

DEVELOPMENT METHOD FOR THE DETERMINATION OF Cr, Cd AND Pb IN EDIBLE SUNFLOWER OIL USING EMULSION EXTRACTION-FAAS

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ABSTRACT

The presence of heavy metals in vegetable oils has negative health effects when consumed by living organisms. As a result, assessing mineral extraction methods is critical for monitoring mineral concentration levels and ensuring oil quality. This study describes a new analytical method for the determination of cadmium (Cd), chromium (Cr), and lead (Pb) in edible sunflower oil using emulsion extraction followed by flame atomic absorption spectroscopy (FAAS). The method is based on the formation of a water-in-oil emulsion by mixing the oil sample with (1, 10^{-2} and 10^{-3} M nitric acid solution for Pb, Cr, and Cd respectively) incorporated with a certain amount of a surfactant Triton-X 100 for Pb and Cr, and Tween 80 for Cd. Once the emulsion was formed, it was broken by centrifuging the mixture at 4000 rpm for 5 minutes. This led to the extraction of metal ions into the aqueous phase which was collected, and introduced to FAAS for metal analysis. Neither an organic solvent was used nor an additional dilution was performed prior to the metal analysis. Various parameters that may affect the extraction efficiency of the target metals were evaluated and optimized. The detection limits were 20.0 $\mu\text{g}/\text{kg}$ for lead, 4.0 $\mu\text{g}/\text{kg}$ for chromium, and 0.2 $\mu\text{g}/\text{kg}$ for cadmium. The standard addition method was used for the construction of the calibration curve to mitigate the potential interferences caused by the sample matrix. The findings confirmed that the proposed sample preparation method combined with FAAS provides a simple and reliable analytical method for the measurement of lead, chromium, and cadmium in edible oils.

KEYWORDS: Emulsion extraction, Heavy metals, Edible oil, Flame atomic absorption spectrometry

1. INTRODUCTION

Heavy metals such as Lead, chromium and cadmium are among the most chemical pollutants that have been included in the priority pollutant list generated by the United States Environmental Protection Agency (USEPA) (Kim, Kim, and Kumar, 2019). These metals can cause several environmental and atmospheric pollution and might be lethal to human too (Bakircioglu, Kurtulus and Yurtsever, 2013),(Mendil *et al.*, 2009). For example, studies show that trace amounts of Cd and Pb in human body can cause kidney dysfunction and lung inflammation which may lead to tissue destruction and obstructive lung function. They can also impact the cardiovascular, nervous and reproductive systems, particularly in children. (Davudabadi Farahani and Shemirani, 2012),(Guney and Zagury, 2014). Long-term exposure to the high levels of Cr can cause

various cytotoxic and genotoxic reactions that affect the immune system (Bagchi, Bagchi, and Stohs, 2001).

Heavy metals can enter our bodies through different ways such as inhalation of polluted air, drinking contaminated water and eating foods containing such metals. For instance, The presence of heavy metals in edible oils has been frequently reported and alarmed. According to the previous studies, the soil where the vegetables are planted and grown for the production of edible oils remains the main source of heavy metals in edible oils (Bakircioglu, Kurtulus, and Yurtsever, 2013). The frequent use of metals-containing fertilizers and pesticides (Ghane *et al.*, 2022), as well as industrial wastes especially from certain types of manufacturing processes such as whitening, hardening, refining and deodorization, and oil processing are the other sources responsible for the soil contamination by heavy metals. It is also proved that trace amounts of heavy metals can

enter the edible oils from the packaging materials containing heavy metals in their composition (Zeiner, Steffan and Cindric, 2005),(Boskou, 2006),(Jamali *et al.*, 2008),(Ghane *et al.*, 2022). As a result, many countries have regulated the heavy metal content in edible oils. For example, the European Union (EU) has set a maximum residual limit (MRL) of 100 µg/kg for different edible oils (EU, 1107/2009).

Metals content in vegetable oils is commonly determined by spectrometric methods, such as flame atomic absorption spectrometry (FAAS) (de Souza *et al.*, 2005),(Bornhorst *et al.*, 2018),(Adhami *et al.*, 2020), graphite furnace atomic absorption spectrometry (GFAAS) (Mohebbi *et al.*, 2018),(Almeida *et al.*, 2019), (Manjusha, Shekhar and Kumar, 2019),(Baldo *et al.*, 2020), inductively coupled plasma mass spectrometry (ICP-MS) (Fu, Xie and Shi, 2018), (Luka and Akun, 2019) and inductively coupled plasma optical emission spectrometry (ICP-OES) (Oner *et al.*, 2021),(Tokay *et al.*, 2021). Among all these techniques, flame atomic absorption spectrometry (FAAS) is much more demanding because of its simplicity, availability, and low cost of analysis. (Lepri *et al.*, 2011),(Bakircioglu, Topraksever and Kurtulus, 2014). On the other hand, the direct determination of heavy metals in vegetable oils is often very challenging due to oil viscosity is basically too high to be injected into the measurement equipment. Besides, their high organic content may impact the method accuracy and selectivity (Valasques *et al.*, 2020), (da Silva *et al.*, 2021),(Bornhorst *et al.*, 2018),(Cassella *et al.*, 2018),(Mdluli, Nomngongo and Mketi, 2022). As a result, various sample preparation techniques, such as microwave-assisted digestion, and several extraction techniques, have been reportedly used to eliminate or reduce the potential interferences caused by the sample matrix (Shariff *et al.*, 2018),(Ni *et al.*, 2018),(Tokay and Bagdat, 2015),(Adhami *et al.*, 2020). In recent years, emulsion, as well as microemulsion formation techniques, have gained considerable attention. The extraction induced by emulsion breaking (EIEB) is an interesting procedure which is becoming more and more demanding due to its simplicity, the ability to perform the calibration with standard aqueous solutions, and short extraction times. (Vicentino and Cassella, 2017), (Cassella *et al.*, 2018). This method is based on the formation and breakage of emulsions prepared

by mixing an oil sample with an aqueous phase, composed of an acid and a surfactant (He *et al.*, 2016),(Valasques *et al.*, 2020). During the emulsion breaking, the aqueous layer is isolated from the oily phase via either heating or centrifugation, and the analyte is released to the aqueous phase (Moreira and de Souza Dias, 2018),(Carneiro *et al.*, 2020). This procedure has proved to be more efficient, faster, simpler and more trustworthy in comparison with the other previously reported methods (Meira and de Souza Dias, 2017).

