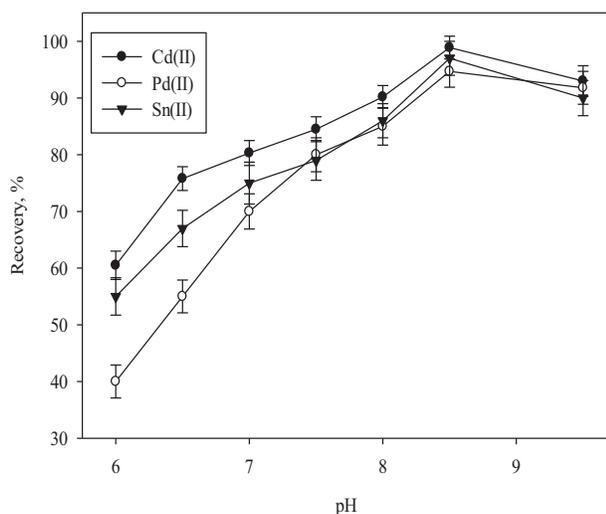
To achieve the maximum recovery of each analyte, different analytical variables including pH, the ionic/nonionic surfactant amounts, the chelating agent amount, the sample volume, ultrasonic time, temperature, and matrix effect were investigated in detail. During the optimization step, a fixed concentration of 20  $\mu$ g L<sup>-1</sup> of each analyte was used, and one-at-a-time strategy was employed.

### 2.3.1. Effect of pH

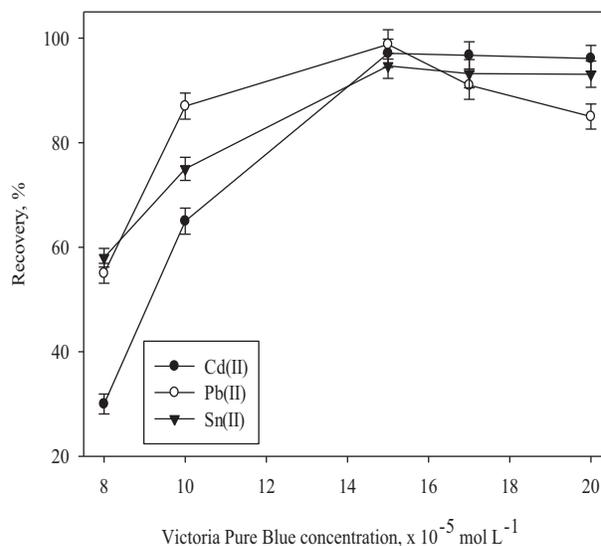
The formation of a hydrophobic stable complex is required for a successful UA-CPE process. For this purpose, pH is the first variable to be optimized, because the complex formation of Cd(II), Pb(II), and Sn(II) with chelating agent mostly depends on their forms at a particular pH. Moreover, the recovery of each analyte is significantly dependent on the pH of the aqueous solution. From the studies conducted in the pH range of 6.0–9.5, the best recovery for each analyte was obtained at pH 8.5. It can be seen in Figure 1 that the recovery increased along with increasing pH in the range of 6.0–8.5 and then gradually decreased. At higher pHs than 8.5, the cause of the signal decrease may be the conversion of the chelating agent, VPB<sup>+</sup>, to carbinol by nucleophilic attack of hydroxyl ions, OH<sup>-</sup>, in alkaline media. Among different buffers such as phosphate, universal Britton–Robinson, and tris-acetate, the best sensitivity was obtained using the tris-acetate buffer. Therefore, tris-acetate buffer at pH 8.5 was used to achieve the best recovery.

