

Vortex-Assisted and Cloud Point Extraction of Cadmium, Lead, Copper and Zinc in Different Personal Care Product Samples

Khan Muhammad Malik^a, Mahboob Ali Rind^a, Nusrat Jalbani^{b*}, Aijaz Panhwar^a, Shahid Bhutto^b, Iftikhar Ahmed^a, Amber Rasheed^a, Durdana Rais Hashmi^b and Humaira Khan^a

^aDr M.A Kazi Institute of Chemistry University of Sindh, Jamshoro, Pakistan

^bPCSIR Laboratories Complex Karachi, Karachi-75280, Pakistan

(received July 6, 2020; revised January 29, 2021; accepted February 4, 2021)

Abstract. A rapid vortex assisted–cloud point extraction (VA–CPE) method was developed to separate cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb) in accordance with important parameters. Cd and Pb was determined in personnel care products (PCPs) by Electrothermal Atomic Absorption Spectrometry (ETAAS), however Cu and Zn was determined by Flame Atomic Absorption Spectrometry (FAAS). Triton X-100 and xylenol orange were used as a chelating agent. The important factors including pH, Ligand Volume (LV), Vortex Time (Vt), Centrifuge Time (Ct), Centrifuge (rpm) and volume of Triton X-100 as well as volume of chloroform and concentration of surfactant were optimized. The Certified Reference Material (CRM) (wheat flour-1567 a) and standard addition recovery test was used to analyze the accuracy of proposed method. Detection limits (LODs) of metals like, Cd, Pb, Cu and Zn were 0.001 mg/L, 0.01 mg/L, 0.05 mg/L and 0.1 mg/L respectively. The method has been successfully applied to real samples.

Keywords: heavy metals, personnel care products, micelle mediated, atomic absorption spectrometry, vortex-assisted extraction

Introduction

A rapid development in cosmetics industry is witnessed in last few decades, *via* production of different cosmetic types required for beautification and care of teeth, nails, hair, skin as well as body (Arshad *et al.*, 2020). However, these personnel care products, as well as other products which are applied on skin are found to possess various unwanted effects since, these unwanted effects are not known by majority of the people.

The health awareness of people has attracted health practitioners as well as researchers to find out unusual side effects of personal care products (Gao *et al.*, 2018). Furthermore, the PCPs products may pose little or no risk, some contain heavy metals which cause serious effects on human health including cancer, reproductive and neurological harm and developmental delays. Personnel care product chemicals enter into the human body through the skin, inhalation, ingestion and internal use. In addition to the risks posed by intentionally added ingredients, PCPs can be contaminated with heavy metals such as arsenic, cadmium, lead, mercury and nickel (Massadeh *et al.*, 2017; Zulaikha *et al.*, 2015). Besides that facts these heavy metals posing serious health issues but the demand of the cosmetics is

increasing in the throughout the world and these PCPs are widely used by all age groups and they are oblivious related to safety issue (Perez *et al.*, 2017).

The health hazards related to Cd, Cu and Zn may cause pneumonia, depression and convulsion ataxia, paralysis, tremor, stomatities, diarrhea and gastrointestinal disorder. Accumulation of toxic metals may take place in human and animals by passing through plants, groundwater and aquatic environment from soils and sediments (Kazi *et al.*, 2018; Jalbani and Soylak, 2014). Heavy metal cadmium (Cd), lead (Pb), copper (Cu) and zinc is considered as highly hazardous metals (Latif *et al.*, 2020; Jongeneel *et al.*, 2018). Severe health as well as environmental effects may be caused due to contamination of heavy metals. For instance, lead discharging into the water from manufacturing, mining and smelting may cause various health problems to humans. Though, depression and lethargy may be caused due to the zinc sufficiency and renal damage and hypertension may be caused by cadmium toxicity (Mesko *et al.*, 2020). Because of heavy metal toxicity, many forms of life may suffer. For the analysis of metals, sample preparation is the most important part.

Several pre-concentration methods including cold-induced aggregation micro-extraction (Gharehbaghi *et al.*, 2009) headspace liquid phase micro extraction

*Author for correspondence;

E-mail:nusratjalbani_21@yahoo.com

(de la Calle *et al.*, 2016; Ghasemi *et al.*, 2011). *In situ* solvent formation micro-extraction (Shokri *et al.*, 2015), dispersive liquid-liquid micro-extraction (DLLME) (Altunay *et al.*, 2019; Li *et al.*, 2009), solid phase extraction (SPE) (Nyaba and Nomngongo, 2020; Mei *et al.*, 2019) and heavy metals detection by cloud point extraction method (CPE) are widely reported using ETAAS/FTAAS method (Zaman *et al.*, 2020; Mortada *et al.*, 2017; Mortada *et al.*, 2013).