In this study, a new application of EIEB was introduced for the extraction of Cr, Cd and Pb from sunflower oil samples. A diluted nitric acid solution containing a certain amount of a surfactant was used as the aqueous phase and the oil sample as the oily phase. Several factors affecting the efficiency of the extraction method such as acidity, volume of the aqueous phase, volume and concentration of surfactant, shaking time, and temperature were thoroughly investigated. At the end of the extraction process, the aqueous phase; which was used as the extractant phase, was directly analyzed by FAAS method.

2. EXPERIMENTAL

2.1. Reagents and solutions

All chemicals and reagents used in this work were of analytical grade. Nitric acid and hydrochloric acid solutions were prepared by direct dilution of their concentrated solutions with appropriate amounts of deionized water. The 10% (v/v) solutions of each surfactant, Tween-40 (HIMEDIA, Mumbai, INDIA), Tween-20, Tween-80, Triton X-114, and Triton X-100 (Merck, Darmstadt, Germany) were prepared in acetonitrile and high-purity deionized water.

Single-element standards containing 1000 µg/mL of each metal, prepared in 5% HNO₃, were used to construct the calibration curves. Pb and Cd were supplied from CHEM-LAB Belgium, and Cr from Merck, Darmstadt, Germany.

Sodium hydroxide (98%) was supplied from ALPHA CHEMIKA, INDIA, nitric acid (69-71%) was purchased from GAINLAND CHEMICAL, UK. Acetonitrile and ethanol (for GC, 99.9 %) from scharlab, Spain). Prior to analysis, the laboratory glassware were kept overnight in a 10% (v/v) nitric acid solution. Afterward, they were rinsed thoroughly with ultra-pure water and dried out.

2.2. Equipment

Flame atomic absorption spectrometry (FAAS) using PG AA 500 spectrometer (London, UK) was used for the quantification of Cd, Cr, and Pb. The spectrometer was equipped with a flame atomizer and deuterium lamp background correction. Cd, Cr, and Pb hollow-cathode lamps (PG Instruments Ltd, Alma Park, Wiboft Lutterworth, United Kingdom), operating at 6 mA with a slit width of 0.6 nm were utilized as the radiation source. All the measurements were conducted at the highest-sensitivity wavelength indicated by the instrument's manufacturer. The wavelengths used were 229.10, 359.74 and 283.61 nm for Cd, Cr and Pb, respectively. The spectrometer was equipped with a 100 mm burner made of titanium alloy to generate an air-acetylene flame with a fuel-oxidant ratio of 1:3 (0.5:1.5 L/min). The water-oil emulsification was carried out in a Stuart Orbital shaker (Model SSL1, Stuart, Keison, UK) and lab centrifuge machine (Model 80-2, wincom, China) was used for emulsion breaking. Other equipment used in this work were as follows, an analytical balance with a resolution of 0.1 mg (Sartorius, Goettingen, Germany), a pH meter (Model 3505 JENWAY, Bibby Scientific Ltd, UK), a digital water bath (Model SWB2D 15 L, Stuart, Keison, UK) and a water purification system (Daihan Labtech co.ltd, Korea).

2.3. Sample preparation

Several samples of edible sunflower oil were supplied from local supermarkets (ZER edible

sunflower oil). The samples were then spiked with the target metals according to the following procedure. For lead, 3 mL of 1000 ppm lead standard solution mixed with 7 mL of ethanol. Then, the mixture was added to 990 g of sunflower oil sample and the entire solution was shaken vigorously. for chromium, a mixture of 1.2 mL of 1000 ppm standard solution and 3.8 mL of ethanol was added to 995 g of sunflower oil sample, and shaken vigorously. for cadmium, 0.5 mL of 1000 ppm Cd standard solution mixed with 3.5 mL of ethanol, and the resulting mixture was added to 966 g of sunflower oil.

2.4. Emulsion extraction procedure

7.0 g of spiked sunflower oil samples was transferred into a polyethylene test tube. Then, solutions of 0.5 mL of surfactant (1.5, 3 and 4%) and 2.0 mL of nitric acid (1, 10^{-2} and 10^{-3} M) (for Cd, Pb and Cr, respectively) were added successively to the test tube. After 15 minutes of shaking, the test tube was put in a water bath set at 45 °C for 2 min, then being shaken for another 3 minutes. Here, acidic water-to-oil emulsions were created, and the target minerals were transferred from the oil phase to the aqueous phase (which served as the extraction solvent). Then, the mixture was centrifuged at 4000 rpm for 2 min, and the aqueous phase was separated from the oil phase placed at the bottom of the test tube. Finally, the collected phase was transferred to another tube for further analysis by FAAS as shown in (Fig. 1).