### 2.3.2. Effect of amount of chelating agent

The Victoria Pure Blue BO (VPB<sup>+</sup>), which is a member of the cationic triphenylmethane group of dyes containing a naphthylamine group with a hydrolysis constant of 2.16 (or  $pK_a$ : 11.84), was selected as chelating agent because it gives stable and suitable ion-pairing complexes with the most metals depending on environment pH. Moreover, as a result of the resonance interaction between the carbocation, R<sup>+</sup>, and lone pairs of electrons on the N-atoms of diethylamino and ethylamino substituents on aryl rings, it is a highly stable reagent with a carbocation stability of  $pK_{R^+}$ : 8.57 even in alkaline pHs, in which  $R^+ + H_2O \leftrightarrow ROH + H^+$ . This high  $pK_{R^+}$  value might be due to delocalization of the carbocationic charge by strong resonance effect of one-NHET and two-NET<sub>2</sub> on the structure of dye. Due to its positive surface charge, it is clear that Sn(II), Pb(II), and Cd(II) ions, which can easily be hydrolyzed and form neutral and anionic hydroxo complexes, Sn(OH)<sub>3</sub><sup>-</sup>, Pb(OH)<sub>3</sub><sup>-</sup>, Cd(OH)<sub>2</sub>, and/or Cd(OH)<sub>3</sub><sup>-</sup> at higher pHs than 6.0 with hydrolysis constants of 3.80, 7.71, and 10.8, respectively, can form stable ion-pair complexes in the presence of CPC as sensitivity enhancer in aqueous micelle media at pH 8.5.<sup>24–26</sup> In this sense, after preconcentration from sample matrix with CPE in the presence of excess SCN<sup>-</sup> and CPC at pH 2.0, ion-pairing reagent, VPB<sup>+</sup>, was successfully used in the determination of low levels of molybdenum with a detection limit of 2.18  $\mu\text{g L}^{-1}$  in the range of 7.5–1800  $\mu\text{g L}^{-1}$ .<sup>27</sup> Furthermore, the reagent has been used successfully in the determination of Sb(V) in the range of 1–250  $\mu\text{g L}^{-1}$  with a detection limit of 0.25  $\mu\text{g L}^{-1}$  after preconcentration by CPE at pH 10, while it is used in the determination of Sb(III) in the range of 10–400  $\mu\text{g L}^{-1}$  with a detection limit of 5.15  $\mu\text{g L}^{-1}$ .<sup>28</sup> In order to achieve the maximum recovery for each analyte, the effect of VPB<sup>+</sup> amount was investigated in the range of (8–20)  $\times 10^{-5}$  mol L<sup>-1</sup>. As can be seen in Figure 2, 15  $\times 10^{-5}$  mol L<sup>-1</sup> of VPB<sup>+</sup> can provide quantitative recovery for each analyte, and concentrations of the VPB<sup>+</sup> higher than 15  $\times 10^{-5}$  mol L<sup>-1</sup> caused no change in the recoveries except for Pb(II) with a slight decrease in signal. Consequently, 15  $\times 10^{-5}$  mol L<sup>-1</sup> of VPB<sup>+</sup> was used to achieve the best recovery.



**Figure 1.** Effect of pH on the recoveries of analytes under the optimized conditions.



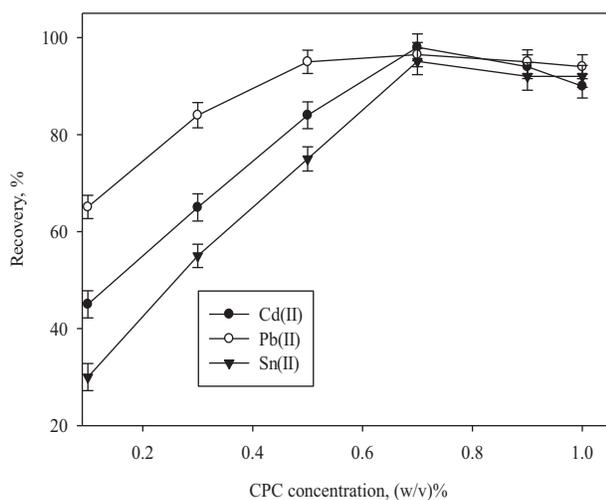
**Figure 2.** Effect of Victoria Pure Blue BO amount on the recoveries of analytes under the optimized conditions.

### 2.3.3. Effect of ionic surfactant amount

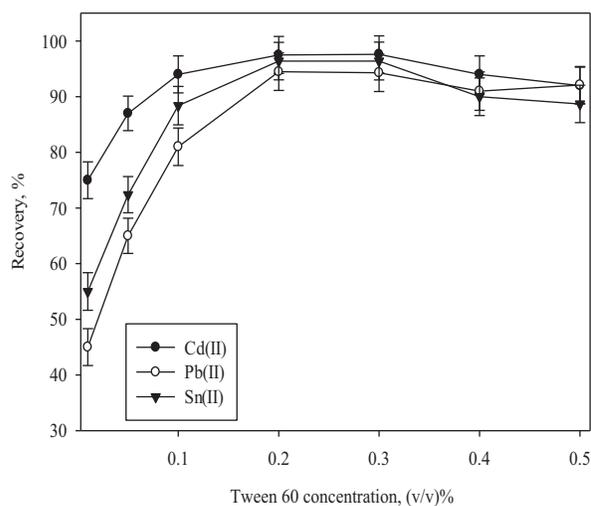
The cationic surfactant (CPC) was used as both a sensitivity enhancer and counter ion in the preconcentration step of the ion-pairing complexes. It can effectively transfer ternary complexes into the micellar phase of extracting agent, Tween 60, above critical micellar concentration (CMC), so as to cause an increase in sensitivity. To ensure this, the effect of CPC in the range of 0.1%–1.0% (w/v) was optimized. From the results obtained in Figure 3, it is understood that the CPC concentration strongly affects the recovery of each analyte. With regard to the CPC concentration, the best recovery for each analyte was observed for 0.7% (w/v) of CPC. Consequently, this value was used to achieve the best recovery.

