

Trace determination of lead in lipsticks and hair dyes using microwave-assisted dispersive liquid–liquid microextraction and graphite furnace atomic absorption spectrometry

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Synopsis

OBJECTIVE: A novel microwave-assisted dispersive liquid–liquid microextraction (MADLLME) technique according to the solidification of a floating organic droplet (SFO) and graphite furnace atomic absorption spectrometry (GFAAS) used for the extraction and determination of lead ions in lipsticks and hair dyes made in different countries. Lipstick and hair dye samples of different brands and colours were collected from local market in Kermanshah, Iran.

METHODS: After sample treatment with microwave-assisted acid digestion, an appropriate mixture of acetone, 1-undecanol and diethyl dithiophosphoric acid was injected rapidly into the aqueous sample containing lead ions, and as a result, cloudy mixture was formed. After centrifugation, the test tube was cooled for few minutes. The solidified 1-undecanol on top of the solution was transferred into a suitable vial and injected into the analytical instrument.

RESULTS: Under the optimum experimental conditions (extraction solvent: 30 μL of 1-undecanol; disperser solvent: 500 μL of acetone; ligand concentration: 0.15% (v/v); pH: \sim 1.5 and without salt added), the enhancement factor of 96 was obtained. The calibration graphs were linear in the range of 0.3–50 $\mu\text{g kg}^{-1}$ with a correlation coefficient (r^2) more than 0.995. The detection limit was 0.1 $\mu\text{g kg}^{-1}$. Consequently, the developed method was successfully applied to extract and determine lead ions in the lipsticks and hair dyes, and favourable results were obtained. The proposed method which applied in cosmetics showed excellent relative recoveries (90–109.7%) with relative standard deviations $<8.3\%$ ($n = 3$) for all samples.

CONCLUSION: The study revealed that the concentration of lead found in lipsticks and hair dyes on the Kermanshah market is far below the recommended limits as applied in Germany (20 mg kg^{-1}) and Canada (10 mg kg^{-1}) and confirmed that very low levels of lead are technically available in the final cosmetic products.

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Résumé

OBJECTIF: Développement d'une nouvelle technique de microextraction liquide-liquide dispersive (MADLLME) assistée par micro-ondes selon la solidification d'une gouttelette organique en suspension (SFO) et de la spectrométrie d'absorption atomique à four graphite (GFAAS), utilisées pour l'extraction et la détermination des ions de plomb dans les rouges à lèvres et teintures capillaires fabriqués dans différents pays. Des échantillons de rouge à lèvres et la teinture des cheveux de différentes marques et couleurs ont été recueillies auprès du marché local à Kermanshah, Iran.

METHODES: Après traitement de l'échantillon par une digestion acide assistée par micro-ondes, un mélange approprié d'acétone, de 1-undécanol et de l'acide dithiophosphorique de diéthyle a été injecté rapidement dans l'échantillon aqueux contenant des ions de plomb et, en conséquence un mélange trouble a été formé. Après centrifugation, le tube à essai a été refroidi pendant quelques minutes. Le 1-undécanol solidifié au-dessus de la solution a été transférée dans un flacon convenable et injecté dans l'instrument d'analyse.

RÉSULTATS: Dans les conditions expérimentales optimales (extraction par solvant: 30 μL de 1-undécanol; dispersion solvant: 500 μL d'acétone, la concentration ligand: 0.15% (v/v); pH: \sim 1.5 et sans sel ajouté), un facteur d'amélioration de 96 a été obtenu. Les graphiques d'étalonnage étaient linéaires dans l'intervalle de 0.3 à 50 $\mu\text{g kg}^{-1}$ avec un coefficient de corrélation (r^2) de plus de 0.995. La limite de détection était de 0.1 $\mu\text{g kg}^{-1}$. Par conséquent, la méthode développée a été appliquée avec succès pour extraire et déterminer des ions de plomb dans les rouges à lèvres et les colorants capillaires et des résultats favorables ont été obtenus. La méthode proposée qui se appliquait dans les cosmétiques a montré des recouvrements relatifs excellents (90–109.7%) avec de déviations standard relatives $<8.3\%$ ($n = 3$) pour tous les échantillons.

