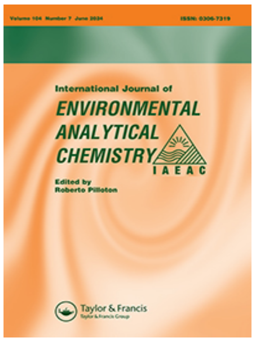

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Development of a dispersive micro-solid phase extraction method based on using cobalamin as a green adsorbent for the extraction of Cd(II) and Pb(II) from oil samples

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ABSTRACT

A dispersive micro-solid phase extraction procedure using cobalamin as a green sorbent has been developed for the extraction of Cd(II) and Pb(II) ions from oil samples. At first, a desired amount of oil sample was dissolved in chloroform. Then, the specified amount of cobalamin was added and vortexed. After centrifuging, the separated solid particles were dissolved in nitric acid solution. Finally, the analytes were analysed by flame atomic absorption spectrometry. Effects of different analytical parameters such as amounts of sample and cobalamin, vortex time, complexing agent amount, type and volume of dissolving solvent, and temperature on the extraction efficiency of Pb(II) and Cd(II) ions were investigated and optimised. Under optimised conditions, calibration curves were established with the linear ranges of 1.5–150 µg Kg^{-1} for Cd(II) and 1–150 µg Kg^{-1} for Pb(II). The detection limits were found to be 0.48 and 0.34 µg Kg^{-1} along with extraction recoveries of 89.1% and 94.8% for Cd(II) and Pb(II) ions, respectively. The proposed method demonstrated good repeatability, with the relative standard deviation ranging from 3.8% to 4.1% ($n = 6$, $C = 10$ µg Kg^{-1} of each cation). Finally, the method was successfully applied to determine the concentrations of Cd(II) and Pb(II) ions in various oil samples.

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Dispersive micro-solid phase extraction; cobalamin; heavy metal ions; oil; flame atomic absorption spectrometry

1. Introduction

Heavy metals can enter the environment and living organisms through both natural processes and human activities [1]. These metals are harmful to the environment and can lead to health problems due to their ability to accumulate in living tissues [2]. Edible oils are necessary for human consumption, as they are used for three purposes: providing energy, acting as a structural component, and producing biological controllers [3,4]. The quality of these oils is dependent on the level of trace metals, as their high levels can accelerate oxidation [5]. These metals may come from the soil in which the plants are grown or may be introduced during the manufacturing process of food samples [6–10]. Also, trace elements can be entered in oils due to contaminations from fertilisers, soil, extraction and refining processes, packaging materials or metal processing equipment

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[11]. Some of these elements such as Ca, Co, Fe, Mg, Mn, and Ni may promote oxidative degradation of the oils. Some other ions, because of their concentrations in oil samples, may have negative impacts on human health [12]. Cadmium and lead are particularly concerning due to their toxicity and potential health risks. They can affect the quality of oils by altering their nutritional value, freshness, preservation properties, storability, and toxicity [13]. As a result, detecting the presence of such elements in edible oils has become increasingly crucial in recent years. Various analytical methods such as graphite furnace atomic absorption spectrometry [14,15], inductively coupled plasma-mass spectrometry [16,17], inductively coupled plasma-optical emission spectrometry [18], flame atomic absorption spectrometry (FAAS) [19,20], and electrochemical methods [21,22] have been used to quantify heavy metals in various oil samples. In this regard, FAAS is widely used for detecting trace levels of metals, but its main drawback is high instrumental detection limits. Also, direct determination of metals in oil is challenging due to their low concentration, high viscosity of the samples, and interferences from organic compounds [23]. Consequently, performing a sample preparation procedure is essential for trace analysis of heavy metals in oil. Several procedures like extraction methods and microwave, wet, and dry digestion were reported [24,25] for this purpose. However, they are time-consuming and prone to contamination and analytes loss [26]. To overcome these issues, analytical chemists use extraction/preconcentration techniques to improve the sensitivity of FAAS in metal determination.