### 2.3.4. Effect of nonionic surfactant amount

The main criterion for the best recovery of the UA-CPE process is nonionic surfactant type and concentration. In the present study, polyoxyethylene sorbitan monostearate (Tween 60) was selected as the extracting nonionic surfactant because of its features like ecofriendliness, low cost, and low cloud point temperature. On the other hand, the surfactant concentration is very important to obtain a high preconcentration factor. When nonionic surfactant concentration increases above the optimal value, the amount of the surfactant-rich phase increases after the UA-CPE, and consequently the preconcentration factor decreases. The phase was also too sticky and more difficult for subsequent handling. In this context, the effect of the Tween 60 concentration on the recovery was investigated in the range of 0.01%–0.5% (v/v) for each analyte. The results are shown in Figure 4. The recovery for each analyte was approximately the same between 0.2% and 0.3% (v/v) of Tween 60. This optimal value, which corresponds to a concentration of  $1.94 \text{ mmol L}^{-1}$ , is above the critical micelle concentration (CMC) of  $0.0206 \text{ mmol L}^{-1}$  ( $27 \text{ mg L}^{-1}$ ). Therefore, a concentration of 0.25% (w/v) was used to achieve the best recovery.



**Figure 3.** Effect of the CPC amount on the recoveries of analytes under the optimized conditions.

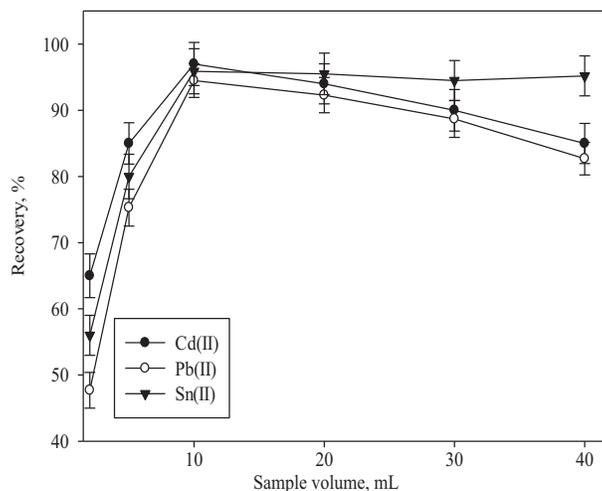


**Figure 4.** Effect of the Tween 60 amount on the recoveries of analytes under the optimized conditions.

### 2.3.5. Effect of sample volume

Because the target analyte concentration in the selected sample is usually low, the sample volume is one of the most important parameters for preconcentration and optimization. To evaluate the effect of sample volume, six

different volumes (2, 5, 10, 20, 30, and 40 mL) of sample were investigated by using model solutions for each analyte under optimal conditions. As can be seen in Figure 5, the recovery for each analyte increases up to 10 mL sample volume. Above this volume, the recovery value of the Sn(II) ion remained stable, but the recoveries of Cd(II) and Pb(II) decreased. Therefore, a sample volume of 10 mL was used to achieve the best recovery.



**Figure 5.** Effect of the sample amount on the recoveries of analytes under the optimized conditions.

### 2.3.6. Effect of equilibrium temperature and ultrasound extraction time

For preconcentration procedure, the temperature of the assay medium is a very important parameter for the formation of micelles. Therefore, the effect of the equilibrium temperature on the recovery for each analyte was investigated in the range of 40–80 °C under ultrasonic effect for 10 min. As a result of the experiments conducted, the separation of the two phases was quantitatively complete at 60 °C and the recovery of each analyte was approximately the same. Consequently, an equilibrium temperature of 60 °C was used to achieve the best recovery. Ultrasound effect is an important stage at which the formation of micelles becomes well dispersed in the aqueous solution. The ultrasound extraction time was defined as the time between the addition of the Tween 60 and the end of sonication. To study this, the effect of ultrasound extraction time on the recovery of each analyte was investigated in the range of 2–20 min. Consequently, optimum ultrasound extraction time was adopted as 10 min. In addition to these experiments, centrifugation time and rate were investigated in the range of 1000–4000 rpm and 2–10 min, respectively, because they are necessary when preconcentrating trace amounts of each analyte with the best percent recovery in a short time. The results obtained show that centrifugation for 5 min at 4000 rpm leads to the best recovery and sensitivity for each analyte.