CONCLUSION: L'étude a révélé que la concentration de plomb trouvé dans les rouges à lèvres et les teintures capillaires sur le marché Kermanshah est bien inférieure aux limites recommandées, appliqué en Allemagne (20 mg kg^{-1}) et le Canada (10 mg kg^{-1}) et a confirmé que des niveaux très bas de plomb sont techniquement disponible dans les produits cosmétiques finis.

Introduction

Over the past years, using cosmetic products increases worldwide at an alarming rate due to unending pursuit for individual beautification and there is a sharp rise in advertisements of these products in electronic media [1]. These products are directly applied to human skin, mainly produce local exposure to certain ingredients. Among the hazardous substances involved in cosmetics, toxic elements are widely diffused in colour make-up products. Lipsticks and hair dyes are typical examples of pigmented make-up products [2]. Lead is widely distributed in the environment regarding to extensively use in consumer products, recycling old products and manufacturing process, worldwide. Recent media reports the presence of lead in various cosmetic products such as lipsticks and hair dyes, also suggested that the potential lead exposure may be harmful due to ordinary use. However, lead may cause serious health problems, including both acute and chronic poisoning, pathological change in multiple organs; it can cause a variety of problems in the cardiovascular system, kidney, bone and liver, even cause cancer whenever excessive amounts of lead accumulate in the human body [3, 4]. It can be stated that lead could pass through the placenta and get into the foetal brain in pregnant women [5]. Lipsticks and hair dyes contain a very minor source of lead in comparing with other sources of lead in the environment such as water, food or air because the amount of lipstick or hair dye which one applies daily is actually very slight.

Nonetheless, one should not exclude the fact that lead accumulates in the body due to over time and repetitive lead-containing lipstick or hair dye application, which lead to significant exposure levels. As a result, exposing to high levels of these products can only be properly verified by conducting population risk assessment exposure studies [6].

The occurrence of lead in cosmetic products can originate from some ingredients naturally containing lead (such as dyes and pigments) or introduced during the production process. Various instrumental techniques including graphite furnace atomic absorption spectrometry (GFAAS) [6], flame atomic absorption spectrometry (FAAS) [2], inductively coupled plasma mass spectrometry (ICP-MS) [7], inductively coupled plasma-optical emission spectrometry (ICP-OES) [8] and laser-induced breakdown spectroscopy (LIBS) [9] are used for the determination of metals in cosmetics. GFAAS appears to be a good alternative for the determination of trace elements, such as lead in lipsticks and hair dyes, because it is one of the most sensitive techniques, with detection limits in the range of $\mu\text{g L}^{-1}$ to ng L^{-1} [10]. Although lower detection limits can be achieved with recent powerful analytical methods, such as liquid chromatography/tandem mass spectrometry (LC-MS/MS), but many analytical laboratories cannot support such equipment because of their relatively high maintenance and repair costs [11].

Determining lead at very low concentrations is often difficult because of insufficient sensitivity of the method as well as the matrix interferences occur during the real sample analysis. Therefore, a preliminary separation and pre-concentration step is often required to enhance the sensitivity of the method. Also, complex samples such as lipsticks and hair dyes require conversion to a form compatible with the instrumentation. Techniques such as coprecipitation [12], liquid-liquid extraction (LLE) [13], solid-phase extraction (SPE) [14], cloud point extraction (CPE) [15], solid-phase microextraction (SPME) [16], liquid-phase microextraction (LPME) [17] and dispersive liquid-liquid microextraction (DLLME) [18, 19] are widely used in the separation and pre-concentration of trace

amounts of lead in different matrices. Advantages and disadvantages of these techniques have already been discussed [20].

Recently, DLLME based on solidification of floating organic droplet (DLLME-SFO) is developed as a novel sample preparation technique, which follows the same principle as the DLLME technique [21]. The main difference between DLLME-SFO and DLLME is that the extraction solvent used in the former is of low melting point and hypotoxicity. In DLLME-SFO, the extraction solvent after DLLME was collected in the top of the test tube and cooled it in an ice bath for 5 min. The solidified extraction solvent was transferred into a suitable vial and immediately melted at room temperature; then it was finally injected into a suitable instrument. The performance of DLLME-SFO was illustrated by extraction of organic and inorganic compounds from different matrices [22–26].

Microwave-assisted acid digestion is considered a good alternative for organic and inorganic compound extraction from solid and semisolid matrices, which provides a more efficient contact between the solid and solvent due to increase of both pressure (which favours penetration and transport) and temperature (improves solubility and diffusivity). The microwave-assisted digestion was combined with dispersive liquid-liquid microextraction (MADLLME) as a sample preparation method from semisolid and solid samples to extract lead from cosmetics.