The major benefits of the CPE technique include, environmental friendly, lowcost, rapid, effective, simple and real samples (personal care products) can easily be measured without interfering effects. This proposed technique reduces or ignores the utilization of toxic organic solvents and on the basis of above facts the technique is termed as “eco-friendly tool (Mortada *et al.*, 2013). The present procedure possesses good reproducibility and repeatability with low limit of detections (LODs) over the other separation procedure since can be used to determine heavy metals in various personal care products.

The major objective for the proposed work was to develop a miniaturized, economic, environmental friendly and vortex-assisted cloud point extraction VA-SPE procedure for the pre-concentration and determination of Cd, Pb, Cu and Zn. Important parameters that affect on percent recovery of metals were optimized using triton X-100 and xylenol orange as chelating agent. The real samples were successfully analyzed by the proposed procedure, CRM (wheat flour-1567 a) and addition recovery test for determination and pre concentration of heavy metals.

Materials and Methods

Chemicals and reagents. All chemicals and reagents used in the present study were of A.R grade and bought from Merck (Darmstadt, Germany). De-ionized water was used for solution preparation and washing of glass wares, nitric acid (65%), triton X-100 and 0.1 % (w/v) xylenol orange as a chelating agent obtained from Merck (Darmstadt, Germany) was used in the present work. For pH adjustment, a phosphate buffer of pH 4.0 was prepared by adding an appropriate amount of sodium di-hydrogen phosphate and disodium hydrogen phosphate. A 0.1 % (w/v) chelating agent xylenol orange (XO) was purchased from Merck, Darmstadt, Germany, and prepared daily in ethanol/water (1/1 v/v).

For validation of the method, CRM (wheat flour-1567 a) (National Institute for Standards and Technology, Gaithersburg, MD, USA) was used.

Instrumentation

A Hitachi Model 8000 Z Flame Atomic Absorption Spectrometer was used for determination of Cu and Zn in under study samples. However, for lead and cadmium measurement ETAAS was used. At suggested conditions, operation of hollow cathode lamps was carried out. Working standard solutions were used for obtaining calibration curves for Cu, Zn (0.5-1.5 mg/L), Cd (1-3 µg/L) and Pb (20-40 µg/L) respectively. The manufacturer's guideline was followed for recommendation of instrumental parameters. For the adjustment of pH of solutions, the digital pH meter model (HI 2211 Ph/ORP) equipped with combined glass calomel electrode was utilized, centrifuge () 4 × 50 mL digital as well as vortex (SCI Logex) were also used in present study.

Sample collection. The 20 samples of personal care products were collected from different super markets of Karachi capital of Sindh and Lahore capital of Punjab. These samples were directly purchase in different products in the year of 2018 and 2019, which were located from the different areas of Karachi and Lahore Pakistan. Therefore, the personal care products samples were stored at room temperature till to further analysis. To check the accuracy of present procedure, a wheat flour CRM (wheat flour-1567 a) was used. The triplicate determinations were carried out for each sample.

Analysis of real samples. A (1.0-3.0) gm of personal care product (cream, face wash, liquid and powder) samples were taken for Cd, Cu, Pb and Zn analysis. A (0.5-1.0) g of certified reference material (CRM) wheat flour 1567a and Bovine Liver Bovine (1577b) was measured exactly transferred in 250 mL conical flask. The nitric acid (HNO₃) was used to digest the samples at the temperature of 250 °C on using sand bath for one hour, to get clear solution. A Whatman no: 42 filter paper was used to filter the resulting cooled solution in 50 mL volumetric flask double distilled water was used to dilute the solution. After that, pH values of the samples were adjusted to required pH and then developed method was followed to determine the concentration of heavy metals using ETAAS/FTAAS. The similar procedure was followed to prepare blanks without sample. Heavy metals were determined from real samples as well as CRM by proposed method.

