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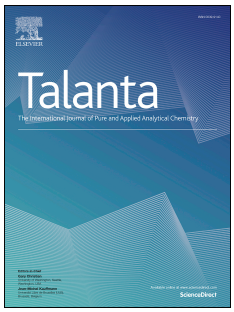


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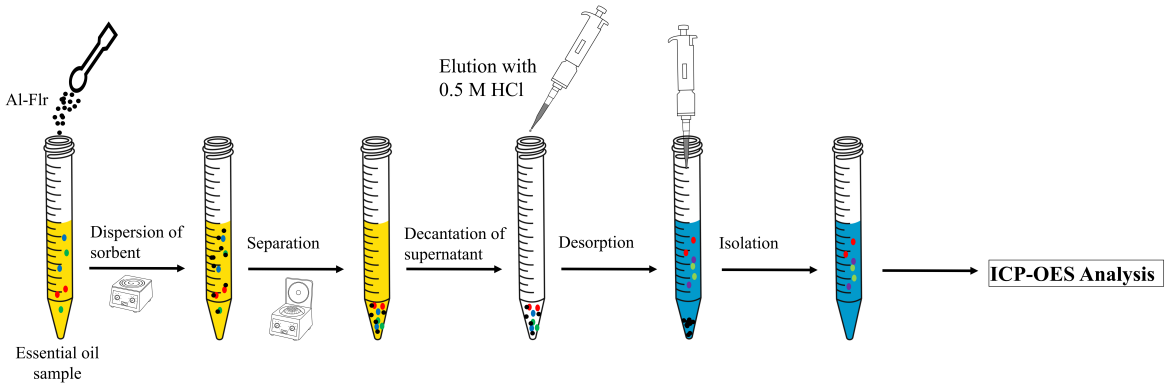

# A Novel Vortex Assisted Dispersive Solid Phase Extraction of Some Trace Elements in Essential Oils and Fish Oil

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## Abstract

In this paper, a novel vortex assisted solid phase extraction procedure combined with inductively coupled plasma optic emission spectrometry was presented for determination of Mn, Cu, Ni, Cr, Cd and Pb directly in oily matrix. The suggested separation and preconcentration method was based on simultaneous sorption of the target analytes from real essential oil matrix onto $\gamma$-$Al_2O_3$ functionalized with fluorescein (Al-Flr) and transfer to aqueous eluent prior to quantification. The effect of different parameters including sorption and elution time, sample volume, eluent type and concentration and interfering ions were investigated. The working conditions were given as follows, vortex agitation for sorption and elution 40 s, sample volume 20 mL, eluent type HCl, eluent concentration 0.3 mol $L^{-1}$. The detection limits were found to be 0.7 µg $L^{-1}$ for Mn, 4.1 µg $L^{-1}$ for Cu, 1.0 µg $L^{-1}$ for Ni, 1.6 µg $L^{-1}$ for Cr, 0.7 µg $L^{-1}$ Cd and 1.0 µg $L^{-1}$ Pb. The evaluation of the accuracy and precision of the method was tested via metallo-organic certified reference material. The recovery values have warranted the accuracy and found between 98.4 – 103.3% with 2.6 – 6.4% relative standard deviation (RSD, %). The sampling frequency of the procedure was calculated as 11.25 $h^{-1}$. Finally, the proposed analytical method was successfully applied on analyte spiked and unspiked apricot, black cumin, pine turpentine, thyme, mint essential oils and fish oil samples without any need of performing mineralization pretreatments.

***Keywords:*** essential oil, dispersive solid phase extraction, ICP OES, alumina, preconcentration

## 1. Introduction

Essential oils are defined as natural complex mixtures including unsaturated and saturated hydrocarbons, phenols, alcohols, aldehydes and terpenes. These oils are characterized by a strong odor and taste by the volatile molecules that have sufficiently high vapor pressure at room temperature and atmospheric pressure. Additionally, these characteristic properties of essential oil are directly related to aromatic plants from which it was derived. The essential oils are extensively utilized in the food, pharmacy and cosmetic industry as aromatizing agents. On the other hand, these fragrant agents have also been used in complementary and alternative therapy for centuries [1-5].