### 2.3.7. Effect of diluting agent volume

The surfactant-rich phase obtained after the UA-CPE is very viscous, because the phase contains a high concentration of Tween 60. In addition, the volume obtained is rather small for determination of the analytes by FAAS. For these reasons, the viscosity of the surfactant-rich phase must be reduced with a suitable solvent, and the volume should be increased. As a result of studies conducted with different solvents (methanol, ethanol, acetonitrile, acetone, hydrochloric acid, acidic methanol, and acidic ethanol), the best and reproducible recovery value for each analyte was obtained using acidic ethanol. The surfactant-rich phase was also diluted to 1.0 mL with acidic methanol to obtain a high preconcentration factor.

### 2.3.8. The matrix effect

Because of the high selectivity provided by FAAS using a hollow-cathode lamp, the low sample recovery can result from the preconcentration step. The cationic and anionic species, which are available as concomitant in the composition of cosmetic samples, may either react with ligand or form a stable complex with metal ions. The recoveries of the analytes may accordingly decrease. The effects of interfering ions on the recoveries of the analytes were investigated using FAAS in the optimized reagent conditions. The results of the study as recovery values and tolerance limits are presented in Table 1. Tolerance limit was defined as the highest amount of foreign ions that produced an error not exceeding  $\pm 5.0\%$  in the three replicate determinations of investigated analyte ions. It is clear that the recovery is quantitative in the range of 95.1%–103.3% with a standard deviation ranging from 0.7% to 1.4%. The tolerance limits were found to be in the range of 75–1000.

**Table 1.** Effect of some foreign ions on the recoveries of analytes under the optimized conditions.

Foreign ions	Tolerance limit [Foreign ions]/[analyte]	Recovery $\pm$ SD %		
		Cd(II)	Pb(II)	Sn(II)
$\text{NH}_4^+$ , $\text{K}^+$ , $\text{Na}^+$	1000	$95.7 \pm 1.2$	$102.1 \pm 1.5$	$97.5 \pm 1.2$
$\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Mg}^{2+}$	800	$97.3 \pm 1.4$	$101.4 \pm 1.2$	$98.4 \pm 1.1$
$\text{SO}_4^{2-}$	700	$98.5 \pm 1.1$	$96.8 \pm 1.4$	$98.9 \pm 1.3$
$\text{Cr}^{3+}$	500	$97.0 \pm 1.3$	$97.2 \pm 1.0$	$95.4 \pm 1.1$
$\text{Al}^{3+}$	450	$101.4 \pm 1.7$	$95.3 \pm 1.1$	$97.7 \pm 1.2$
$\text{Cu}^{2+}$	400	$95.8 \pm 0.9$	$96.0 \pm 1.1$	$101.8 \pm 1.3$
$\text{Cl}^-$	350	$97.7 \pm 1.1$	$97.4 \pm 1.3$	$102.4 \pm 1.4$
$\text{As}^{3+}$	250	$102.3 \pm 1.2$	$102.9 \pm 1.2$	$95.3 \pm 1.0$
$\text{Co}^{2+}$	150	$101.6 \pm 1.1$	$95.5 \pm 0.9$	$97.6 \pm 1.3$
$\text{Fe}^{3+}$	125	$95.1 \pm 0.7$	$103.3 \pm 0.9$	$95.8 \pm 1.2$
$\text{Zn}^{2+}$	75	$97.2 \pm 1.2$	$102.4 \pm 1.2$	$95.4 \pm 1.1$

### 2.4. Analytical features

Analytical figures of merit of the method (regression equation, linear working range, the limit of detection, limit of quantitation, precision, and enrichment factor) were achieved after the proposed preconcentration process was applied to a serial standard solution of each analyte under optimized reagent conditions. The limits of detection (LOD) and quantification (LOQ), defined as the ratio of three and ten times the standard deviation of the blanks ( $\sigma_{blank}$ ) to the slope of the calibration graphs ( $m$ ) constructed for Cd(II), Pb(II), and Sn(II) were determined by analysis of a blank solution. The LOD obtained from  $3\sigma_{blank}/m$  for Cd(II), Pb(II), and Sn(II) were 3.70, 1.35, and  $0.45 \mu\text{g L}^{-1}$ , respectively. The LOQ obtained from  $10\sigma_{blank}/m$  for Cd(II), Pb(II), and Sn(II) were 12.2, 4.5, and  $1.5 \mu\text{g L}^{-1}$ , respectively. The sensitivity enhancement factor, which is calculated by using the ratio of the slopes of calibration curves obtained with and without the preconcentration, was 75.8, 126.5, and 98.2 for Cd(II), Pb(II), and Sn(II), respectively. The precision as the percent relative standard deviations (RSDs%) was generally lower than 4.2% for Cd(II) ( $30 \mu\text{g L}^{-1}$ ), Pd(II) ( $25 \mu\text{g L}^{-1}$ ), and Sn(II) ( $15 \mu\text{g L}^{-1}$ ). The other analytical features of the method are also demonstrated in Table 2.