Cloud point extraction (CPE) procedure. In a 50 mL volumetric flask, an amount of standard or sample solution matched within 1 mL of Triton X-100 (10% v/v) were added, mixed with chloroform 10 mL then solutions were vortex for 2 min at room temperature (30 °C) as well as centrifuges. The separation of two phases occurred and accompanied by centrifugation (4000 rpm for 20 min) collected upper layer and lower layer was discarded as well as blank prepared under similar conditions.

Statistical analysis. Statistical analysis was performed by computer program of excel and this was used to calculate the minimum, maximum, mean, standard deviation and descriptive statistics.

Results and Discussion

Influences of pH. The pH plays extremely important role in getting quantitative recovery of heavy metals in cloud point extraction work, which was carried out in present work (Hsu *et al.*, 2020; Zhang *et al.*, 2019). The pH range of 3.0 – 9.0 was used to investigate the effects of pH on the recovery of Cd, Pb, Cu, and Zn on xylenol orange ligand. The recovery amount for understudy metals including Cd, Cu, Pb and Zn was achieved at pH 4.0 (Fig. 1.). Since, pH value of 4.0 was selected for conducting further studies using the phosphate buffer.

Influence of ligand volume. The effect of ligand volume is also an essential parameter for developed procedure.

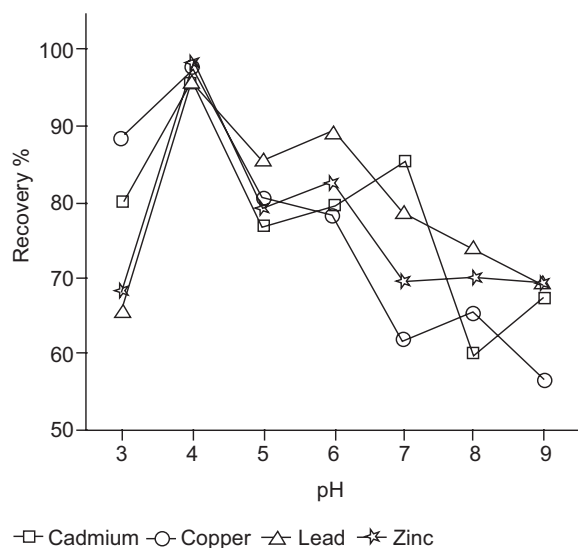


Fig. 1. Result of pH on the recovery of cadmium, lead, copper and zinc.

The experimental data illustrates that the % recovery of the studied metals was reduced at the beginning and then increased with an increase in ligand volume (Fig. 2). The percent recoveries of metals were obtained at 1000 $\mu\text{g/L}$ of ligand volume which was chosen as the optimal value for this study.

Effect of surfactant concentration. To ensure the percent recovery of heavy metals, concentrations of Triton X-100 surfactant were tested. The effect of TX-100 concentration on the percent recovery of trace and toxic metals were explored 0.5–1.0 (w/v) % range as shown in Fig. 3. The % recovery of metals were increased by increasing of TX-100 concentrations up to higher concentration. In order to % recovery of metals on surfactant TX-100 was found to be higher at 1% (w/v) concentrations. Thereafter, 1% concentration, % recovery of all metals was fall down. Therefore, 1.0 % was chosen for further study of experiments.

Effect of incubation time (It) and equilibration temperature (ET). In order to obtain best percent recovery of metals, incubation time and temperature effect were optimized and investigated. With the help of micellar media, cloud point extraction was performed as well as to spend the minimum achievable incubation time and equilibration temperature to complete the reaction and proficient phase separation. In the proposed research, incubation time (It) as well as equilibration

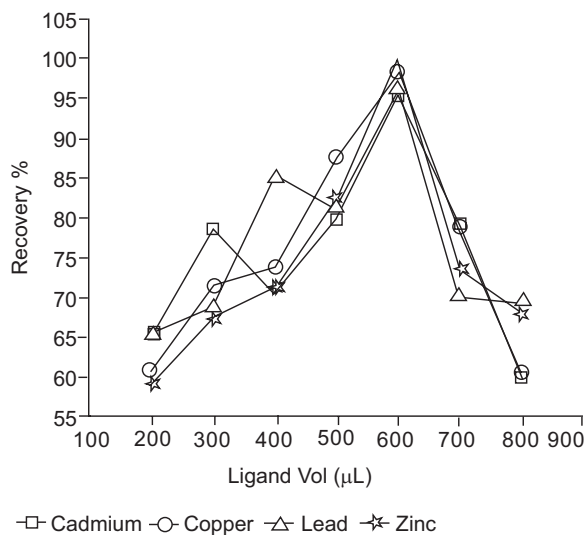


Fig. 2. Result of the ligand volume on the extraction efficiency of cadmium, lead, copper and zinc.