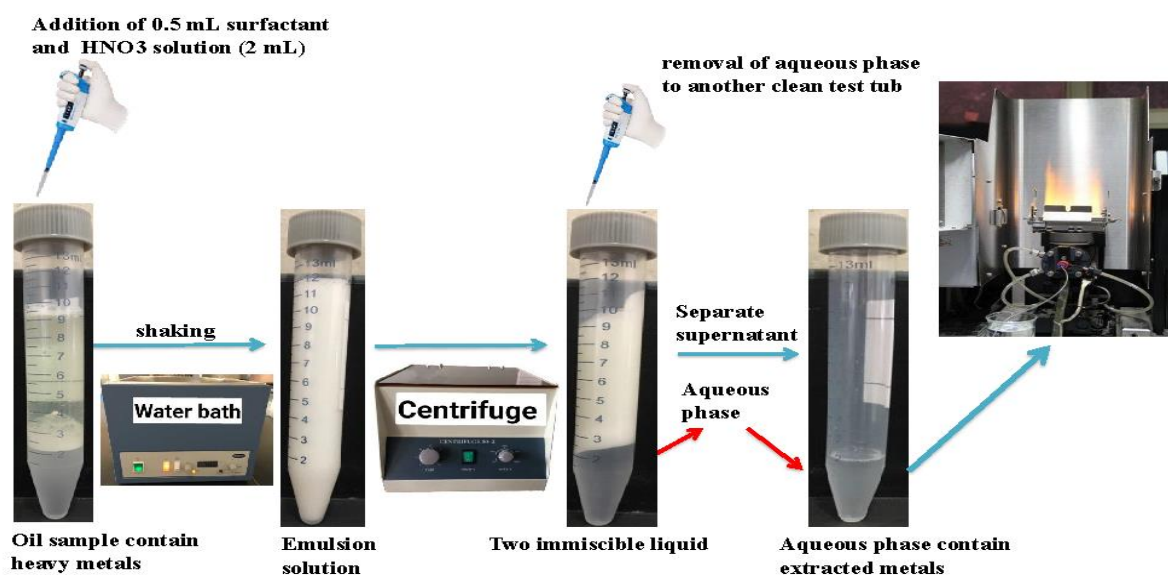


Fig. (1): Emulsion extraction procedure.

3. RESULTS AND DISCUSSION

3.1. Effect of aqueous phase acidity

In order to study the effect of pH of aqueous phase on the extraction of Cr, Cd, and Pb cations from the oil phase, series of experiments were designed and conducted. In short, 2 mL of different concentrations of HNO₃ (2.5 M to 10⁻¹⁰ M) was added to 7.0 g of oil sample together with 0.5 mL of 2% surfactant (Triton-X 100). The target metal ions were extracted and quantified, according to the presented results in Fig 2, 0.001, 0.01 and 1 M were best

concentrations of nitric acid to obtain optimal pH (for Cr, Pb, and Cd, respectively). Relatively low acid concentrations are sufficient to extract metals that are held by weak bonds (Drosaki and Anthemidis, 2022),(Robaina, Brum and Cassella, 2012),(Pereira *et al.*, 2013). But in stronger bonds between metals and organic and oily matrix, high concentrations of nitric acid are required (Drosaki and Anthemidis, 2022),(Adolfo *et al.*, 2020),(Valasques *et al.*, 2018).

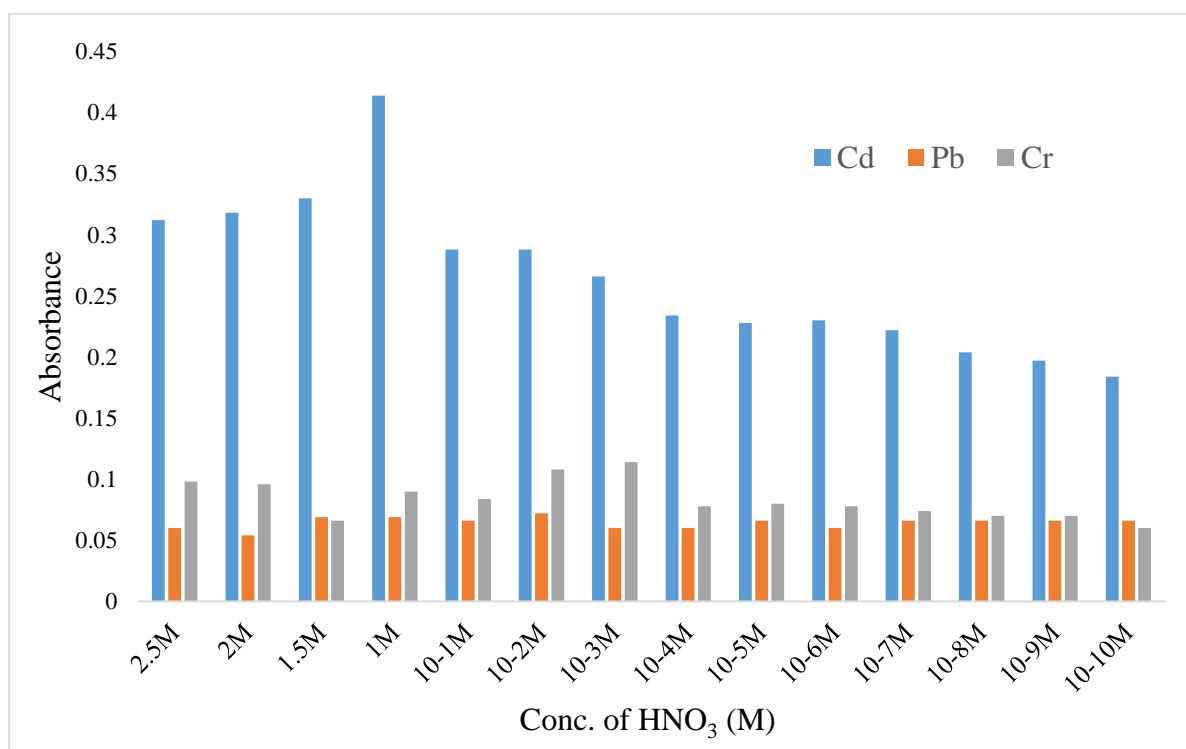


Fig. (2): Effect of acidity on the absorbance of Cd, Cr and Pb obtained from extraction. Cd, Pb and Cr concentrations, 0.25, 1.5 and 0.6 mg/kg.