The aim of this study was the development of a sensitive analytical method for the determination of lead in cosmetics by GFAAS, after sample treatment with microwave-assisted acid digestion and pre-concentration with the DLLME-SFO procedure. After optimization of the method, this method was used for determination of lead ions in lipsticks and hair dyes made in different countries.

Experimental

Reagents and standards

The chelating agent, diethyl dithiophosphoric acid (DDTP) with the density of 1.17 kg L^{-1} , was purchased from Merck company. 1-undecanol, 2-dodecanol and 1-decanol as the extraction solvent, methanol (MeOH, for spectroscopy), acetone (AC, suprasolv) and acetonitrile (AN, HPLC grade) as a disperser solvent, NaCl (analytical grade), HNO_3 (65%, suprapure), H_3BO_3 (99.97%) and HF (47%, suprapure) were purchased from Merck company. All solutions were prepared with ultrapure water (six times distilled and also double deionized with $18.2 \text{ M}\Omega \text{ cm}^{-1}$ resistivity) that was purchased from Shahid Ghazi Pharmaceutical Co. (Tabriz, Iran). Stock standard solution of lead with a concentration of 1000 mg L^{-1} was prepared by dissolving appropriate amount of lead nitrate from Merck (Darmstadt, Germany). The working standard solution was prepared by appropriate dilution of the stock standard solution. Lipstick and hair dye samples of different brands and colours were collected from local market (Kermanshah, Iran). Selected samples were made from China, France, Turkey, the U.S.A. and Iran.

Instrumentation

A Model nov AA 400 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany), equipped with deuterium background correction, a transversely heated graphite tube atomizer and an MPE 60 autosampler, was used in all measurements of lead integrated absorbance. The lead hollow cathode lamp (Analytik Jena, Jena, Germany) was run under the conditions which recommended by the manufacturer (current: 5 mA). Also, the wavelength

Table 1 The graphite furnace temperature programme for lead determination

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (mL min ⁻¹)
Drying	90	1	10	500
Drying	110	1	5	500
Pyrolysis	500	10	15	500
Atomization	1900	0	3	0
Cleaning	2500	0	2	1000

(283.3 nm), the slit bandwidth (0.8 nm) had conventional values. Pyrolytic graphite-coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.026) were used for all measurements. The instrumental parameters and temperature programme for the graphite atomizer are presented in Table I. Argon (99.999%) was purchased from Air Products (UK) as a purge and protective gas with a flow rate of 500 mL min⁻¹ during all stages, except during atomization, when the flow was stopped. All measurements were based on the peak height. The microwave experiments were performed in a microwave oven (Ethos Sel, Milestone, U.S.A.) equipped with two magnetrons of 800 W, high pressure rotor with capacity for twelve closed vessels and automatic temperature sensor. The pH values were measured with a Metrohm pH meter (Model: 692, Herisau, Switzerland) supplied with a glass-combined electrode. The Hettich Zentrifugen (EBA20, Tuttingen, Germany) was used for centrifuge.

Sample digestion

The cosmetic samples have been digested according to previous reports [7]. A mass of 100 mg of lipstick or hair dyes sample was weighed by a microwave vessel liner; subsequently, 7 mL of nitric acid and 2 mL of hydrofluoric acid was added. The liners were placed in vessels, closed with a sealed cap and put into the microwave oven. The vessels were heated to 130°C for 15 min and held at this temperature for 3 min. Then, the temperature ramped to 200°C and was held at this temperature for 35 min. After this step, vessels were cooled at 50°C and vented; then, 30 mL of 4% boric acid aqueous solution was added to each sample and the vessels were further heated in the microwave at 180°C for 8 min and held at this temperature for 10 min, to complex and dissolve any insoluble fluorides. After cooling and venting, the solutions were diluted to a final volume of 50 mL by adding distilled water. An aliquot of 5 mL of the resulting solution was subjected to the DLLME-SFO procedure.