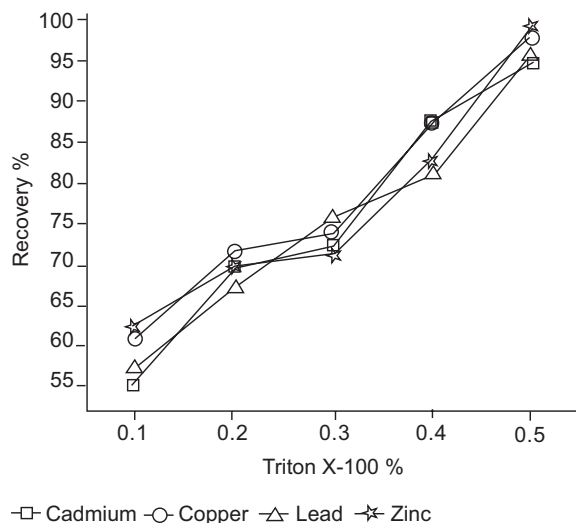


Fig. 3. Result of the Triton concentration on the extraction efficiency of cadmium, lead, copper and zinc.

temperatures (Et) were observed in the range of 5–20 min and 25–40 °C respectively.

Effect of centrifugation time. In order to get clear separation of two layers aqueous phase and organic phase the centrifuge time and rpm were investigated and optimized. The best extraction was carried out with the help by centrifuge and also to employ best possible centrifuge time and rpm for complete separation of phases. In this study, good separation was occurred at 20 min and rpm 4000 rpm respectively and was chosen for subsequent study.

Interference study. The proposed method (Fawzia *et al.*, 2020; Bahadir *et al.*, 2014), and the influence of cations, anions, various alkali metals and alkaline earth metals, on the detection of trace and toxic metals was calculated. Solutions of separate preparation of interfering species and target analyte were carried out and then developed method was used to apply to them as mentioned in the part “Application”. Table 1 shows the experimental data. These results indicated that these

Table 1. Consequence of matrix ions

Ions	Added as	Concentration mg/L	% Recovery
Cd	Cd (NO ₃) ₂	20	97.3
Cu	Cu(NO ₃) ₂	20	95.5
Pb	Zn(NO ₃) ₂	25	97.8
Zn	Pb(NO ₃) ₂	25	96.4

bulging ions cannot interfere to determine trace and toxic metals in current study.

Analytical performance. To facilitate validity of the proposed method, calibration graph was acquired linear for Cd 1-3.0 µg/L, Pb 20-50 µg/L and for Cu, Zn 0.5-1.2 mg/L with a regression values of (0.995, 0.9998). The detection limit was measured depending on the triplicate of the standard deviation of the readings of blank. Detection limit for heavy metals (values in brackets) Cd (0.01 mg/L), Pb (0.01 mg/L), Cu (0.05 mg/L) and Zn (0.1 mg/L) were determined with the pre-concentration factor of 50. The satisfactory results were obtained by proposed method by using suggested method.

Accuracy of method. So, as to validation of method, the accuracy of the proposed procedure was estimated by analyzing of standard addition recovery test and Certified Reference Material (CRM) Wheat Flour (1567a) and Bovine Liver (1577b) for extraction and determination of trace and toxic metals. For certified reference material (CRM) and standard addition method, the proposed method was applied and then subjected to ETAAS/FAAS. The results are summarized in Table 2 and 3.

Comparison of proposed procedure with other pre-concentration techniques. The proposed method of cloud point extraction (CPE) which is micelle mediated was compared with the other published article based on pre-concentration techniques for the evaluation of heavy metals i.e., Cd, Cu, Pb and Zn. Low detection limit and high pre-concentration factor was shown by this proposed procedure (Table 4).

Application to real samples. The measurement of content of heavy metals under study included zinc, lead, copper and cadmium. Lead and cadmium has the highest concentration in PCPs. However, Cu and Zn

Table 2. The results of certified reference material i.e. wheat flour (1567a) and Bovine liver (1577b) (N=6) mg/Kg

Metals	Wheat flour (1567a)		
	Certified value	Found value	% RSD
Cadmium	0.026 ± 0.002	0.025±0.001	4.01
Copper	2.1 ± 0.2	2.07±0.12	5.80
Zinc	11.6 ± 0.4	11.8±0.45	3.81
	Bovine liver (1577b)		
Lead	0.129	0.128±0.008	6.25

Table 3. Standard addition recovery/test in sugar samples for determination of Cd, Cu, Pb and Zn.