Despite their broad variety of bioactivities such as antimicrobial, antioxidant, antihistaminic, antienflamatuar, antifungal and anticancer [6, 7], the essential oils are quite sensitive to heat, moisture and oxygen. The mentioned parameters led to polymerization and oxidation reactions with the catalytic properties of elements in the oil matrix. Thus, the essential oils lost quality, freshness and uniqueness [8-10]. Considering the wide range of anthropogenic applications in several industries and health, the presence of organic and inorganic contaminants of essential oils should be monitored with high accuracy and precision.

Trace element quantification has frequently been a problematic challenge in oil samples because of hydrophobic matrix [11-13]. The small amounts of analytes and complex organic matrix renders the sample preparation step critical for the analysis. In literature, there are various sample preparation procedures based on wet/dry ashing [14, 15], acid extraction [16], transfer of the analyte by a chelating agent to aqueous phase [13] and microextraction by deep eutectic solvents [17, 18] for oil matrix. These well-established matrix eliminating procedures may be seen quite effective, but excessive use of hazardous reagents, the possibility of analyte loss or contamination and explosion risks restrict the applications. On the other hand, the procedures that allow direct aspiration of the diluted or emulsified oil sample have been reported [19]. In most cases, these optional procedures cause problems in excitation powers and led to difficulties in calibration.

Solid phase extraction (SPE) is frequently used for the separation and preconcentration of inorganic and organic species. The simplicity, drastically reduction in the use of organic reagents, the opportunity of on-line or off-line link up with analytical techniques, shortening the analysis time, versatility in sorbent selection/modification and achievability of high enrichment factor make the procedure popular and attractive [20, 21]. Moreover, dispersive solid phase extraction (d-SPE) that was firstly proposed by Anastassiades et al. [22], appreciates the application by adding more superior features. d-SPE is based on the addition of sorbent material into an aliquot to isolate the target analyte(s), dispersion by external energy such as vortex, magnetic stirring or ultrasound and then separation for elution. In this case, d-SPE increases the contact area between the sample and sorbent and improves the extraction kinetics. On the other hand, it prohibits blockage of flow in the cartridge, pipette tip or disc applications [23, 24].

Our survey of the literature showed that there is no solid phase extraction based sample preparation method for elemental analysis of essential oils. Consideringly, it is aimed to

elaborate a simple, accurate, precise and reliable vortex assisted d-SPE based sample preparation method for Mn, Cu, Ni, Cr, Cd and Pb prior to ICP OES detection. In this scope, γ-alumina was employed as solid support and modified using fluorescein. The newly synthesized and the characterized sorbent (Al-Flr) was used for simultaneous separation and preconcentration of target analytes from hydrophobic essential oil matrix. The parameters including oil sample-sorbent contact time, sample volume, eluent type, concentration and eluent-sorbent contact time were tested for effective sorption and elution cycle. Finally, the optimized methodology was applied on analyte spiked and unspiked apricot, black cumin, pine turpentine, thyme, mint essential oils and fish oil.

## 2. Materials and Methods

### *2.1.Instrumentation*

Determination of the target analytes was achieved by Perkin Elmer 7300 DV axial inductively coupled plasma-optical emission spectrometer (Waltham, MA, USA) equipped with standard quartz torch, cyclonic spray chamber, concentric nebulizer and Perkin Elmer S10 auto sampler (Waltham, MA, USA). The optical system was purged with Ar and analytical lines were 257.610 nm for Mn, 327.393 nm for Cu, 231.604 nm for Ni, 267.716 nm for Cr, 228.802 nm for Cd and 220.353 nm for Pb. Additionally, the operation parameters were set as recommended by the manufacturer. The modification period of the sorbent was monitored PG Instrument T80+ UV–Vis spectrometer (Leicestershire, UK) at 490 nm. Jeol Neoscpoe JCM-5000 benchtop scanning electron microscope (SEM) (Peabody, MA, USA) and PerkinElmer Spectrum 65 Fourier transform infrared attenuated total reflectance (FTIR-ATR) (Waltham, MA, USA) were employed for imaging and record of spectra to characterize the sorbent, respectively. An XH-C vortex (Wincom, Shanghai, China) was utilized for dispersion of the sorbent. Additionally, a Sartorius TE214S electronic balance (Bradford, MA, USA), Biosan ES-20 orbital shaker (Riga, Latvia), Elektro-mag M815 P centrifuge (Istanbul, Turkey) and Carbolite muffle furnace (Hope Valley, UK) were used for the experiments. CEM Mars 5 microwave digestion system (Matthews, NC, USA) was utilized to mineralize the essential oil samples during conventional analysis.