Therefore, to accurately determine trace levels of heavy metals in samples, it is necessary to use extraction procedures effectively before analysing with analytical instruments. Various techniques have been developed for this purpose, including solid-phase extraction (SPE) [1,27,28], cloud point extraction [29,30], dispersive SPE (DSPE) [31,32], solid-phase microextraction [33,34], single-drop microextraction [35,36], homogeneous liquid–liquid extraction [37,38], dispersive liquid–liquid microextraction [39,40], and hollow-fibre liquid-phase microextraction [41,42]. These methods are used to separate and preconcentrate heavy metal ions by accounting for the presence of matrix effect in the samples. In the last decades, microextraction techniques were very popular for separating and concentrating trace amounts of inorganic and organic substances. These methods offer benefits such as short extraction time, minimum consumption of organic solvents, and high concentration factor [43–46].

Several studies were conducted to assess the effectiveness of various adsorbent materials in eliminating, extracting, and preconcentrating different heavy metals from diverse sources [47–52]. The most commonly used extraction techniques involving the use of adsorbents are SPE, DSPE, and dispersive micro-solid phase extraction (D-µSPE) [53–56]. These methods typically involve mixing the sample solution with the adsorbent and then using small amounts of organic solvents to break up the interactions between the solid particles and analytes, causing the analytes to detach from the particles. DSPE and D-µSPE have been widely used for separation and preconcentration of trace analytes due to their high extraction efficiency, short extraction time and low use of organic solvents [57–59]. However, these methods are often associated with the issues such as inadequate adsorption and incomplete desorption.

Cobalamins, also known as vitamin B12, is the compound that contains cobalt and is essential for human health [60]. Vitamin B12 is crucial for the human body, as it plays an essential role in the nervous system, red blood cell formation, DNA synthesis, and myelin sheath growth [61]. The deficiency of this vitamin can lead to severe health issues such as megaloblastic anaemia and nervous system disorders. The human body cannot store vitamin B12, and any excess amount is quickly excreted due to its water-soluble nature. Therefore, it needs to be recieved daily, and the recommended daily intake for adults is 2.4 µg per day.

In this study, a simple D-µSPE method was developed for the extraction of Cd(II) and Pb(II) ions from oil samples by using cobalamin as an adsorbent. In the proposed method, to solve the problem of incomplete desorption of the analytes, which can lead to decreasing extraction efficiency, the evolution of the analytes from the sorbent surface was replaced by dissolution of the sorbent in nitric acid solution. After extraction, the cobalamin particles were collected at the bottom of the tube after centrifuging. The supernatant was discarded, and the collected particles were dissolved in nitric acid solution. Therefore, the proposed method requires no desorption step, which is time-consuming and requires sonication or vortexing. In this study, for the first time, cobalamin was used to extract heavy metal ions from oil samples. Easy operation, short extraction time, high extraction efficiency, and inexpensiveness can be the major advantages of the proposed procedure

2. Materials and methods

2.1. Reagents and solutions

Ethyl acetate, acetonitrile (ACN), nitric acid, methanol, chloroform, $Pb(NO_3)_2.6\,H_2O$, $Cd(NO_3)_2.6\,H_2O$, and 8-hydroxyquinoline (8-HQ) with the highest purity were provided from Merck (Darmstadt, Germany). Cobalamin was gift from Daana Pharmaceutical Company (Tabriz, Iran). The preliminary experiments indicated that the analyte contents of a sunflower oil were lower than the limits of detection (LODs) of the method. Therefore, 100 g of this oil was leached with 100 mL HNO_3 (5%, v/v) solution for two times and used as a Pb- and Cd-free oil sample (blank oil) in optimisation of the proposed method. A stock solution containing Pb(II) and Cd(II) ions was prepared by dissolving $Pb(NO_3)_2.6\,H_2O$ and $Cd(NO_3)_2.6\,H_2O$ in acetone at a concentration of 100 mg L^{-1} for each cation and used to spike the samples. Moreover, a mixed standard solution of the analytes was prepared at a concentration of 3 mg L^{-1} for each cation, and injected into FAAS three times daily for quality control of the detection system. The obtained signals were used to calculate the extraction recoveries (ERs) of Pb(II) and Cd(II) ions.

2.2. Real samples

Oil samples including omega 3, olive, almond, hazelnut, and sunflower oils were bought from local sellers in Tabriz, Iran. Also, fish oil capsules were provided from local pharmacies (Tabriz, Iran). The contents of the capsules were removed with the aid of a syringe. The samples were subjected to the microextraction methods without treatment.