3.2. Effect of extractant phase volume

The volume of the extractant phase is an important parameter affecting the extraction process in two different ways. On one hand, its volume should be large enough so that a fine and uniform dispersion of the aqueous phase in the oil phase is achieved. On the other hand, it should be as low as possible so that a high concentration factor is obtained. Therefore, it is important to find the optimal volume of extractant phase to establish a balance between these two effects. To do so, different volumes of

nitric acid solution 0.001, 0.01 and 1 M (for Cr, Pb, and Cd, respectively), ranging from 1.5 to 3.5 mL were added to 7 mL of the sunflower oil samples. As indicated in **Fig. 3**, the best extraction efficiency was achieved at extractant volume of 2 mL. It should be noted that the volumes smaller than 2 mL were not studied, as the volume of the remaining aqueous solution, which contains the extracted metals, was too small to be introduced to the FAAS. So, 2 mL of extractant phase was used in the following experiments.

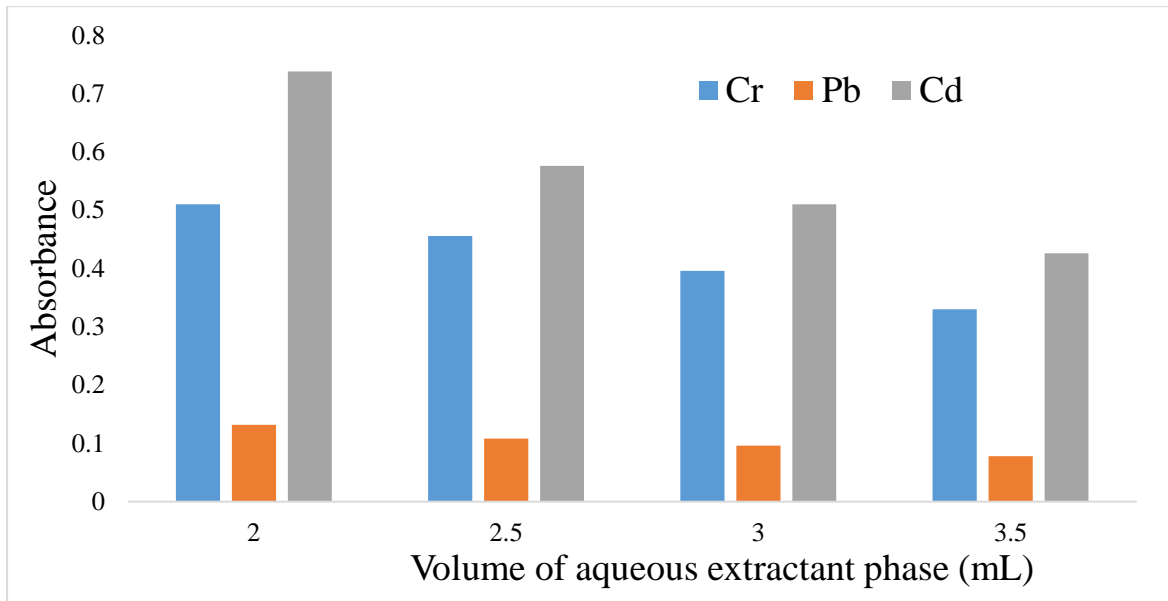


Fig (3): Effect of volume of aqueous extractant phase on the absorbance of Cd, Cr, and Pb obtained from extraction. Cd, Pb and Cr concentrations, 0.25, 1.5 and 0.6 mg/kg spiked to oil sample.

3.3. Effect of surfactant type, concentration, and volume

Emulsifying agents play a very important role in emulsion formation. Besides, they can increase the stability of the emulsion by reducing the surface tension of the oily and aqueous phases (Camera *et al.*, 2022). So, several surfactants including Tween-20, Tween-40, Tween-80, Triton X-114, and Triton X-100 were chosen to study the impact of surfactant type on the extraction efficiency of Cr, Cd and Pb metals. To this end, 2.0 mL of extracting phase with

optimal pH relevant to each metal and 0.5 mL of each surfactant (2% w/v) were added separately to 7.0 g of sunflower oil samples. After the formation of the emulsion the two phases were separated by the centrifuge, and the aqueous phase containing the target metals was analyzed by FAAS. The results, which are presented in **Fig. 4**, showed that Triton-X 100 provided higher extraction efficiencies for Pb and Cr, while Tween 80 had a profound impact on the extraction of Cd.