### *2.2.Reagents and Samples*

All reagents were of analytical grade and used without further purification. Purification of water was achieved using a reverse osmosis system. The laboratory ware used was kept in 10% (v/v) nitric acid, rinsed with purified water and dried in a dust-free environment.

Fluorescein, γ-$Al_2O_3$ and n-hexane were purchased from Merck (Darmstadt, Germany). A 25 mL portion of fluorescein solution at 1.0 mg $mL^{-1}$ concentration was prepared in methanol for modification of γ-$Al_2O_3$. Conostan S-21 metallo-organic multi element standard (900 mg $kg^{-1}$, SCP Science, Quebec, Canada) was used to prepare working solutions of Mn, Cu, Ni, Cr, Cd and Pb by proper dilution in n-hexane and to spike the real essential oil samples for testing the suggested procedure. Additionally, individual Conostan metallo-organic standards of Fe, Zn, Mg and Ca (1,000 mg $kg^{-1}$, SCP Science, Quebec, Canada) were employed for interference studies. An aqueous multi element standard solution of Merck (1,000 mg of each element per liter, Darmstadt, Germany) was employed to establish calibration curves for target analytes.

Apricot, black cumin, pine turpentine, thyme, mint essential oil and fish oil samples were commercially available in Balikesir, Turkey and stored at +4 °C until analysis. In the real matrix analysis, 4.0 g of essential oil sample was weighed in a volumetric flask and diluted to 10.0 mL with n-hexane to reduce the viscosity. The dilution of the samples was realized just before analyses.

*2.3.Modification of γ-alumina*

A 10 g portion of γ-alumina was suspended in 25 mL of 0.5 mol $L^{-1}$ $HNO_3$ solution to remove impurities for 1 h. Afterward, the mixture was filtered and γ-alumina was sequentially washed with pure water until neutralized. The neutralized γ-alumina and fluorescein solution were taken in a flask and agitated for 1 h at room temperature. Lastly, the sorbent (Al-Flr) was filtered off, washed to remove unsorbed fluorescein and dried at room temperature till constant weight.

The least time needed for modification of alumina was determined spectrophotometrically. In this scope, 1 mL of fluorescein solution was pipetted from the liquid phase and absorbance measurement was achieved at 490 nm. The absorbance monitoring was carried out hourly for 5 h.

The determination of surface coverage of Al-Flr was achieved by the thermal desorption method [25]. Accordingly, accurately weighed 500.0 mg Al-Flr was transferred to muffle furnace and combusted at 550 °C for 5 h. After that, the residue was allowed to cool inside the furnace till 100 °C and transferred to desiccator. The difference in sorbent mass before and after combustion was used to determine the chelating fluorescein amount. The ignition was applied on Al-Flr in triplicate. Additionally, bare alumina was treated similarly as blank sample.

*2.4.Effect of Parameters on Sorption and Elution*

The parameters effective on sorption and elution of the target analytes including extraction time, sample volume, eluent type, eluent concentration and elution time were optimized according to the one factor at a time (OFAT) procedure. In optimization experiments, the Al-Flr amount was 500.0 mg and dispersion was carried out at 3000 rpm. The standard solutions of the target analytes were prepared in n-hexane at 30.0 µg $L^{-1}$ concentration by dilution of Conostan metallo-organic multi element standard. The experiments of each variable were assayed in triplicate. The analysis of aqueous eluents was realized by ICP OES. Optimal conditions of each variable were defined as those at which the maximum recovery for the target analytes was obtained.