2.3. Instruments

A Shimadzu AA-6300 flame atomic absorption spectrometer (Kyoto, Japan) was used to determine heavy metal ions. An air-acetylene flame was used in the determination of the analytes concentration. Radiation sources for lead and cadmium were hollow-cathode lamps from Hamamatsu Photonics (Shizuoka, Japan). They were operated at the wavelengths of 217.0 and 228.8 nm (resonance line) with the currents of 15 and 10 mA, respectively. An L46 vortex mixer (Netherland) and a D-7200 (Hettich) centrifuge were used to assist the extraction process.

2.4. Extraction procedure

A 0.25 g analytes-free oil sample was spiked with 10 µg Kg^{-1} of each cation in an 8-mL glass test tube. Then, 3 mL of chloroform and 200 µL of 5 mmol L^{-1} 8-HQ were added. To the obtained homogeneous solution, 6 mg cobalamin was added. It was vortexed for 4 min and then centrifuged at a rate of 8000 rpm for 5 min. The particles of cobalamin were separated. To dissolve the adsorbent particles and transform the analytes into solution, 220 µL nitric acid solution (5%, v/v) was added, and vortexed for 30 s. Two portions of 100 µL aliquots were removed and injected into the FAAS.

3. Results and discussion

Various practical factors including the amount of oil, the amount of cobalamin, vortex time, volume of ACN, complexing agent concentration, and temperature were assessed using a 'one-factor-at-a-time' approach to study their impact on the extraction efficiency to determine the optimal conditions of the proposed method. The detailed discussion of these parameters can be found in the following sections. It should be noted that in the optimisation process, 0.25 g of analytes-free sunflower oil (spiked with 10 µg kg^{-1} of each cation) diluted by 3 mL chloroform was used as the working solution.

3.1. Optimization of oil amount

To study the effect of the sample weight on the ERs of the analytes, various amounts (100–400 mg) of the analytes-free oil spiked with 10 µg kg^{-1} of each cation were mixed with 3 mL chloroform and subjected to the proposed extraction procedure. The findings in Figure 1(a) demonstrate that ERs of the analytes are noticeably impacted within the range of 100–250 mg, then remain relatively consistent till 350 mg, and thereafter decrease. It can be concluded that the larger amount of oil leads to the higher viscosity of sample and decreasing ERs of the analytes. Consequently, 250 mg was selected as the optimum amount of oil for the subsequent experiments.

3.2. Optimization of adsorbent amount

In this study, at first, the specified amount of cobalamin was added into the diluted oil (250 mg oil in 3 mL chloroform). The selected heavy metal ions can be extracted *via* possible interactions such as van der Waals, surface adsorption, and polar–polar