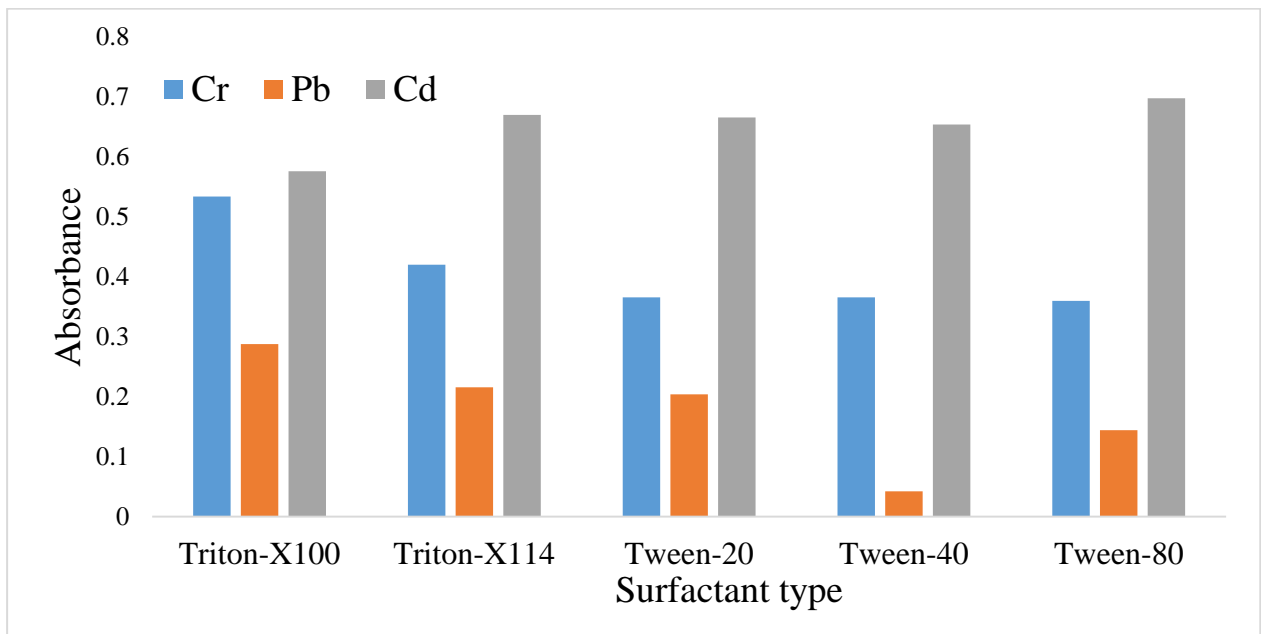


Fig. (4): Effect of surfactant type on the absorbance of Cd, Cr, and Pb obtained from extraction. Cd, Pb and Cr concentrations, 0.25, 1.5 and 0.6 mg/kg.

The concentration of surfactants is another important factor that can influence the extraction efficiency. In order to find the ideal concentration of the surfactant, 0.5 mL of of the selected surfactants at different concentrations ranging from 0.25 to 5% w/v

were examined. Looking at **Fig. 5**, The optimal surfactant concentration for Cr and Pb was 1.5 and 3.5% of Triton-X 100, respectively, and the ideal surfactant concentration was 4.5% of Tween-80 for Cd,

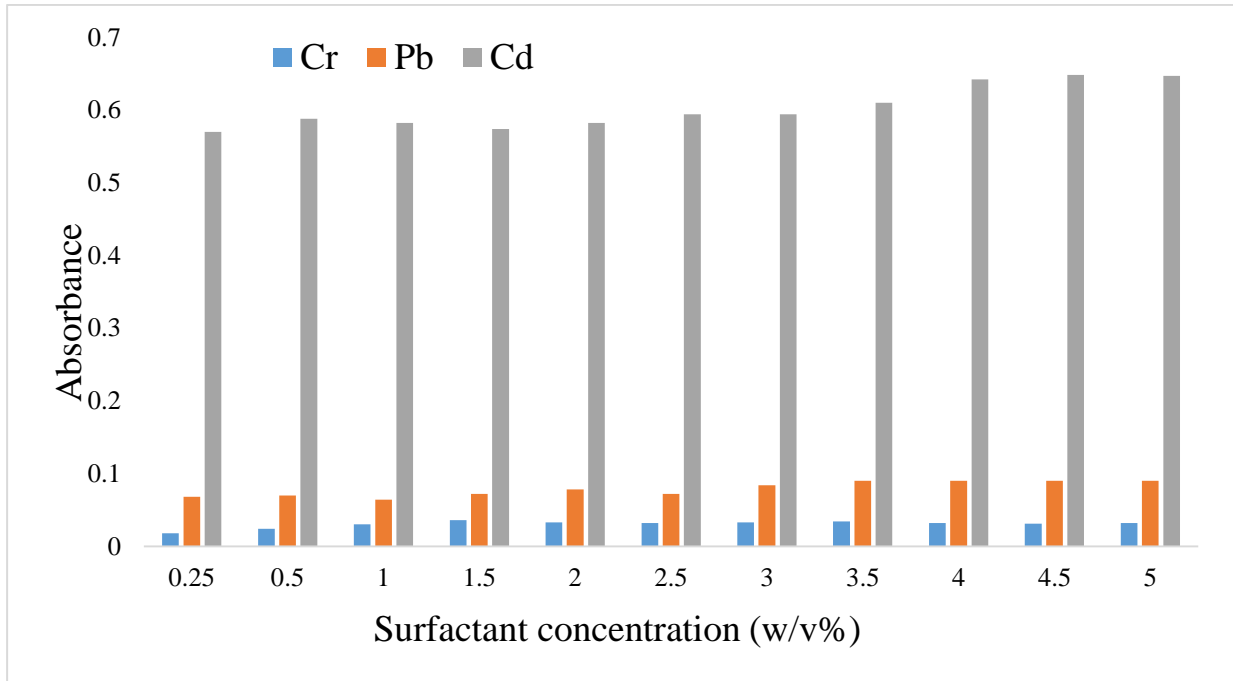


Fig. (5): Effect of surfactant concentration on the absorbance of Cd, Cr, and Pb obtained from extraction. Cd, Pb and Cr concentrations, 0.25, 1.5 and 0.6 mg/kg.

Once the optimal surfactant concentration was determined for each metal, the effect of surfactant volume on the extraction efficiency was studied and optimized. To this end, different surfactant volumes ranging from 0.25 to 2.5 mL were examined. As demonstrated in **Fig. 6**, increasing the surfactant volume beyond 0.5 mL caused a considerable reduction in the absorbance value for all studied metals. The pH

of the aqueous layer is impacted by surfactant solution volume, which lowers extraction efficiency. The volume of the extracted aqueous phase, on the other hand, increases as the surfactant solution volume increases, which causes a decrease in the concentration of heavy metals removed in the aqueous phase. Therefore, 0.5 mL of surfactant was used for all three metals in the rest of this study.