*2.5.Dispersive Solid Phase Extraction Procedure for Essential Oils*

Simultaneous separation and preconcentration of Mn, Cu, Ni, Cr, Cd and Pb were achieved with *d*-SPE in essential oil matrix at room temperature. Accordingly, a 10 mL portion of essential oil solution was placed in a 50 mL conical tube containing 500.0 mg of Al-Flr. The mixture was subjected to dispersion by vortex agitation at 3000 rpm for 40 s for sorption of the target analytes. After vortexing, the mixture was centrifuged at 5000 rpm for 2 min and the supernatant was removed by decantation. The sorbent was washed with n-hexane to

remove any oil residue. Then, 5 mL of 0.3 mol $L^{-1}$ HCl solution was added on air-dried Al-Flr for desorption of the analytes. The sorbent was dispersed in eluent for 40 s by vortexing at 3000 rpm. Finally, the phase separation was accelerated by centrifuging the mixture at 5000 rpm for 2 min, the sorbent was collected at the bottom of the tube and the aqueous phase was pipetted for ICP OES analyses. The blank solutions were subjected to the same separation procedure as samples and each sample was analyzed in triplicate.

*2.6.Comparative Study*

The investigated oil samples were subjected to microwave-assisted acid digestion procedure prior to ICP OES detection of the target analytes as a comparative method. The digestion pretreatment was based on a procedure from the previous literature [26]. Accordingly, 0.2 g of essential oil was weighed in a digestion tube, 5 mL of concentrated $HNO_3$ was added and capped according to manufacturer recommendation. The microwave unit heating was performed with three stage temperature and pressure controlled program at 1200 W as follow: (i) ramp of 10 min to reach 130 °C with maximum 140 psi pressure and held for 10 min, (ii) ramp of 10 min to reach 150 °C with maximum 200 psi pressure, held for 10 min and ventilation for 10 min, (iii) ramp of 20 min to reach 160 °C with maximum 200 psi pressure and held for 20 min. After digestion, the samples were vented for 15 min and diluted to 10 mL in volumetric flasks with purified water. The digestion procedure was carried out in triplicate for each sample and the reagent blanks were prepared in each lot of samples. Analysis of the digests was achieved using ICP OES..

## 3. Results and Discussion

*3.1.Characterization of Al-Flr*

SEM and FT-IR analysis were employed in the characterization process to identify morphological differences and the functional groups on bare and the fluorescein modified γ-alumina particles.

Fig. 1 illustrates the SEM images of bare (a) and fluorescein modified (b) γ-alumina. It can be easily seen that wrinkling formation was seen on modified γ-alumina image. This proved increasing in porosity and surface area of solid support by coverage with functional groups.

The FT-IR spectra of γ-alumina before and after modification were given in Fig. 2a. The broad absorption band at 3430 $cm^{-1}$ in both spectrums can be attributed to the stretching of Al-O group. The newly appeared peaks 2917 and 2850 $cm^{-1}$ on Al-Flr spectrum emphasize the modification. The bands could be assigned to C-H vibrations. Additionally, the frequencies at 1700 $cm^{-1}$ and 1624 $cm^{-1}$ correspond to the C=O stretching of carboxylic acid and the aromatic C=C stretching in fluorescein structure, respectively. Moreover, decrease in the intensity of peaks proved the modification of γ-alumina with fluorescein.

The amount of fluorescein loaded on γ-alumina was determined according to the thermal desorption method. The fluorescein mass that covered the γ-alumina was found to be 31.8±2.6 mg $g^{-1}$ Al-Flr. The surface coverage value was also expressed in mole as 0.10±0.01 mmol $g^{-1}$. Obviously, the results confirmed the modification of γ-alumina with fluorescein.

*3.2.Modification Period*

The period needed for modification of sorbent is an important parameter for separation and preconcentration studies. A short preparation/synthesis process provides advantages to SPE procedure. Consideringly, decrease in absorbance value of fluorescein solution was monitored during modification over periods ranging from 30 min and 5h. The absorbance values versus time data were plotted in Fig. 2b. The obtained values clearly showed that 30 min modification period was sufficient for the preparation of Al-Flr particles.