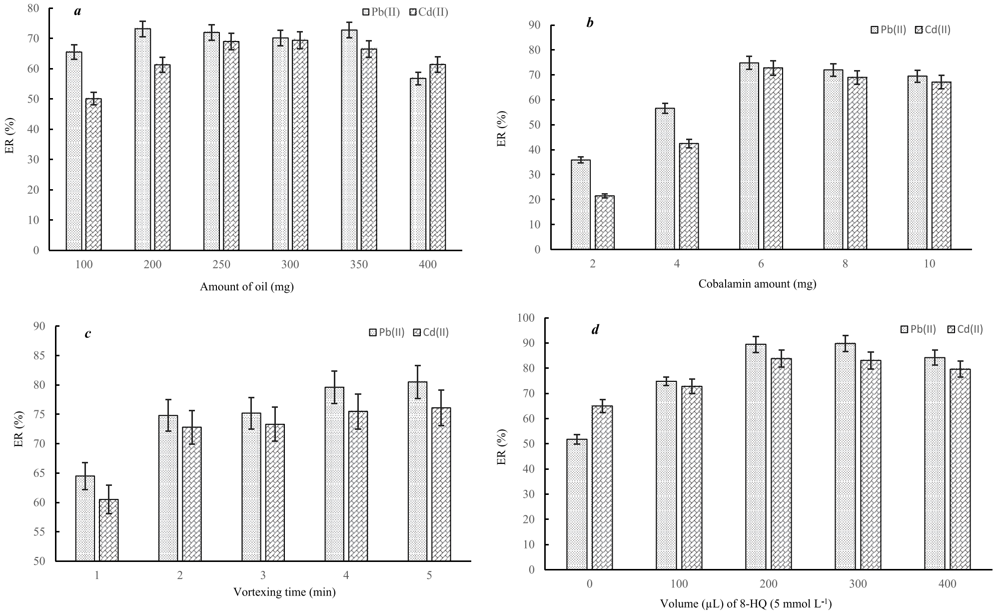

Figure 1. (a) Effect of amount of oil on the ERs of the analytes. Extraction conditions: sample, blank oil spiked with 10 μg kg^{-1} of each Cd(II) and Pb(II); chloroform volume, 3 mL; cobalamin amount, 8 mg, vortexing (extraction time), 2 min; 8-HQ (100 μL, 0.1 mol L^{-1}); and desorption solvent (volume), ACN (220 μL). The error bars represent standard deviations for three replicates ($n = 3$). (b) Effect of cobalamin amount on the ERs of the analytes. Extraction conditions: 250 mg of the analytes-free oil containing 10 μg kg^{-1} of each Cd(II) and Pb(II) ions was dissolved in 3 mL chloroform; and the other conditions were the same as those used in Figure 1(a). (c) Study the effect of vortexing time on the ERs of Cd(II) and Pb(II) ions. Extraction conditions: cobalamin, 6 mg; and the other conditions were the same as those used in Figure 1(b). (d) Study the effect of concentration of 8-HQ on the ERs of Cd(II) and Pb(II) ions. Extraction conditions: vortexing time, 4 min; and the other conditions were the same as those used in Figure1(c).

interactions. Therefore, the amount of the adsorbent is an important parameter that determines the adsorption capability of the method. To obtain maximum ERs for the analytes, various amounts of cobalamin ranging from 2 to 10 mg were utilised in the method. As illustrated in Figure 1(b), the ERs increase as the amount of cobalamin increase till 6 mg, remain approximately constant in the range of 6–8 mg and then decrease. Therefore, using 6 mg of cobalamin results in maximum ERs. Decreasing ERs at the amounts more than 6 mg is occurred because of the aggregation of the adsorbent particles. As a result, 6 mg cobalamin was used in the other optimisation steps.

3.3. Optimization of vortexing time

Optimization of extraction time is important since a suitable extraction method should have high ER along with short extraction time. In this work, agitation of solution with the aid of vortex plays an important role in dispersing the fine particles of cobalamin into solution. In this study, the impact of vortexing time was investigated within the range of 1–5 min, with the same rate of agitation. Based on the results in Figure 1(c), ERs are increased with time increasing the time till 4 min. The ERs for vortexing time of 5 min are comparable with those of vortexing time of 4 min. As a result, the vortexing time of 4 min is enough for extraction of the analytes, and it was used in the further experiments.

3.4. Effect of complexing agent concentration

The extraction process can be facilitated when the selected analytes are complexed with a suitable chelating agent, because the formed complexes are adsorbed onto the surface of adsorbent more than the heavy metal ions. 8-HQ, is one of the most popular, low toxic, antibacterial and versatile organic compound. In addition, it has been known as one of the most sensitive ligands used as a preconcentration agent in analytical chemistry [62]. To investigate this issue, 8-HQ was selected to induce complexation of Pb(II) and Cd(II) ions. So, 8-HQ should be added to the solution in sufficient concentration to quantitatively complex the metal ions in the medium. Therefore, optimisation of the concentration of 8-HQ is very important. The effect of the concentration of 8-HQ on the ERs of Pb(II) and Cd(II) ions was investigated by changing the volume of 8-HQ solution (5 mmol L^{-1}) from 0 to 400 µL. The results in Figure 1(d) indicate that ERs increase up to 200 µL and then decrease gradually. Based on this consideration 200 µL of 8-HQ solution (5 mmol L^{-1}) was selected as the sufficient volume to achieve high ERs of the selected ions, and it was used in the next experiments.