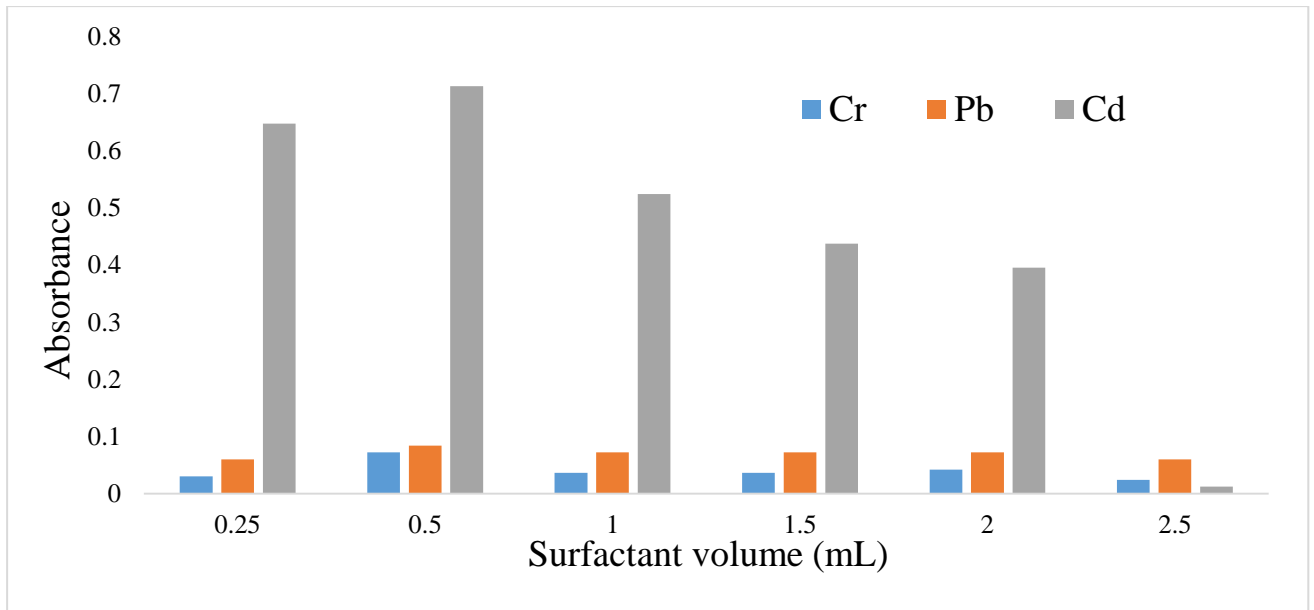


Fig. (6): Effect of surfactant volume on the absorbance of Cd, Cr, and Pb obtained from extraction. Cd, Pb and Cr concentrations, 0.25, 1.5 and 0.6 mg/kg.

3.4. Effect of shaking time

Shaking the mixture of oil sample and the aqueous extractant helps disperse the aqueous phase in the oil phase more uniformly and generate the emulsion faster. However, shaking the mixture for a long time will increase the total time of measurement. So, in an attempt to determine the best shaking time, different

shaking times from 3 min to 18 min were investigated. **Fig. 7** shows the obtained absorbance values for each extracted metal at different times. As indicated, the extraction efficiency increased gradually by increasing the shaking time from 3 min to 15 min and became stable afterward. So, 15 min was chosen as the best shaking time in this work.

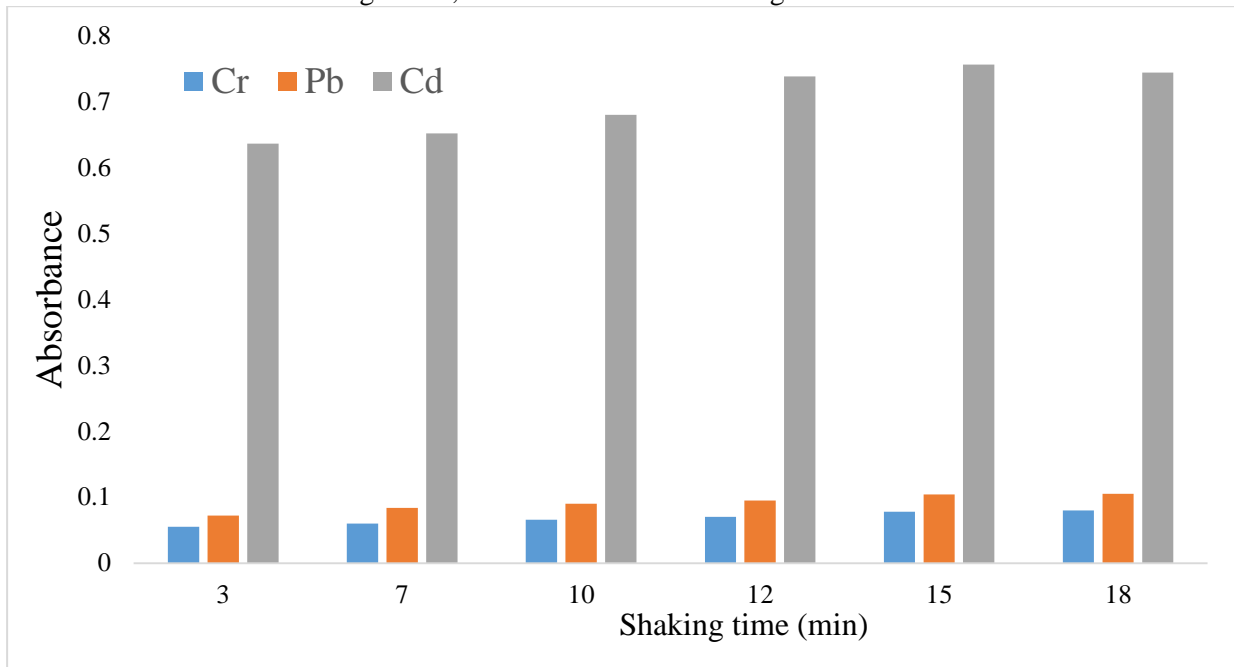


Fig. (7): Effect of shaking time on the absorbance of Cd, Cr, and Pb obtained from extraction. Cd, Pb and Cr concentrations, 0.25, 1.5 and 0.6 mg/kg.