DLLME-SFO procedure

For the DLLME-SFO, an aliquot of 5 mL of the extract obtained by microwave-assisted digestion placed in a glass centrifuge tube. Five hundred microlitre of acetone (disperser solvent), containing 30 µL of 1-undecanol (extraction solvent) and 5 µL of DDTP (chelating agent), was injected rapidly into a sample solution using a 1.0-mL syringe (Gastight, Hamilton). A cloudy solution (resulting from the dispersion of the fine droplets of 1-undecanol in the aqueous sample) was formed in the test tube. In this step, the lead ions react with DDTP and extract into the fine droplets of 1-undecanol. The mixture was then centrifuged for 3 min at 4000 g. The fine drop-

lets of organic solvent float at the top of the test tube due to difference in the density between the aqueous phase and organic solvent. The test tube was then transferred into an ice bath for cooling. After 4 min, the extraction solvent solidified and was then transferred into a conical vial, where it melts quickly at room temperature. Finally, 20 µL of this organic phase using an auto-sampler was injected into the GFAAS and was submitted to the temperature programme of Table I.

Results and discussion

In the experimental procedure, some important parameters which usually affect the extraction performance were optimized. As mentioned above, at first step, a microwave procedure was used to remove the analyte from the matrix and clean the sample. In the second step, the analytes in the aqueous solution were extracted by the DLLME-SFO procedure. The parameters affecting the DLLME-SFO procedure such as the extraction and disperser solvents, as well as their volumes, addition of salt, extraction time, pH and concentration of chelating agent were optimized. For this purpose, 5 mL of an aqueous solution containing analyte concentrations of about 5 µg L⁻¹ was used.

Effect of the type and volume of extraction solvent

The selection of appropriate extraction solvent was essential for the development of an efficient DLLME-SFO procedure. The extraction solvent should have a lower density than water, a lower melting point than room temperature, a low solubility in water and high extraction efficiency for the target analytes. Therefore, to choose the best extraction solvent to achieve optimum results for the DLLME-SFO method, three extraction solvents, namely 1-undecanol, 2-dodecanol and 1-decanol were investigated. These solvents have a melting point close to or below room temperature. Average recoveries ($n = 3$) and standard deviations (SD) for different extraction solvents are shown in Fig. 1. The results revealed that 1-undecanol has the highest absorbance in comparison with the other tested solvents. Therefore, 1-undecanol was chosen for further experiments.

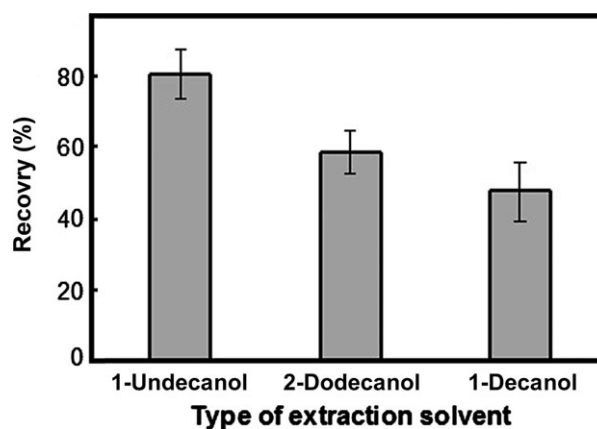


Figure 1 Effect of the type of extraction solvent on the absorbance of Pb(II) obtained from MADLLME-SFO. Extraction conditions: volume of extraction solvent, 30 mL; sample amount, 100 mg; volume of disperser solvent (acetone), 500 µL; floated phase volume, 25 ± 2 µL; DDTP concentration, 0.15% (v/v); pH, 1.5; concentration of lead, 5.0 µg L⁻¹; room temperature.

To select the optimum volume of 1-undecanol, several experiments were performed using 500 μL of acetone and different volumes of 1-undecanol. It was observed that by increasing the volume of 1-undecanol from 35 to 75 μL , the volume of the floated phase increases from 25 to 63 μL , whereas the absorbance was decreased accordingly. A volume of <35 μL of 1-undecanol resulting in a floated volume <25 μL was insufficient for determination by the GFAAS. Thus, to have a high enhancement factor and good repeatability, 30 μL of 1-undecanol was selected as the optimum volume of the extracting solvent.

Effect of the type and volume of disperser solvent

Similar to conventional DLLME, the main criterion for disperser solvent in DLLME-SFO is its miscibility with both water and the extraction solvent. Therefore, acetone, acetonitrile and methanol were selected as disperser solvent, and the effect of these solvents on the performance of DLLME-SFO was investigated. The results showed, under the same experimental conditions, acetone resulting in a higher absorbance compared to methanol and acetonitrile, therefore, was selected as disperser solvent.