3.5. Study the nature and volume of desorption/dissolving solvent

Desorption of the analytes from the surface of cobalamin after the extraction is also an important process in the proposed DµSPE. Therefore, in the following, to achieve optimal extraction efficiency, it is necessary to desorb the adsorbed complexes from the surfaces of cobalamin particles totally. For this purpose, various solvents were investigated, including methanol, nitric acid 5% (*v/v*), and ACN, and the results are shown in Figure 2(a). Nitric acid 5% (*v/v*) was selected as the best solvent for this step. In the following, the different concentrations (1–10%, *v/v*) of nitric acid was investigated, and the amounts of the desorbed analytes were determined. According to the results shown in Figure 2(b), 5% (*v/v*) is the suitable concentration. The volume of nitric acid solution is another crucial factor that can impact the efficiency of the method. It is noticeable that to analysis the extracted amounts of the analytes by home-made injection system, at least 100 µL solution is needed for each cation. Therefore, to explore the effect of nitric acid solution volume, its volume was altered between 220 and 370 µL. The experiments indicated that the ERs remained approximately constant, but the analytical signals decreased by increasing the acid volume due to dilution effect. Therefore, 220 µL was selected as the optimum volume.

3.6. Effect of temperature

The effectiveness of the proposed method can be influenced by temperature as it can enhance mass transfer of the analytes and extraction rate by increasing the kinetic energy of molecules and changing the analyte diffusion coefficients. To investigate its impact on the ERs, different temperatures ranging from 25°C to 45°C were examined. The findings

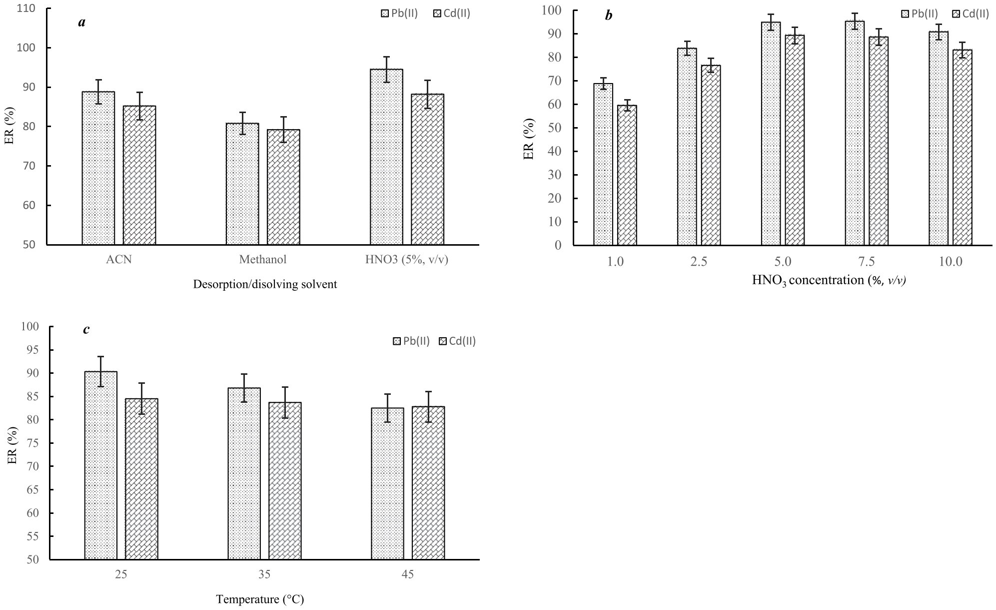

Figure 2. (a) Effect of desorption/dissolving solvent kind on the ERs of Cd(II) and Pb(II) ions. Extraction conditions: 8-HQ, 200 µL (5 mmol L^{-1}); and the other conditions were the same as those used in Figure 1(d). (b) Effect of concentration of nitric acid solution on the ERs of the analytes. Extraction conditions: are the same as those used in Figure 2(a), except 200 µL 8-HQ solution and 220 µL nitric acid solutions were used as the complexing agent and dissolving solvent volumes, respectively. (c) Effect of temperature on the ERs of the analytes. Extraction conditions: are the same as those used in Figure 2(b), except nitric acid solution (5%, v/v) was used as the dissolving solvent.

(Figure 2(c)) reveal that altering the temperature does not have a positive effect on the extraction efficiency. Thus, the optimum extraction temperature was determined to be 25°C (ambient temperature).