*3.3.Optimization of Separation and Preconcentration Conditions*

The analytical parameters including extraction time, the type and concentration of eluent, sample volume and matrix effect was tested to find the best conditions for quantitative separation and preconcentration of Mn, Cu, Ni, Cr, Cd and Pb from the oily phase. All the experiments were assayed in triplicate. The percent recoveries were calculated by the following equation:

$$\text{Recovery, \%} = \frac{w_f}{w_i} x100$$

where $w_f$ is the amount of each analyte (ng) in the final solution and $w_i$ is the amount of each analyte (ng) in the initial solution.

*3.3.1. Effect of Extraction Time*

Extraction time is a significant factor affecting the extraction efficiency and speed of analysis. In order to have quantitative extraction with satisfactory precision, the effect of vortex time on dispersing the sorbent into the oil sample was investigated. The parameter was performed with 5.0 mL oily solutions including 150.0 ng of Mn, Cu, Ni, Cr, Cd and Pb in triplicate. The contact times of 10, 20, 30, 40 and 50 s were examined for sorption of the target analytes, while all parameters kept constant and the recovery results were depicted in Fig. 3a. The obtained outcomes showed that quantitative sorption for Mn, Cu and Cd were achieved in only 10 s. On the other hand, the quantitative sorption was attained in 30 s for Ni and Pb and 40 s for Cr. The relatively short extraction periods indicate that the passage of the target analytes from the oily phase to Al-Flr has rapid kinetics of equilibrium. Additionally, this also indicates that Al-Flr sorbent is highly suitable for the separation of the target analytes from the oily phase. Considering the findings, 40 s vortexing time was selected for simultaneous separation and preconcentration of the target analytes in next experiments.

*3.3.2. Choice of type and concentration of the eluent*

The eluent solution plays an important role in the effective desorption of the retained analytes. In order to achieve simultaneous desorption of the target analytes, 5 mL solutions of $HNO_3$, HCl and $CH_3COOH$ at 0.5 mol $L^{-1}$ concentration; EDTA solution at pH 8 and 0.1 mol $L^{-1}$ concentration and 1.0 % thiourea solution in 0.5 mol $L^{-1}$ HCl was tested on 150 ng of each analyte loaded Al-Flr. As the recovery results were summarized for each analyte in Fig. 3b, the acceptable recoveries were obtained with HCl solution.

Then, the effect of HCl concentration was also explored between 0.1 and 0.5 mol $L^{-1}$ on desorption of the analytes and the recoveries depicted in Fig. 3c. The results evidenced that

5.0 mL of 0.3 mol $L^{-1}$ HCl solution would be sufficient for desorption of the analytes simultaneously and used in all further studies.

### *3.3.3. Effect of Elution Time*

In the current study, the vortex agitator was employed to disperse of Al-Flr in eluent solution as in sorption. Similarly, the effect of elution time was tested with 5.0 mL of 0.3 mol $L^{-1}$ HCl solution on 150 ng analyte loaded Al-Flr ranged from 10 to 50 s with 10 s intervals. The plot of recoveries versus time in Fig. 3d shows that stripping of the analytes was achieved quantitatively in 40 s, simultaneously.

### *3.3.4. Effect of Sample Volume*

The sample volume has an important role in the separation of analytes from the essential oil matrix by dispersive solid phase extraction as it also affects the preconcentration factor. In this purpose, to find out the possibility of separation and preconcentration of the target analytes from large volumes of oily samples by the suggested procedure, sample solutions including 150 ng of analytes with volumes ranged from 5.0 to 50.0 mL was tested at selected conditions. It was found that the recoveries were 101.0±3.9 for Ni, 101.9±2.2 for Cr, 101.5±5.1 for Cd and 101.2±1.3 for Pb up to 20.0 mL and 102.0±6.3 for Cu up to 30.0 mL sample volume as depicted in Fig. 3e. The recoveries were decreased swiftly with increasing sample volume for each analyte. Considering, the maximum applicable volume for simultaneous operation as 20.0 mL and eluent volume as 5.0 mL, the preconcentration factor was achieved as 4 by this method. However, a 10 mL portion of oil solution was used for the analysis in further experiments for convenience.