### 2.5. The accuracy and analytical applications

The validity of the method was primarily evaluated by analysis of the certified reference materials like Clay CRM051-050 metals on soil and SRM 1548a typical diet for Cd(II), Pb(II), and Sn(II) values. The results of the

**Table 2.** The instrumental operation conditions of FAAS and analytical figures of merit of the method.

Analyte	Regression equation	Linear range $\mu\text{g L}^{-1}$	<sup>1</sup> LOD $\mu\text{g L}^{-1}$	<sup>2</sup> LOQ $\mu\text{g L}^{-1}$	<sup>3</sup> EF	Wavelength h (nm)	<sup>4</sup> LC (mA)	<sup>5</sup> BH (mm)	<sup>6</sup> SB (mm)	Air/C <sub>2</sub> H <sub>2</sub> flow rates (L min <sup>-1</sup> )
Cd(II)	Abs = $1.03 \times 10^{-3}[\text{Cd(II)}] + 4.6 \times 10^{-4}$	12-330	3.70	12.2	75.8	228.8	8	7	0.7	15.0/1.8
Pb(II)	Abs = $4.56 \times 10^{-3}[\text{Pb(II)}] + 3.48 \times 10^{-4}$	4-200	1.35	4.50	126.5	283.3*	10	7	0.7	15.0/2.0
Sn(II)	Abs = $7.42 \times 10^{-3}[\text{Sn(II)}] + 2.14 \times 10^{-4}$	1-275	0.45	1.50	98.2	286.3**	10	9	0.7	15.0/3.0

<sup>1</sup> The limits of detection, <sup>2</sup> The limits quantification, <sup>3</sup> Enhancement factor, <sup>4</sup> Lamp current, <sup>5</sup> Spectral bandwidth, <sup>6</sup> Burner height.

\*The more sensitive resonance line of 217.0 nm for Pb was not used in this study, due to causing fluctuations arising from noise in the analytical results.

\*\*In a similar way, the more sensitive resonance lines of 224.6 and 235.5 nm for Sn were not used in this study, due to causing fluctuations in the analytical results, so as to lead to poor precision in especially low concentrations.

study are shown in Table 3, and there was good agreement between the certified and observed values for each analyte. The accuracy was also investigated by standard addition method for each analyte. In this context, different concentrations of Cd(II), Pb(II), and Sn(II) ions were spiked in the CRMs and selected cosmetics samples. The method was then applied to these mixtures. The results obtained are extensively given in Tables 3 and 4. The recovery values for 20 and 30  $\mu\text{g L}^{-1}$  concentrations of Cd(II) were 95.4%–101.2% and 97.5%–102.7%, respectively. The recovery values for 10 and 20  $\mu\text{g L}^{-1}$  concentrations of Pb(II) were 96.3%–101.8% and 97.0%–101.3%, respectively. The recovery values for 15 and 25  $\mu\text{g L}^{-1}$  concentrations of Sn(II) were 96.5%–98.4% and 97.8%–100.9%, respectively.

Furthermore, the precision of the proposed procedure was investigated by means of the parameters of repeatability and reproducibility. To assess repeatability (the intraday precision), five replicate measurements of each analyte at levels of 20 and 40  $\mu\text{g L}^{-1}$  were made on the same day. In conclusion, the mean concentrations of Cd(II) were  $20.3 \pm 0.4$  and  $39.5 \pm 0.9 \mu\text{g L}^{-1}$  with a RSD ranging from 2.5% to 2.9%, respectively. The mean concentrations of Pb(II) were  $19.4 \pm 0.8$  and  $40.6 \pm 1.3 \mu\text{g L}^{-1}$  with a RSD ranging from 2.4% to 3.2%. The mean concentrations of Sn(II) were  $20.5 \pm 0.3$  and  $40.9 \pm 1.1 \mu\text{g L}^{-1}$  with a RSD ranging from 1.9% to 2.6%.

To assess reproducibility (the interday precision), the same concentrations of each analyte were measured for five consecutive days. In conclusion, the mean concentrations of Cd(II) were  $19.8 \pm 0.3$  and  $39.7 \pm 0.9 \mu\text{g L}^{-1}$  with a RSD ranging from 2.2% to 2.5%. The mean concentrations of Pb(II) were  $19.5 \pm 0.7$  and  $40.8 \pm 1.2 \mu\text{g L}^{-1}$  with a RSD ranging from 2.2% to 2.7%. The mean concentrations of Sn(II) were  $39.7 \pm 0.4$  and  $41.1 \pm 1.3 \mu\text{g L}^{-1}$  with a RSD ranging from 2.3% to 2.7%.