3.7. *Study of interferences*

In order to investigate possible coexistence of ions interfering effect in the extraction and detection of Pb(II) and Cd(II) ions in the studied samples, the working solution was supplemented with various concentrations of different cations and anions. The implemented method was done and any ion that caused a ±5% variation in the analytical signals of the analyte, it was considered as an interfering agent. Table 1 summarises the results, indicating that high concentrations of the chosen ions do not significantly affect the ERs of the analytes. As a result, this method can be considered as a selective analytical approach for detecting the studied cations.

3.8. *Adsorption capacity of sorbent*

To determine the adsorption capacity of the used sorbent for the selected heavy metal ions, 0.25 g analytes-free oil sample was spiked with 10 mg Kg^{-1} of each cation, and 3 mL

Table 1. Tolerance limits of interferent/analyte ratios of coexisting ions in determination of Pb(II) and Cd(II) ions using the proposed method.

	Tolerance limit of interferent/analyte ratio	
Species	Pb(II)	Cd(II)
Fe^{3+}	1500	1750
Pt^{2+}	1250	1500
Co^{2+}	500	500
Ni^{2+}	750	1000
Mg^{2+}	2000	1500
Cu^{2+}	750	750
Zn^{2+}	500	1000
Ca^{2+}	2000	2000
Al^{3+}	2500	2000
K^{+}	1250	1250
SO_4^{2-}	1750	2000
NO_3^{-}	2000	2000
Cl^{-}	300	1500

of chloroform and 2 mL of 5 mmol L^{-1} 8-HQ were added. A 6 mg cobalamin was added to the solution and shaken for 40 min and then centrifuged at a rate of 8000 rpm for 5 min. The obtained supernatant was diluted five folds, and concentrations of the analytes in the supernatant were determined. The calculated adsorption capacities ($n = 3$) were 124.8 ± 2.2 and 116.2 ± 1.8 mg g^{-1} for Pb(II) and Cd(II), respectively.

3.9. *Analytical performance of the method*

The developed method was assessed for its analytical performance, and the results are presented in Table 2. The process of constructing calibration graphs involved analysing analytes-free oil spiked with the analytes at 10 different concentration levels within the range of 0.5–200 µg kg^{-1}. The linearity of the graphs was maintained in the concentration ranges of 1–150 and 1.5–150 µg kg^{-1} for Pb(II) and Cd(II) ions, respectively. The LODs for Pb(II) and Cd(II) ions, calculated as 3 times of standard deviation of blank (S_B) divided into the slope of calibration graph (m), were 0.34 and 0.48 µg kg^{-1}, respectively. The limits of quantification (LOQs) were also obtained as 10 S_B/m, which were found to be 1.0 and 1.5 µg kg^{-1} for Pb(II) and Cd(II), respectively. The relative standard deviations were calculated and obtained in the range of 3.8–4.9% for intra- ($n = 6$) and inter-day ($n = 6$) precisions.

Table 2. Quantitative characteristics of the method for the studied heavy metal ions.

					RSD%[e]		
Analyte	LR[a] (µg Kg^{-1})	r^2[b]	LOD[c] (µg Kg^{-1})	LOQ[d] (µg Kg^{-1})	Intra-day ($n = 6$)	Inter-day ($n = 6$)	ER ± SD[f]
ZPb(II)	1–150	0.9931	0.34	1.0	3.8	4.5	94.8 ± 3.6
CCd(II)	1.5–150	0.9988	0.48	1.5	4.1	4.9	89.1 ± 3.7

[a] Linear range.
[b] Coefficient of determination.
[c] Limit of detection.
[d] Limit of quantification.
[e] Relative standard deviation at a concentration of 10 µg Kg^{-1} of each cation.
[f] Extraction recovery ± standard deviation ($n = 3$).

Table 3. Analysis of certified reference material (Enviro MAT HU-1 oil) for the determination of the Cd(II) and Pb(II) ions with the proposed method.

Analyte	Certified concentration (μg g^{-1}) ± SD[a] ($n = 3$)	Found concentration (μg g^{-1}) ± SD ($n = 3$)	t-value[b]
Cd(II)	15 ± 1	15.3 ± 0.7	0.52
Pb(II)	20 ± 1	18.8 ± 0.8	2.1

[a] Standard deviation.