3.5. Effect of temperature

The effect of temperature on the formation and stability of the emulsion can be investigated from the aspect that increasing the temperature can reduce the viscosity and surface tension of the oil phase and hence facilitate the formation of water droplets in the oil. On the other hand, increasing the temperature can break the generated emulsion, reducing the contact time between the oil phase and the aqueous phase (Camera *et al.*, 2022). So, In order to find the

optimum temperature, different oil samples were extracted in the same experimental conditions at different temperatures from ambient temperature to 60 °C. As indicated in **Fig. 8**, for almost all studied metals, temperatures higher than 40 °C led to a significant decrease in the absorbance value which can be attributed to the breaking of the emulsion. As a result, 40 °C was chosen as the optimal temperature.

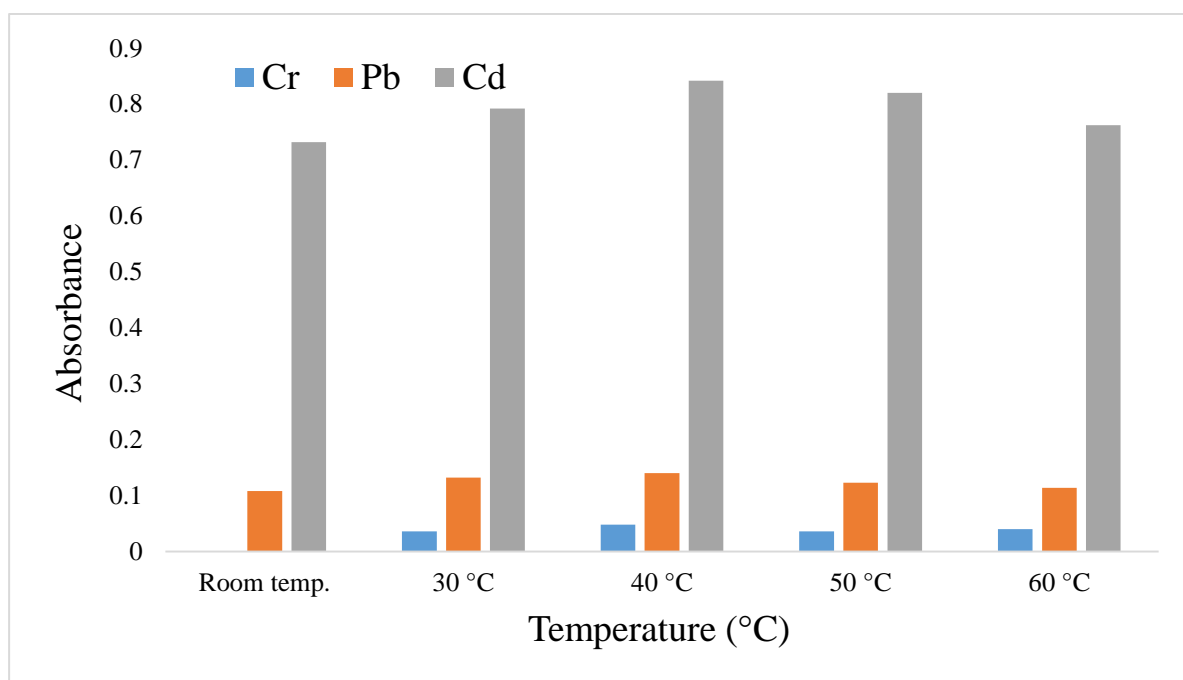


Fig. (8): Effect of temperature on the absorbance of Cd, Cr, and Pb obtained from extraction. Cd, Pb and Cr concentrations, 0.25, 1.5 and 0.6 mg/kg.

3.6. Effect of sample amount

Basically, increasing the sample quantity will increase the chance of analyte extraction by the extractant phase. However, to reduce the use of chemicals and avoid large sample volumes, it is necessary to find out the ideal sample amount. For this purpose, different amounts of oil samples ranging from 3.0 to 10.0 g were weighed accurately and transferred to different test tubes. Then, the same amount of extractant and surfactant solutions were added to each tube,

and the extracted metals were quantified by the proposed method. As can be seen in **Fig. 9**, the analytical signal increased remarkably by increasing the sample weight up to 7.0 g and afterward remained unchanged. This is probably because of the higher stability of generated emulsion at bigger sample volumes. So, a sample size of 7.0 g opted for the analysis of target metals using the presented method.