To test its analytical applicability, the method was applied to determination of Cd(II), Pb(II), and Sn(II) levels in various cosmetic samples including shampoo, conditioner, hair dye, lipstick, nail polish, gel, powder, foundation, eyeliner, and skin cleanser by standard addition method. The results of the study were compared in terms of the analyte contents. The mean metal contents were arranged in the following decreasing order: Cd(II) > Pb(II) > Sn(II) for hair dye, nail polish, and skin cleanser; Pb(II) > Sn(II) > Cd(II) for shampoo, foundation, gel, and lipstick; Cd(II) > Sn(II) > Pb(II) for powder and eyeliner; and Sn(II) > Cd(II) > Pb(II) for conditioner. The further results are presented in Table 4. It can be seen that the RSDs obtained for Cd(II), Pb(II), and Sn(II) in these samples are 1.7%–2.5%, 1.9%–2.9%, and 1.3%–2.1%, respectively.

Finally, a comparison of the proposed procedure with other methods reported in the literature for determination of Cd(II), Pb(II), and Sn(II) by atomic spectrometric and other techniques is given in Table 5.<sup>29–35</sup> The method shows a lower or comparable detection limit, good precision, and high sensitivity enhancement factor with respect to other studies in the literature, and does not require any costly equipment. The chemicals and equipment have features like low cost, low toxicity, simplicity, and robustness of the operational conditions. For these reasons, the method can be generally applicable for routine analytical laboratories.

**Table 3.** The analysis results of certified reference materials (CRMs) by the proposed method (n: 5).

Analytes	Clay CRM051-050 metals on soil ( $\mu\text{g kg}^{-1}$ )			SRM 1548a typical diet ( $\mu\text{g kg}^{-1}$ )			<sup>a</sup> F-value	<sup>b</sup> Student's t-value		
	Added ( $\mu\text{g L}^{-1}$ )	Certified value	Found	Recovery %	Added ( $\mu\text{g L}^{-1}$ )	Certified value			Found	Recovery %
Cd(II)	-		$40.3 \pm 1.3$	95.4	-		$35.4 \pm 0.9$	101.2	2.45, 2.57	1.05, 0.87
	20	42.2	$60.7 \pm 1.8$	97.2	20	$35 \pm 1.5$	$55.5 \pm 1.7$	100.9	-	-
	30		$70.8 \pm 2.2$	98.1	30		$64.6 \pm 1.9$	99.4	-	-
Pb(II)	-		$42.5 \pm 1.7$	96.3	-		$42.5 \pm 0.8$	96.6	1.78, 2.11	0.75, 1.3
	10	44.1	$52.9 \pm 1.9$	97.8	10	$44 \pm 0.9$	$52.3 \pm 1.2$	97.1	-	-
	20		$63.1 \pm 2.4$	98.5	20		$62.9 \pm 1.3$	98.4	-	-
Sn(II)	-		$79.0 \pm 3.1$	96.5	-		$16.7 \pm 2.6$	97.3	2.74, 1.90	1.20, 0.95
	15	81.9	$94.6 \pm 3.3$	97.6	15	$17.2 \pm 2.6$	$32.7 \pm 2.9$	101.6	-	-
	25		$105.2 \pm 3.7$	98.4	25		$41.8 \pm 3.1$	99.2	-	-

<sup>a</sup>The critical  $F_{(4,4)}$  value is 6.39 for 95% confidence level and four degrees of freedom.

<sup>b</sup>The critical t-value is 2.31 for 95% confidence level and four degrees of freedom.

Table 4. Recovery and determination of the analytes from the cosmetic samples after the preconcentration (n: 5).