Added values	Found values	% Recovery
*Cadmium (Cd)		
0.0	9.61±0.87
2.0	11.2±0.71	96.6
**Copper (Cu)		
0.0	0.146±0.02
0.8	0.942±0.05	99.6
*Lead (Pb)		
0.0	295±3.2
20	326±15.6	97.3
**Zinc (Zn)		
0.0	0.248±0.01
0.5	0.741±0.03	99.1

**µg/mL, *µg/L

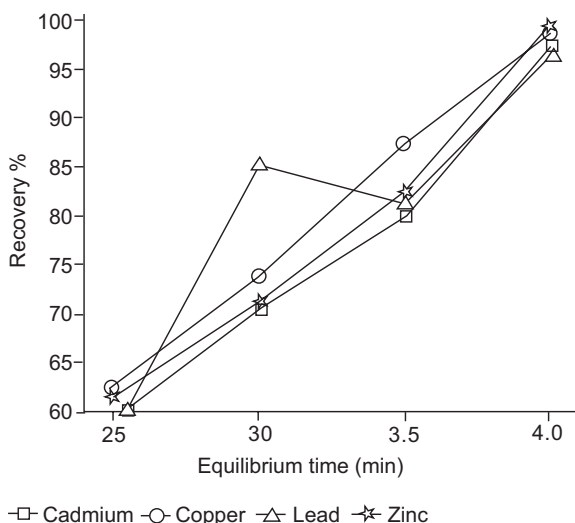


Fig. 4. Result of the equilibrium time on the extraction efficiency of cadmium, lead, copper and zinc.

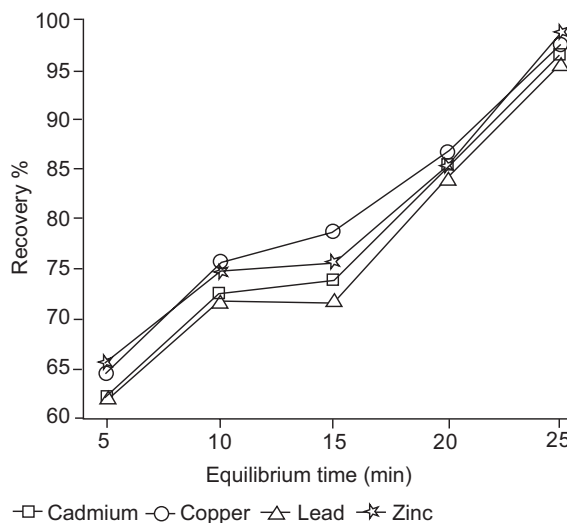


Fig. 5. Result of the incubation time on the extraction efficiency of cadmium, lead, copper and zinc.

have the least concentration in PCPs products. No significant difference was found between lower as well as higher cost cosmetics regarding heavy metals contents measured as shown by T-Test ($P < 0.05$). The proposed method was selected to cover the toxic metals contents. The selected cosmetic items were whitening cream; whitening gel and whitening scrub are the most popular skin whitening creams which are being used throughout Pakistan. The regular consumption of studied cosmetic products may affect on human skin which may lead to dermal problem and many other health issues. Skin contact is regarded as the most important aspect for PCPs because of the various products are used to superficial skin. For this reason, several factors i.e., characteristics of the mixtures determined but minimal absorption of heavy metals to the skin is observed. Cosmetics may be orally exposed to mouth and from hand to mouth connect with heavy metals present in

Table 4. Comparison of proposed technique with other reported pre-concentration methods for cadmium, copper, lead and zinc.