To investigate the effect of acetone volume on the extraction efficiency, several volumes of acetone in the range of 300–1000 μL containing different volumes of 1-undecanol were studied. Increasing the volume of 1-undecanol by increasing the volume of acetone is necessary to obtain the constant volume of the floated phase (25 ± 2 μL) in all experiments. According to the results, the absorbance increased by increasing the volume of acetone from 300 to 500 μL (Fig. 2). It seems that, in smaller volumes of acetone, the cloudy state could not be formed well; thereby, the absorbance was low. On the other hand, using more than 500 μL of acetone, the solubility of analyte in water increases and, in turn, it causes a decrease in the extraction recovery. According to the obtained results, a volume of 500 μL was selected as the optimum volume of the acetone for further studies.

Effect of the sample pH

The pH of the aqueous phase has a unique role in the extraction efficiency as it affects the metal–chelate formation and its subse-

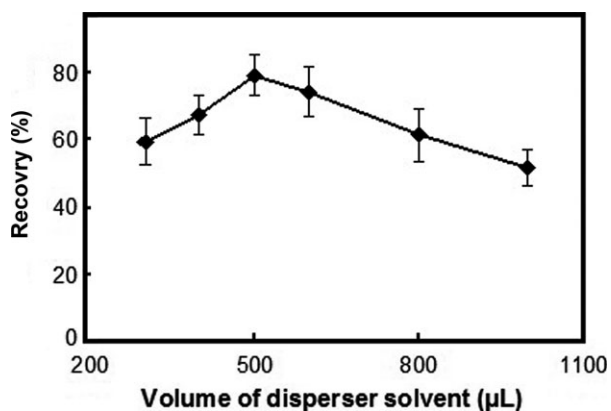


Figure 2 Effect of volume of disperser solvent on the absorbance of Pb(II) obtained from MADLLME-SFO. Extraction conditions: similar to those in Fig. 1, except for type of extraction solvent, 1-undecanol.

quent extraction. The effect of pH on the complex formation and extraction of lead from water samples was studied in the range of 1.0–7.0. The absorbance of Pb^{2+} complex with DDTP reaches a maximum in the pH range of 1–4 and it reduced at the higher pH values (Fig. 3). On the other hand, because the sample solution and aqueous solution of diethyldithiophosphoric acid were acidic (pH \sim 1.5), in the present study, the use of an acidic solution for the pH adjustment, being the contamination sources, was not necessary. Therefore, all experiments were conducted without adding the acid.

Effect of the DDTP concentration

DDTP is a well-known chelating agent for lead extraction with the formation of a stable 2:1 complex with Pb^{2+} ion. The influence of DDTP concentration was carried out in the range of 0.02–0.4% (v/v), and the other variables remained constant. It was found that the absorbance of lead increases with increasing DDTP concentration from 0.02% to 0.1% (v/v) and it kept constant upon further

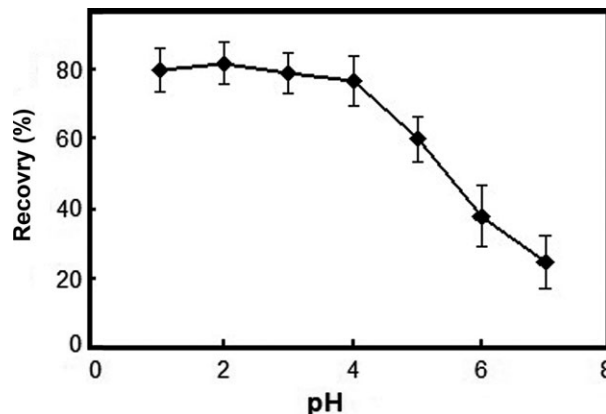


Figure 3 Effect of pH on the absorbance of Pb(II) obtained from MADLLME-SFO. Extraction conditions are similar to those of Fig. 2.