### *3.4.Matrix Effect*

Separation and preconcentration procedures may be significantly affected by the composition of the sample matrix. The interfering species may compete with the analyte in the process of sorption and as a conclusion avoiding the resin to form chelates with target analytes. In order to explore the selectivity of the method, the effect of Fe, Zn, Mg and Ca on separation and preconcentration of the target analytes from oily samples were tested. Hence, the known concentration of each metallo organic interferant was added individually on the hydrophobic model solution containing fixed 150 ng of studied analytes and the solution was subjected to the suggested d-SPE procedure under optimal conditions. Error of ±10 % in the recovery of the target analytes was considered tolerable. The tolerance limits for coexisting species were given in Table 1. As can be seen, large amounts of Fe, Zn, Mg and Ca have no significant effect on the separation and preconcentration of Mn, Cu, Ni, Cr, Cd and Pb from essential oil samples. The proposed vortex-assisted d-SPE protocol showed high selectivity for the interference-free separation and preconcentration of the target analytes in the oil samples.

### *3.5.Performance Characteristics*

Limit of detection (LOD) was calculated by the ratio of three standard deviations of 7 independent runs measurements of blank solutions to the slope of the calibration curve for each target analytes ($3s_b/m$). LODs were found to be 0.7; 4.1; 1.0; 1.6; 0.7 and 1.0 µg $L^{-1}$ for Mn, Cu, Ni, Cr, Cd and Pb, respectively. The calibration curves were constructed externally

and were linear in the range of 10.0-50.0 µg $L^{-1}$ with coefficient of determination ($r^2$) >0.995 for all analytes. To establish accuracy and precision, metallo-organic multi-element standard fortified model solutions were analyzed according to optimized conditions. The results were given in Table 2. It is clearly seen that the found values of the analytes presented good concordance with added amounts and recoveries were between 98.4 – 103.3%. Additionally, the precision was expressed as the percent relative standard deviation (RSD, %) and the values were between 2.6 – 6.4%. Thus, the obtained sufficient accuracy and precision values evidenced that the developed method can effectively separate and preconcentrate the target analytes in essential oil samples. Moreover, the student-t test showed that there is no significant difference between added and found amounts at 95% confidence level.

In view of single sample analysis in each cycle, the overall time required for simultaneous separation and preconcentration of Mn, Cu, Ni, Cr, Cd and Pb in 10 mL oily solution; (i) 40 s vortexing with sample and 2 min centrifuge in sorption step, (ii) 40 s vortexing with eluent and 2 min centrifuge in elution step, resulted in a sampling frequency of 11.25 $h^{-1}$.

*3.6.Applications*

The suggested procedure was implemented on various essential oils including apricot, black cumin, pine turpentine, thyme and mint oil samples for simultaneous separation and preconcentration of Mn, Cu, Ni, Cr, Cd and Pb. Additionally, a fish oil sample was also analyzed according to the given scheme. Analyses were carried out on analyte spiked and unspiked oil samples and the results were given in Table 3. The suitability, applicability and reliability of the method were evaluated via results of samples spiked with known amount of target analytes. The recovery percentages of the method were in the range of 90.2-104.3% for Mn, 91.5-105.7% for Cu, 93.6-104.2% for Ni, 96.1-101.7% for Cr, 95.5-105.6% for Cd and 94.7-109.9% for Pb. On the other hand, spiked analyte amounts (µ) were compared to experimental values ($\bar{x}$) using the Students t-test whether or not there is a significant difference. One sample t test was employed for each analyte and oil sample, individually. The results showed that experimental t values ($|\mu - \bar{x}|$) were less than theoretical ones ($\frac{ts}{\sqrt{N}}$). As it emerged, the obtained data proved that there is no evidence of systematic error in the suggested methodology at 95% confidence level. Consequently, it can be concluded that the proposed method is capable of simultaneous separation and preconcentration of Mn, Cu, Ni, Cr, Cd and Pb in troublesome essential oil samples.