Metals	Methods	Enrichment factor (EF)	Limit of detection (LOD) µg/L	Reference
Cd	SPµE, UA-CPE-D-µ-SPE/ICP-OES, CPE	120, 150, 42	0.15, 0.08, 0.37	(Nyaba and Nomngongo, 2020; Panhwar <i>et al.</i> , 2015; Galbeiro <i>et al.</i> , 2014).
Cu	RP-SHS-LLME-FAAS	22.7	6.9	(Hassan <i>et al.</i> , 2020)
Pb	UA-CPE-D-µ-SPE/ICP-OES	145	0.06	(Nyaba <i>et al.</i> , 2020)
Zn	CPE	43	2.3	(Galbeiro <i>et al.</i> , 2014)

Table 5a. Analytical results for personal care products

Samples ID	Samples description	Results (mg/Kg)			
		Cd	Pb	Cu	Zn
1c	Garnier micellar cleansing water	9.49±0.47	195±1.52	N.D	0.11±0.03
2c	Olay essentials complete care UV fluid	3.44±0.47	206±2.5	N.D	0.31±0.02
3c	Hemani argan scrub	4.53 ±0.51	171 ±1.8	N.D	0.21±0.03
4c	Hemani herbals rose water spray	5.64 ±0.55	231±2.8	N.D	N.D
5c	Grainer anti-dark circle eye roller	9.61 ±0.87	295±3.2	0.14±0.02	0.25±0.01
6c	Loreal skin expert,pure clay detoxifying gel	7.64±0.61	279±2.7	0.31±0.03	N.D
7c	Neutrogena black head remover scrub	8.80±0.24	185 ±3.5	N.D	0.15±0.02
8c	Fruit therapy (body and face bar) by body care essentials	10.9±0.11	147±1.8	0.15±0.01	0.12±0.03
9c	Apricot oil by aura crafts	16.6±0.37	860±1.5	0.14±0.04	0.19±0.02
10c	Radiance (sea salt mask/scrub) by organic secrets	9.15± 0.4	268±1.2	N.D	0.42 ±0.04
WHO		0.3**µg/L	10 **µg/L	50-120 *mg/Kg	101-113 *mg/Kg

these cosmetics. Although, inhalation contact of heavy metals is normally believed to be insignificant (Sani *et al.*, 2016). Thus, toxic and trace metals in cosmetic samples were found above maximum safe limit and considered to be negligible impacts on human health. If these heavy metals like (Cd, Cu, Pb and Zn) cause serious health problems and toxic effects when taken in higher amounts. Likewise, heavy metals may be deposited in the mouth of the human which cause long term health issues. Different sorts of cosmetics, food ingestion, manufacturing methods, industrial sources of heavy metals are responsible for exposure of heavy metals to human health (Achary *et al.*, 2017). Because of inaccuracy of these PCPs in developing countries like Pakistan are sold in the brand name of national as well as international reputed companies in various shops of the country. Believing the various sales situations, affecting the content of heavy metals quantity of personal care products attached with lacking of policy on PCPs in Pakistan, and also marked with bogus PCPs products, markets tolerate non-regulations and the unsupported trust that authentic and safer products are found in the superior and more luxurious markets like the superstores as compared to the smaller and less costly market such as, open market.

Conclusion

Various components are present in the products used for the purpose of beauty. These components enhance fair color complication that get better the quality of life of people related to infection avoidance, self confidence level, and beauty enhancement. The local products (Pakistan made) contains high level of trace and toxic metals which is very harmful for human health, However, Pakistan cosmetic Industries having Guideline and

Standard Operating Procedures (SOPs) but they are not fulfilling the specific standards they are just applying basic guidelines throughout their cosmetic industries. In recent trend, cosmetic industries are expanding, the safety of beauty components as well as products is being kept reviewing by the related authorities. In terms of improvement of products quality, the role should also be played by the consumer by updating with knowledge and responsive of the components present in the products used by them. The proposed cloud point extraction method depending on mixed micelle mediated was developed has been successfully applied on real samples for determination of Cu, Ni and Pb in personal Care Product samples by Electrothermal/Flame Atomic Absorption Spectrometry (ETAAS/FAAS). The major benefits of the procedure are; environmental friendly, more efficient, less expensive, fast, best efficiency of extraction and utilization of less chemical as well as reagents. Due to such facts and figures, this proposed method is achieved as a simple and environmental friendly. The satisfactory results were obtained by proposed method applied successfully on certified reference material and real samples.

Conflict of Interest. The authors declare no conflict of interest.

References

- Achary, M.S., Satpathy, K.K., Panigrahi, S., Mohanty, A.K., Padhi, R.K., Biswas, S., Prabhu, R.K., Vijayalakshmi, S., Panigrahy, R.C. 2017. Concentration of heavy metals in the food chain components of the near shore coastal waters of Kalpakkam, southeast coast of India. *Food Control*, **72**: 232-243.