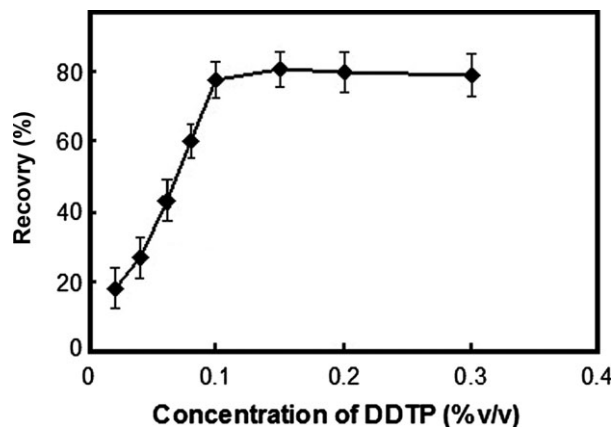


Figure 4 Effect of concentration of DDTP on the absorbance of Pb(II) obtained from MADLLME-SFO. Extraction conditions are similar to those of Fig. 2.

increase in concentration (Fig. 4). Thus, the concentration of 0.15% (v/v) of DDTP was then used in subsequent experiments.

Effect of the salt addition and extraction time

For investigating the effect of ionic strength on the performance of DLLME-SFO, various experiments were performed by adding different amounts of NaCl (0–5%). Other experimental conditions were kept constant. By increasing NaCl, the volume of floating phase increases, because of the decrease in solubility of the extraction solvent in the presence of salt. Therefore, the enrichment factor slightly decreases. No significant effect on extraction recovery was observed when different amounts of sodium chloride were added into the sample solution. As a result, all the extraction experiments were carried out without salt added.

In DLLME-SFO, extraction time is defined as the time between injection of a mixture of disperser and extraction solvents in the sample solution and starting to centrifuge the resulting cloudy solution. The resulting data show that the extraction time has no significant effect on the extraction efficiency for the target analyte. It was found that, after the formation of the cloudy solution, the contact area between the extraction solvent and the aqueous phase was considerably larger, delineating why the extraction equilibrium could be established very fast.

Effect of the coexisting ions

The effect of various interfering ions on the determination and recovery of lead was also investigated. However, each interfering ion was added to 5 mL of aqueous solution containing $5.0 \mu\text{g L}^{-1}$ of lead, and the tolerable amount of each ion was determined after applying the presented method. The tolerable amount is defined as the maximum concentration could cause a change of <5% in signal compared to the signal of lead without any interference. As indicated in Table II, the lead recoveries were almost quantitative in the presence of the excessive amounts of the possible interfering cations and anions.

Analytical figures of merit

The analytical parameters for lead determination in lipstick and hair dye samples were obtained under optimal experimental conditions. Analytical characteristics of the optimized method, including linear range, limit of detection, repeatability (intraday), reproducibility (interday) and enhancement factor are shown in Table III.

Table II Effect of potentially interfering ions on the recovery of $5.0 \mu\text{g L}^{-1}$ Pb(II)

Interferent	Potentially interfering ions to analyte ratio	Range of recoveries (%)
Na^+ , K^+ , Li^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- , SCN^-	10 000	95.2–104.5
Co(II) , Fe(II) , Zn(II) , Hg(II) , Cu(II) , Cr(III) , Ag(I)	500	96.1–102.6
Cd(II) , Sn(IV)	200	98.0–99.5
As(V) , Cr(VI)	300	94.2–97.6
As(III)	100	93.8

Table III Analytical characteristics of MADLME-SFO-GFAAS for determination of Pb(II) in cosmetics

Parameter	Analytical feature
Linear range ($\mu\text{g kg}^{-1}$)	0.3–50
r^2	0.9955
Limit of detection ($\mu\text{g kg}^{-1}$) (3σ , $n = 7$)	0.1
RSD ^a % (intraday, $n = 7$)	3.2
RSD % (interday, $n = 7$)	4.7
Enhancement factor	96

^aPb(II) concentration was $5 \mu\text{g kg}^{-1}$ for which RSD was obtained.