[b] $t_{critical} = 4.30$ at a confidence level of 95%, $n = 3$.

These findings suggest that the proposed method is highly sensitive and repeatable and has low LODs and LOQs, which make it suitable for determining the selected cations in different oil samples. To test the accuracy of the proposed method, three repeated determinations were carried out on EnviroMAT HU-1 oil, a certified reference material. The results obtained (Table 3) are in a good agreement with the certified values for Cd(II) and Pb(II) ions, indicating that the proposed method is reliable. The findings were validated by t-test which displayed a good agreement between the confirmed and determined values.

3.10. Analysis of real samples

The applicability of the developed procedure was studied in determination of the studied ions in different oil samples including omega 3, fish oil, almond oil, hazelnut oil, olive oil, and two sunflower oils (I and II). The concentration of Pb(II) in fish oil, almond oil, olive oil, and sunflower oil II were found 4.1 ± 0.2, 21.2 ± 0.9, 3.1 ± 0.1 and 3.9 ± 0.2 μg Kg^{-1} ($n = 3$), respectively. The concentration of Cd(II) in fish oil, almond oil, hazelnut oil, olive oil, and sunflower oil II were found 7.8 ± 0.3, 28.1 ± 2.0, 11.7 ± 3.0, 12.5 ± 0.5 and 8.4 ± 0.3 μg Kg^{-1} ($n = 3$), respectively. Concentration of Pb(II) was lower than LOD of the method in omega 3, hazelnut oil, and sunflower oil (I). Also, the concentration of Cd(II) was lower than LOD of the method in omega 3.To assess the effect of matrix effect on the performance of the method, the selected samples were spiked at 10 and 50 μg Kg $^{-1}$ concentrations of each analyte. The results are presented in Table 4 along with their respective standard deviations. The results indicate that the suggested approach performance is not significantly influenced by the sample matrices. As it can be observed in Table 5, both Cd(II) and Pb(II) ions are successfully recovered from all samples at the range of 86.3–101.5%. Therefore, this method is deemed reliable for analysing these ions in various types of oil samples.

Table 4. Matrix effect study for the selected ions in different oil samples. Analyte contents of the samples were subtracted.

	Mean relative recovery ± standard deviation ($n = 3$)						
Analyte	Omega 3	Fish oil	Almond oil	Hazelnut oil	Olive oil	Sunflower oil (I)	Sunflower oil (II)
All samples were spiked with each analyte at a concentration of 10 μg Kg^{-1}							
Pb(II)	86.3 ± 3.6	92.0 ± 4.1	90.7 ± 3.7	94.7 ± 4.1	91.7 ± 3.9	101.5 ± 4.0	93.9 ± 3.8
Cd(II)	91.7 ± 4.0	93.1 ± 4.1	90.2 ± 3.7	90.7 ± 3.9	90.5 ± 3.7	94.5 ± 3.9	95.1 ± 3.8
All samples were spiked with each analyte at a concentration of 50 μg Kg^{-1}							
Pb(II)	89.7 ± 3.6	95.6 ± 3.9	91.6 ± 3.8	95.5 ± 4.0	91.8 ± 3.7	98.4 ± 3.7	94.7 ± 3.6
Cd(II)	93.5 ± 4.0	93.2 ± 3.9	92.3 ± 3.8	90.5 ± 3.8	94.2 ± 3.9	95.1 ± 3.8	94.4 ± 3.7

Table 5. Evaluation of greenness of the proposed method using AES.

DSPE-FAAS	
	PPs
Reagents	
Chloroform (3 mL)	2
8-HQ	1
Cobalamin	0
HNO_3 (5%, v/v), 220 µL	2
	∑ 5
Instruments	
FAAS	1
Vortex	1
Centrifuge	1
Waste	3
	∑ 6
Total PPs	11
AES score	89