- Arshad, H., Moniba Z.M., Shah, M.H., Abbasi, A.M. 2020. Evaluation of heavy metals in cosmetic products and their health risk assessment. *Saudi Pharmaceutical Journal*, **28**: 779-790.
- Altunay, N., Elik, A., Gurkan, R. 2019. Monitoring of some trace metals in honeys by flame atomic absorption spectrometry after ultrasound assisted-dispersive liquid microextraction using natural deep eutectic solvent. *Microchemical Journal*, **147**: 49-59.
- Bahadir, Z., Bulut, V.N., Ozdes, D., Duran, C., Bektas, H., Soylak, M., 2014. *Journal of Industrial and Engineering Chemistry*, **20**: 1030-1034.
- De la Calle, I., Pena-Pereira, F., Lavilla, I., Bendicho, C. 2016. Liquid-phase microextraction combined with graphite furnace atomic absorption spectrometry: a review. *Analytica Chimica Acta*, **936**: 12-39.
- Fawzia, I. E., Dalia, E. M., Omnia, A.A., El-Shamy, M.R., Mishrif. 2020. Study the adsorption properties of magnetite nanoparticles in the presence of different synthesized surfactants for heavy metal ions removal. *Egyptian Journal of Petroleum*, **29**: 1-7.
- Gao, P., Tingting, L., Liming, J., Badmatsybenov, Y., Zhaohan, Z., Yingqiu, D., Yujie, F., Baoshan, X. 2018. Bio-accessible trace metals in lip cosmetics and their health risks to female consumers. *Environmental Pollution*, **238**: 554-561.
- Galbeiro, R., Garcia, S., Gaubeur, I. 2014. A green and efficient procedure for the pre-concentration and determination of cadmium, nickel and zinc from freshwater, hemodialysis solutions and tuna fish samples by cloud point extraction and flame atomic absorption spectrometry. *Journal of Trace Elements in Medicine and Biology*, **28**: 160-165.
- Gharehbaghi, M., Shemirani, F., Farahani, M.D. 2009. Cold-induced aggregation microextraction based on ionic liquids and fiber optic-linear array detection spectrophotometry of cobalt in water samples. *Journal of Hazardous Materials*, **165**: 1049-1055.
- Ghasemi, E., Sillanpaa, M., Najafi, N.M. 2011. Headspace hollow fiber protected liquid-phase micro extraction combined with gas chromatography– mass spectroscopy for speciation and determination of volatile organic compounds of selenium in environmental and biological sample. *Journal of Chromatography, A*, **1218**: 1 380-386.
- Hassan, M., Erbas, Z., Alshana, U., Soylak, M., 2020. Ligandless reversedphase switchablehydrophilicity solvent liquid-liquid micro extraction combined with flameatomic absorption spectrometry for the determination of copper in oil samples. *Microchemical Journal*, **156**: <https://doi.org/10.1016/j.microc.2020.104868>.
- Hsu, J.P., Chen, Y.C., Wu, C.T. 2020. Detection of the trace level of heavy metal ions by pH-regulated conical nano channels. *Journal of the Taiwan Institute of Chemical Engineers*, **109**: 145-152.
- Jalbani, N., Soylak, M. 2014. Ligandless surfactant mediated solid phase extraction combined with Fe₃O₄ nano particle for the pre-concentration and determination of cadmium and lead in water and soil samples followed by flame atomic absorption spectrometry: multivariate strategy. *Ecotoxicology and Environmental Safety*, **102**: 174-178.
- Jongeneel, W.P., Delmaar, J.E., Bokkers, B.G.H. 2018. Health impact assessment of a skin sensitizer: analysis of potential policy measures aimed at reducing geraniol concentrations in personal care products and household cleaning products. *Environment International*, **118**: 235-244.
- Kazi, T.G., Afridi, H.I., Murk, B., Asma, A. 2018. A rapid ultrasonic energy assisted pre-concentration method for simultaneous extraction of lead and cadmium in various cosmetic brands using deep eutectic solvent: a multivariate study. *Ultrasonics Sonochemistry*, 2018doi.org/10.1016/j.ultsonch.2018.10.016.
- Latif, A., Sheng, D., Sun, K., Si, Y., Azeem, M., Abbas, A., Bilal, M. 2020. Remediation of heavy metals polluted environment using Febased nanoparticles: mechanisms, influencing factors and environmental implications. *Environmental Pollution*, 114728. doi.org/10.1016/j.envpol.2020.114728.
- Li, S., Cai, S., Hu, W., Chen, H., Liu, H. 2009. Ionic liquid-based ultrasound assisted dispersive liquid–liquid micro extraction combined with electrothermal atomic absorption spectrometry for a sensitive determination of cadmium in water samples. *Spectrochimica Acta Part B: Atomic Spectroscopy*, **64**: 666-671.
- Massadeh, A. M., El-khateeb, M. Y., Ibrahim, S. M. 2017. Evaluation of Cd, Cr, Cu, Ni and Pb in selected cosmetic products from Jordanian, Sudanese, and Syrian markets. *Public Health*, **149**: 130-137.
- Mei, M., Pang, J., Huang, X., Luo, Q. 2019. Magnetism-reinforced in-tube solid phase micro extraction for