Table IV Lead concentration in lipstick and hair colour cream samples and in a certified reference material

Sample	Origin country	Added ($\mu\text{g kg}^{-1}$)	Found mean \pm SD ($\mu\text{g kg}^{-1}$) ($n = 3$)	Relative recovery (%)
Lipstick	U.S.A.	0	455.4 ± 63.6	–
		20	473.8 ± 55.7	92.0
		50	506.5 ± 61.3	102.2
	China	0	276.0 ± 19.7	–
		50	321.5 ± 22.1	91.0
		100	368.7 ± 29.5	92.7
	Germany	0	208.3 ± 17.7	–
		40	252.2 ± 31.3	109.7
		80	286.7 ± 25.6	98.0
	Turkey	0	288.1 ± 33.7	–
		30	320.5 ± 35.1	108.0
		60	346.2 ± 44.9	96.8
France	0	316.3 ± 27.4	–	
	20	337.5 ± 38.8	106.0	
	50	363.3 ± 41.5	94.0	
Iran	0	305.5 ± 26.7	–	
	50	354.8 ± 33.5	98.6	
	100	401.7 ± 39.6	96.2	
Hair dye	China	0	67.2 ± 7.5	–
		10	76.8 ± 8.1	96.0
		20	88.1 ± 6.8	104.5
	Italy	0	72.2 ± 5.3	–
		15	85.9 ± 6.0	90.0
		30	103.3 ± 8.8	103.6
	France	0	76.4 ± 5.9	–
		20	95.6 ± 7.3	96.0
		40	115.4 ± 9.2	97.5
	Iran	0	55.3 ± 4.1	–
		10	66.1 ± 5.2	108.0
		50	106.6 ± 8.7	102.6
CRM NIST 1571 (Orchard Leaves)		45 ± 3.1^a (mg kg^{-1})	43.2 ± 3.6 (mg kg^{-1})	96.0

^aCertified value of Pb(II).

The calibration graph was linear in the range of $0.3\text{--}50 \mu\text{g kg}^{-1}$ of lead. The limit of detection, defined as $C_L = 3 S_B/m$ (where C_L , S_B and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively), was $0.1 \mu\text{g kg}^{-1}$. Repeatability (intraday) and reproducibility (interday) of method based on seven replicate measurements of $5 \mu\text{g kg}^{-1}$ of

Pb (II) were 3.2% and 4.7%, respectively. The enhancement factor was obtained from the slope ratio of calibration graph after and before extraction, which was about 96.

Lead determination in lipstick and hair dyes

The lead concentration in 6 different brands of lipstick and four different brands of hair dye samples from several different manufacturers/countries was determined by the proposed method. The lead concentrations ranged from 208 to 455 $\mu\text{g kg}^{-1}$ for the lipsticks and 55 to 72 $\mu\text{g kg}^{-1}$ for hair dyes. The detailed results are depicted in Table IV. Certified reference materials similar to lipsticks and hair dyes were not available; thus, the presences of lead in these samples were confirmed by spiking lead at the different concentration levels. The relative recoveries of lead from lipsticks and hair dyes at spiking level of different amounts of lead are represented in Table IV. The quantitative results show that the method is accurate and reliable and could be applied for the determination of lead in cosmetic samples. In addition, the accuracy of the proposed methodology was evaluated by analysing a certified reference material (CRM) NIST 1571 (Orchard Leaves), with certified lead content of $45 \pm 3.1 \text{ mg kg}^{-1}$, and the analytical results are added to Table IV. As is obvious from Table IV, the determined value of $43.2 \pm 3.6 \text{ mg kg}^{-1}$ is in satisfactory agreement with the certified value.

Lead content was determined in six tested lipstick samples, the highest lead content was $455 \mu\text{g kg}^{-1}$, and the lowest was $208 \mu\text{g kg}^{-1}$. This variation in the concentration of lead may be attributed to the quality of the raw materials used in the production of the lipsticks. The amount of lead in hair dye samples of dif-

ferent brands is almost identical. The FDA has established 20 mg kg^{-1} as the maximum amount of lead allowed in colour additives used to make cosmetics for external use, produced using good manufacturing practices. However, there exists no legislation for regulating the level of toxic metals in lipsticks and hair dyes produced in the U.S.A., China, Germany, Turkey, France, Italy and Iran.

Conclusions

A simple and fast analytical method for the determination of lead content in lipstick and hair dye samples by GFAAS after MAD-LLME-SFO has been proposed and validated. The experimental results revealed that this method provides good enhancement factor and good linearity over the investigated concentration range. The performance of this procedure in the extraction of lead from cosmetics was also favourable. The data presented in this work provide useful information about lead content in cosmetic products from different countries in the world. Overall, the study revealed that the concentration of lead found in lipsticks and hair dyes on the Kermanshah market is far below the recommended limits as applied in Germany (20 mg kg^{-1}) and Canada (10 mg kg^{-1}) [27] and confirmed that very low levels of lead are technically available in the final cosmetic products.

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