Samples	Cd(II) ( $\mu\text{g kg}^{-1}$ )			Pb(II) ( $\mu\text{g kg}^{-1}$ )			Sn(II) ( $\mu\text{g kg}^{-1}$ )					
	Added	Found	Recovery %	RSD %	Added	Found	Recovery %	RSD %	Added	Found	Recovery %	RSD %
Hair dye	-	4.5 ± 0.1	-	2.3	-	2.10 ± 0.06	-	2.8	-	0.90 ± 0.01	-	1.9
	25	28.3 ± 0.6	95.7	2.0	15	16.3 ± 0.4	95.3	2.4	20	20.1 ± 0.4	96.2	1.8
Nail polish	-	5.8 ± 0.1	-	2.5	-	3.9 ± 0.1	-	2.6	-	1.70 ± 0.03	-	2.0
	25	30.2 ± 0.6	98.2	2.2	15	18.4 ± 0.5	96.5	2.5	20	20.8 ± 0.4	95.9	1.8
Skin cleanser	-	3.6 ± 0.7	-	2.1	-	3.10 ± 0.07	-	2.5	-	1.50 ± 0.03	-	1.8
	25	29.3 ± 0.5	101.5	1.7	15	17.8 ± 0.4	98.1	2.2	20	21.9 ± 0.3	102.1	1.5
Shampoo	-	3.9 ± 0.1	-	2.3	-	9.2 ± 0.2	-	2.3	-	5.30 ± 0.08	-	1.6
	25	27.8 ± 0.6	96.1	2.2	15	23.4 ± 0.4	96.7	2.0	20	24.6 ± 0.3	97.3	1.4
Foundation	-	4.20 ± 0.08	-	1.9	-	6.5 ± 0.1	-	1.9	-	5.90 ± 0.01	-	2.1
	25	30.1 ± 0.5	95.4	1.7	15	22.0 ± 0.3	102.5	1.8	20	24.9 ± 0.4	96.5	1.8
Gel	-	3.30 ± 0.06	-	1.8	-	3.8 ± 0.1	-	2.4	-	3.40 ± 0.06	-	1.7
	25	27.2 ± 0.5	96.3	1.7	15	18.9 ± 0.4	103.4	2.1	20	22.4 ± 0.3	95.9	1.4
Lipstick	-	5.7 ± 0.1	-	2.4	-	8.6 ± 0.2	-	2.2	-	6.9 ± 0.1	-	1.6
	25	30.2 ± 0.6	98.4	2.1	15	22.8 ± 0.5	96.9	1.9	20	26.3 ± 0.3	97.8	1.3
Powder	-	11.1 ± 0.3	-	2.5	-	2.70 ± 0.08	-	2.9	-	9.80 ± 0.2	-	1.8
	25	37.1 ± 0.8	102.7	2.2	15	16.9 ± 0.4	95.5	2.6	20	28.7 ± 0.5	96.4	1.7
Eyeliner	-	10.3 ± 0.2	-	2.3	-	6.1 ± 0.1	-	2.7	-	7.7 ± 0.1	-	2.0
	25	36.7 ± 0.7	103.8	2.0	15	20.1 ± 0.5	95.4	2.4	20	28.4 ± 0.5	102.5	1.6
Conditioner	-	9.9 ± 0.2	-	2.4	-	8.3 ± 0.2	-	2.6	-	12.4 ± 0.2	-	1.9
	25	34.2 ± 0.6	97.9	1.9	15	23.9 ± 0.5	102.6	2.3	20	32.9 ± 0.6	101.7	1.7

**Table 5.** Comparison of the proposed method with other reported methods for preconcentration and determination of the analytes.

Samples	Analyte(s)	Analytical detection technique	Linear working range, $\mu\text{g L}^{-1}$	Detection limit, $\mu\text{g L}^{-1}$	RSD %	<sup>a</sup> EF	References
Beverages	Cd Pb	GFAAS	2.5–10 20–200	0.05 1.40	- -	- -	29
Solid samples	Cd	CEFC/FAAS		0.45	3.2	50	30
Vegetables	Pb	SPE/ICP-OES	1.25–50	0.10	8.4	94.9	31
Pharmaceutical ingredients	Cd	ASV	5–200	0.76	4.7		32
	Pd		5–200	1.90	5.7		
Tap water and tea samples	Cd	SPE/GFAAS	216–3000	1.44	3.2	50	33
Foods	Sn	ICP-AES	500–5000	200	11.3	-	34
Corn seeds	Sn	ICP-MS	-	0.36	13.1	-	35
Cosmetic samples	Cd	UA-CPE/FAAS	12–330	3.70		75.8	This work
	Pb		4–200	1.35	$\leq 4.2$	126.5	
	Sn		1–275	0.45		98.2	

<sup>a</sup> EF: Enhancement factor, ICP-MS: Inductively coupled-plasma-mass spectrometry, GFAAS: Graphite furnace atomic absorption spectrometry, CEFC/FAAS: Carrier element free co-precipitation/Flame atomic absorption spectrometry, SPE/ICP-OES: Solid phase extraction-inductively coupled plasma optical emission spectrometry, ASV: Anodic stripping voltammetry, SPE/GFAAS: Solid phase extraction-graphite furnace atomic absorption spectrophotometry, ICP-AES: Inductively coupled plasma atomic emission spectrometry.