- the online determination of trace heavy metal ions in complex samples. *Analytica Chimica Acta*, **1090**: 82-90.
- Mesko, M.F., Novo, D.L.R., Costa, V.C., Henn, A.S., Marlon, E., Flores, M. 2020. Toxic and potentially toxic elements determination in cosmetics used for makeup: a critical review. *Analytica Chimica Acta*, **1098**: 1-26.
- Mortada, W. I., Kenawy, I. M.M., Abdel-Rhman, M. H., El-Gamal, G. G., Moalla, S. M. N. 2017. A new thiourea derivative [2-(3-ethylthioureido) benzoic acid] for cloud point extraction of some trace metals in water, biological and food samples. *Journal of Trace Elements in Medicine and Biology*, **44**: 266-273.
- Mortada, W.I., Hassanien, M.M., El-Asmy, A.A. 2013. Speciation of platinum in blood plasma and urine by micelle-mediated extraction and graphite furnace atomic absorption spectrometry. *Journal of Trace Elements in Medicine and Biology*, **27**: 267-272.
- Nyaba, L., Nomngongo, P.N. 2020. Determination of trace metals in vegetables and water samples using dispersive ultrasoundassisted cloud pointdispersive μ -solid phase extraction coupled with inductively coupled plasma optical emission spectrometry. *Food Chemistry*, **322**: 126749.
- Panhwar, A.H., Kazi, T.G., Afridi, H.I., Arain, S.A., Naeemullah, B.K.D., Arain, M.S. 2015. New solid phase micro extraction method using organic ligand in micropipette tip syringe system packed with modified carbon cloth for pre-concentration of cadmium in drinking water and blood samples of kidney failure patients. *pectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **138**: 296-302.
- Perez, A.L., Nembhard, M., Monnot, A., Bator, D., Madonick, E., Gaffney, S.H. 2017. Supplementary dataset for child and adult exposure and health risk evaluation following the use of metal and metalloids-containing costume cosmetics sold in the United States. *Data in Brief*, **13**: 129-131.
- Sani, A., Gaya, M.B., Abubakar, F.A. 2016. Determination of some heavy metals in selected cosmetic products sold in kano metropolis, *Nigeria. Toxicology Reports*, **3**: 866-869.
- Shokri, M., Beiraghi, A., Seidi, S. 2015. *In situ* emulsification micro extraction using a dicationic ionic liquid followed by magnetic assisted physiosorption for determination of lead prior to micro-sampling flame atomic absorption spectrometry. *Analytica Chimica Acta*, **889**: 123-129.
- Zhang, Q., Chen, H., Xu, C., Zhu, H., Zhu. Q. 2019. Heavy metal uptake in rice is regulated by pH-dependent iron plaque formation and the expression of the metal transporter genes. *Environmental and Experimental Botany*, **162**: 392-398.
- Zaman, B.T., Turan, N.B., Bakirdere, E.G., Topal, S., Sagsoz, O., Bakirdere, S. 2020. Determination of trace manganese in soil samples by using eco-friendly switchable solvent based liquid phase micro extraction-3 holes cut slotted quartz tube-flame atomic absorption spectrometry. *Microchemical Journal*, **157**: <https://doi.org/10.1016/j.microc.2020.104981>.
- Zulaikha, S.R., Sharifah, N.S.I., Praveena, S.M. 2015. Hazardous ingredients in cosmetics and personal care products and health concern: a review. *Public Health Research*, **5**: 7-15.