3.11. The compatibility of the developed method with the principles of green chemistry

The evaluation of analytical methods in the context of green chemistry is difficult because of the diversity of analytes and analytical methods, the complexity of sample matrices, and the special analytical criteria that need to be studied like LOD and precision. Therefore, the presence of procedures and instruments to calculate and provide an answer to whether an analytical method can be regarded as green or not is necessary. Tools such as Analytical Eco-Scale (AES) [63], Green Analytical Procedure Index (GAPI) [64], and National Environmental Methods Index (NEMI) [65] are used to assess the greenness of analytical methods. In this study, AES tool, based on assigning penalty points (PPs) to parameters of the analytical protocol, was used for the estimation and assessment of the environmental impact or ‘greenness’ of the proposed method. The PPs concern the amounts of the used reagents, hazards related to the use of reagents and solvents, generated waste, and consumed energy. The sum of these PPs should be calculated and was subtracted from 100. According to AES guidelines, an ideal green method should have a score of 100. The values higher than 75 are considered the method as a green procedure. All of the involved

parameters in the proposed method listed in Table 5 and PPs were considered for each factor. Considering the score equal to 89, it can be concluded that the method presented in this study represents an excellent greenness and can be used for the routine analysis of the studied heavy metal ions with a minimal detrimental impact on human health and environment.

3.12. Comparison of the developed method with the published methods

A comparison of the proposed procedure for determination of Cd(II) and Pb(II) ions in oil samples with the other published methods for the mentioned ions from different samples is demonstrated in Table 6. In comparison with other methods, the LRs of the proposed method are wider. The repeatability of the proposed

Table 6. Comparison of the proposed method with the other methods used in preconcentration and determination of Cd(II) and Pb(II) ions.

Metal ions	Sample preparation method	Sample	LR[a] (μg Kg^{-1})	LOD[b] (μg Kg^{-1})	RSD[c] (%)	Detection system	Ref.
Cd(II)	Ultrasound-assisted emulsification	Edible oils	–	0.013	8	ICP-MS[d]	[66]
Cd(II)		Edible oils	–	0.3	0.6–1.6	FAAS[f]	[67]
Pb(II)	RP-UALLME[e]			1.5	1–1.6		
Cd(II)		Fish oil/current article	–	0.12	<3.6	ICP-OES[h]	[68]
Pb(II)	RP-DLLME[g]			0.58			
Cd(II)	Microwave Digestion	Vegan Milk and Oils	–	0.73	<3.6	ICP-OES	[69]
Pb(II)				17			
Cd(II)	SPE[i]	Water samples	100–5000	54	3.01	ICP-OES	
Cd(II)	RP-DLLME	Fish and olive oil samples	3.77–162	0.75		SQT[j]-FAAS	
Cd(II)	ultrasound-assisted emulsification	Edible oils		0.013	8	ICP-MS	
Pb(II)	DμSPE[k]	Oils	1–150	0.34	3.8	FAAS	This study
Cd(II)			1.5–150	0.48	4.1		

[a] Linear range.
[b] Limit of detection.
[c] Relative standard deviation.
[d] Inductively coupled plasma mass spectrometry.
[e] Reversed-phase ultrasonic assisted liquid-liquid microextraction.
[f] Flame atomic absorption spectrometry.
[g] Reversed-phase dispersive liquid-liquid microextraction.
[h] Inductively coupled plasma optical emission spectroscopy.
[i] Solid phase extraction.
[j] Slotted quartz tube.
[k] Dispersive micro-solid phase extraction.

method is good, and the RSDs are comparable with those of the reported methods. These results show that the presented procedure has several advantages over the other reported methods like being simple, sensitive, efficient, reliable, low cost, and less hazardous for the environment. The LODs of the developed procedure are comparable with those of the mentioned methods. It is noted that in some reported methods in Table 5, high sensitive instruments such as ICP-MS which is inherently more sensitive than FAAS were used. Hence, this method can be recommended for extracting and preconcentrating of the heavy metal ions in oil samples.

4. Conclusions

This study developed an extraction procedure based on cobalamin as a green adsorbent in the analysis of Cd(II) and Pb(II) ions in various oil samples by FAAS. The proposed D-μSPE method needs no desorption step, which requires vortexing or sonication and is time-consuming. Short extraction time, easy operation, inexpensiveness, and high extraction efficiency can be the outstanding advantages of the proposed procedure. Furthermore, after examining numerous oil samples and one certified reference material, it was found that the proposed method provided accurate and reliable outcomes.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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