### 3. Experimental

#### 3.1. Instrument

The elements (Cd, Pb, and Sn) were determined by flame atomic absorption spectrophotometer (FAAS) (Shimadzu AAS-6300 model, Japan) with deuterium background correction. An ultrasonic bath (UCS-10 model, Seoul, Korea), maintained at the desired temperature and ultrasonic power (40 kHz, 300 W), was used for the UA-CPE procedure. A centrifuge (Universal-320, UK) with 50-mL calibrated centrifuge tubes (Isolab, Germany) was used to accelerate the separation of the aqueous and surfactant-rich phases after the UA-CPE procedure. A digital pH-meter equipped with a glass-calomel electrode (pH-2005, JP Selecta, Barcelona, Spain) was used for pH measurements.

#### 3.2. Standard solutions and reagents

All the chemicals were used of analytical grade and were purchased from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany). Unless otherwise stated, all reagents and solutions were prepared with ultrapure water (18.2 M $\Omega$  cm) obtained from a Labcanco water purification system (Kansas City, KS, USA). The stock solutions of Cd(II), Pb(II), and Sn(II) of 1000  $\mu\text{g L}^{-1}$  were prepared by dissolving appropriate amounts of CdCl<sub>2</sub> ( $\geq 99.0\%$ , w/w), Pb(NO<sub>3</sub>)<sub>2</sub> ( $\geq 99.0\%$ , w/w), and SnCl<sub>2</sub> × 2H<sub>2</sub>O ( $\geq 98.0\%$ , w/w) (Sigma) in diluted HNO<sub>3</sub> or HCl (2.0%, v/v) solutions and completing with ultrapure water. Standard working solutions of the each ion (0–500  $\mu\text{g L}^{-1}$ ) for construction of calibration curves and 20  $\mu\text{g L}^{-1}$  for the optimization experiments were prepared by stepwise dilution of the stock solutions in appropriate ratios. An ionic surfactant solution,

cetylpyridiniumchloride (CPC) of 2.5% (w/v), was prepared by dissolving an appropriate amount of CPC (Merck) in water and diluting to 100 mL in a flask. A nonionic surfactant solution, polyoxyethylene sorbitan monostearate (Tween 60) (Sigma) of 1.0% (v/v), was prepared by diluting 1.0 mL of pure compound in 10 mL of ethanol and diluting to 100 mL with water. Victoria Pure Blue BO solution ( $\geq 95.0\%$  for HPLC assay, VPB<sup>+</sup>) of  $3.0 \times 10^{-3} \text{ mol L}^{-1}$ , which is also known as 4-diethylamino)-alpha-4-ethylamino-1-naphthyl)benzylidene) cyclohexa-2,5-dien-1-ylidene) diethylammonium chloride, was prepared by dissolving an appropriate amount of the reagent (Sigma) in water and diluting to 100 mL in a flask. The following steps were followed to prepare Tris-acetate buffer solution at pH 8.5. Dissolve 0.294 g of calcium chloride (CaCl<sub>2</sub>) (Merck) and 12.11 g of tris (hydroxymethyl) aminomethane in the water. Adjust the pH with 5 mol L<sup>-1</sup> acetic acid and dilute to 1.0 L with water. All glassware, pipettes, and plastic tubes were kept in 10% (v/v) HNO<sub>3</sub> in an ultrasonic bath for 2 h, and then rinsed five times with water before the start of the experiment.

### 3.3. Samples and certified reference materials

The cosmetic samples used in this study (shampoo, conditioner, hair dye, lipstick, nail polish, gel, powder, foundation, eyeliner, and skin cleanser) were bought in a local cosmetics store in Sivas, Turkey. Two certified reference materials (CRMs), Clay CRM051-050 metals on soil and SRM 1548a typical diet, supplied from Reference Materials and Proficiency Testing (RTC), were used to validate the accuracy of the proposed method.

### 4. Conclusions

In the current study, a simple and efficient UA-CPE approach is presented and its analytical utility is demonstrated for the determination of Cd(II), Pb(II), and Sn(II) in cosmetic samples by FAAS. Thus, the nonionic surfactant Tween 60 as extracting agent was successfully applied for the preconcentration of the selected analytes. The method is more ecofriendly and faster and has a higher sensitivity enhancement factor when compared with conventional LLE methods. All the results obtained by using the optimized conditions confirm the practicality and viability of the procedure, providing an important tool for quantification of low levels of Cd(II), Pb(II), and Sn(II) in cosmetic samples. After the validity was verified by analysis of two CRMs, the method was successfully applied to the analysis of the analytes in various cosmetic samples. In addition, the method shows features such as simplicity, quickness, and relatively low cost when compared to sensitive, but expensive, time consuming, poor precision especially at low concentrations, and complicated techniques such as ASV, GFAAS, ICP-OES, ICP-MS, CE-, GC-, and/or LC-MS at normal or reverse phase mode.

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