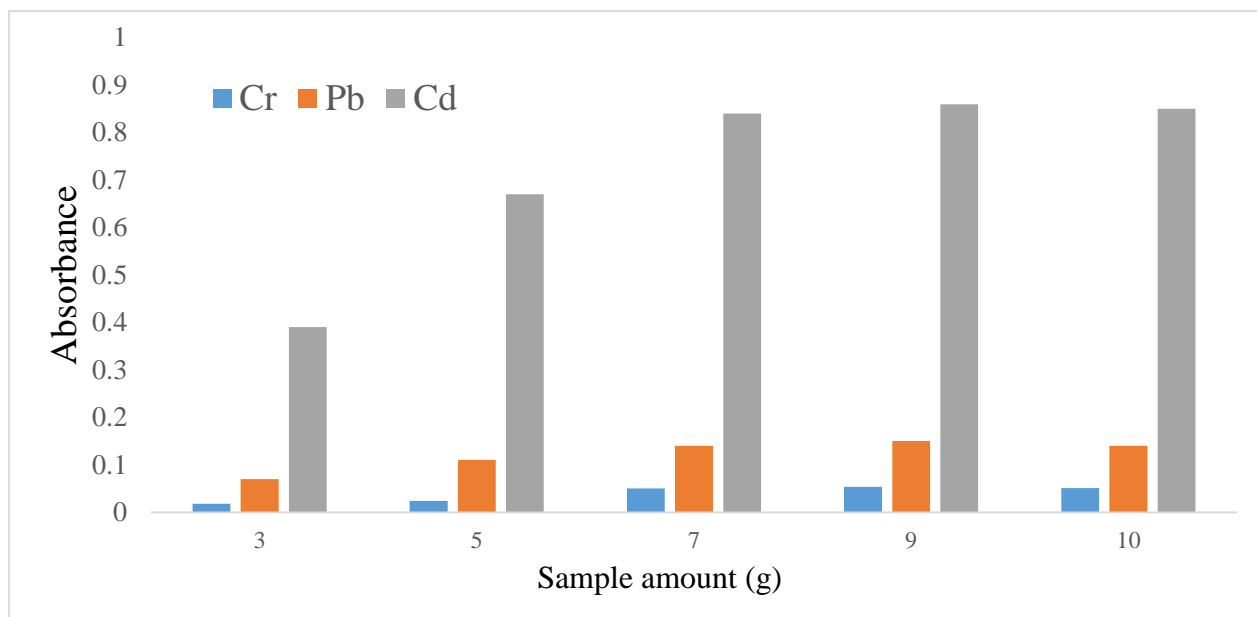


Fig. (9): Effect of sample amount on the absorbance of Cd, Cr, and Pb obtained from extraction. Cd, Pb and Cr concentrations, 0.25, 1.5 and 0.6 mg/kg.

3.7. Analytical figures of merit

The analytical performance of the optimized protocol was evaluated by determination of figures of merit. Table 1 shows the estimated figures for each metal. As indicated, the calibration curves were linear in the range of 0.7-5000 $\mu\text{g}/\text{kg}$ for Cd, Cr, and Pb. The detection limits, which were defined as $\text{LOD} = 3$

SB/m (where LOD, SB, and m are the detection limit, the standard deviation of the blank, and the slope of the calibration plot, respectively), were 0.2, 4, and 20 $\mu\text{g}/\text{kg}$ for Cd, Cr and Pb, respectively. To check the correctness of the proposed method, sunflower oil samples were analyzed using EIEB-FAAS method.

Table (1): The analytical figure of merit of the emulsification extraction-FAAS for determination of Cd, Cr, and Pb.

Element	LOD($\mu\text{g}/\text{kg}$)	LR	R^2	ER%	EF
Cr	4.0	13-2500	0.99	52	4.7
Cd	0.2	0.7-1000	0.99	70	3.3
Pb	20	70-5000	0.99	45	2.1

LOD: limit of detection, LR: the linearity of range, ER: extraction recovery (1 ppm for each element), EF: enrichment factor (1 ppm for each element); experimental condition: 7.0 mL oil sample, 2.0 mL of an acid aqueous phase, 0.5 mL of surfactant, 15 min shaking time.

3.10. Comparison of emulsion extraction with other related techniques

The effectiveness of the optimized emulsion extraction method for the determination of chromium, cadmium, and lead was compared with some formerly reported methods. According to Table 2, the present method's reproducibility was better or comparable to other techniques. However, the present method

requires smaller amounts of chemicals and produces less chemical waste compared to the other methods. Furthermore, a relatively high EF can be obtained using a small sample quantity. In summary, the suggested method has clear advantages over the conventional extraction methods and digestion procedures which makes it very suitable for routine analysis. For example, unlike conventional chemical and microwave

digestion, no special equipment is required. Only a small amount of sample would be enough to extract and quantify the concerned materials,

there is no toxic chemical involved in the measurement which is well in accordance with green chemistry goals.

Table (2): Analytical performance of the presented method and some similar methods for extraction of heavy metal in edible oil.

Methods	Element	LOD ($\mu\text{g}/\text{kg}$)	R ²	LR ($\mu\text{g}/\text{kg}$)	References
Deep eutectic solvent microextraction-FAAS	Pb, Co, Ni and Mn	2.4	0.99	5-60	(Soylak and Koksak, 2019)
Emulsion breaking-induced extraction-GF-AAS	Na, Al, Ti, Cr, Cu and Zn	1.1	0.99	10-100	(da Silva <i>et al.</i> , 2021)
Emulsion breaking-induced extraction-GF-AAS	Cd, Pb	1.5-3.3	0.98-0.99	5-20	(Leal <i>et al.</i> , 2022)
Emulsion extraction -FAAS	Cd, Cr and Pb	0.2-20	0.99	0.7-1000	Our work

4. CONCLUSION

In this work, a new application of EIEB method was introduced for the quantification of cadmium, chromium, and lead in edible sunflower oil using FAAS. The EIEB method used was based on the formation of an emulsion, following the breaking of the emulsion by a centrifuge. Analytical reliability indicators such as sensitivity, linear correlation coefficients, limits of detection, and recovery were calculated for the determination of Cd, Cr, and Pb in oil samples, and the results were found satisfactory. The proposed method had distinctive advantages such as simplicity, speed, environmental friendliness, and low cost of analysis compared to conventional sample preparation methods. The method involved little sample manipulation, reducing the risk of cross contamination. In addition, since a low temperature was used during the emulsion formation, there was little concern about the loss of analytes due to evaporation. Furthermore, the proposed method was quite environmentally friendly as it reduces the use of concentrated acids, toxic chemicals, and solvents. Consequently, the presented method is a suitable alternative to the existing analytical methods for the reliable determination of Cd, Cr, and Pb in edible oil samples.

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