The concentration of Ni in oil samples was found to be lower than its corresponding limits of detection value except for apricot oil which was found to be 1.2±0.1 µg $kg^{-1}$. Similarly, Pb content of the oil samples was also below the detection limit except for pine turpentine oil (3.9±0.2 µg $kg^{-1}$). The minimum and maximum concentrations of Mn were found as 2.1±0.3 µg $kg^{-1}$ in fish oil and 43.8±1.7 µg $kg^{-1}$ in black cumin oils, respectively. The analytes Cu and Cr were quantified in all samples in the range 15.1(±1.2) – 43.0(±0.6) µg $kg^{-1}$ and 4.7(±0.4) – 15.6(±0.4) µg $kg^{-1}$, respectively. Mint oil had the highest concentration of Cd as 19.9±1.9 µg $kg^{-1}$; while those of other oils ranged from 3.7(±0.3) to 16.2(±0.5) µg $kg^{-1}$. The differences in detected levels of Mn, Cu, Ni, Cr, Cd and Pb in the analyzed oil samples may be attributed to the natural background of the analytes in sources or manufacturing processes.

*3.7.Comparison of the d-SPE procedure*

To confirm the reliability of the suggested procedure, a conventional method based on mineralization of the oil matrix was utilized for sample analysis. The results obtained from the suggested and conventional procedures were given in Table 4. As can be seen, the obtained data were in good agreement for each procedure. Additionally, the experimental *t* values were calculated between 0.69-2.74 for Mn, 0.26-1.81 for Cu, 0.31-1.68 for Cr and 0.54-2.74 for Cd where the critical *t* value is 2.78 at 95% confidence level. Consequently, the Students *t*-test proved the absence of significant differences at certain confidence level. On the other hand, in terms of sensitivity, the analytes including Ni and Pb could not be determined after microwave-assisted digestion in the samples. This strongly depends on the dilution effect in the mineralization step. Hence, the results obtained with the proposed procedure evidentially demonstrated that this methodology overrides the conventional method without matrix decomposition.

Moreover, the performance of the vortex assisted d-SPE procedure was compared with limited available separation and/or preconcentration reports for oily matrix and the data were given in Table 5. As can be seen that the suggested procedure is the single separation and preconcentration method for essential oil samples and possesses the fastest equilibrium time in parallel with the highest sample frequency except the result reported in the literature [27], which was only elaborated for Cu and has the minimum initial oil amount ratio to final solution volume. Deep eutectic solvent used liquid phase microextraction [28] and dispersive liquid-liquid microextraction [29] procedures present the highest initial oil amount (g) ratio to final solution volume (mL) as 140, approximately. Unfortunately, both of the procedures offer the quantification of only Pb and Cd, individually by ETAAS. The limits of detection and precision obtained using the dispersive solid phase extraction procedure were better than or comparable with those reports [15, 27-33]. Considering the solid phase extraction related reports [32-33], the proposed method shows a greener profile and allows stripping off the target analytes with an environmentally friendly eluent solution. Additionally, the amount of Al-Flr used in this study is lower than the sorbent amount used in the report [32] due to the large surface area of γ-alumina. Furthermore, a couple of analytes were determined in all of the compared reports [15, 27-33]. However, it is worth noting that the suggested methodology can separate, preconcentrate and quantify Mn, Cu, Ni, Cr, Cd and Pb, simultaneously.

The mentioned characteristics are key of interest for routine quality control analysis. In the light of comparison, this separation and preconcentration method may be applied easily, swiftly and successfully for pretreatment of essential oil matrix for reliable results.

## 4. Conclusion

The present work demonstrates the effectiveness of newly synthesized and characterized fluorescein modified γ-alumina sorbent for simultaneous separation and preconcentration of Mn, Cu, Ni, Cr, Cd and Pb from essential oils prior to ICP OES detection. Sorption and elution of the target analytes were found to be rapid and the suggested procedure has been the most promising solid phase extraction methodology for oily matrix reported till date without decomposition, emulsification or dilution. Another advantage of the procedure is that metallo

organic standards were not required to construct calibration graphs. Additionally, drastic or time-consuming standard addition or internal standard calibrations were also not needed for quantification.

No interference of Fe, Zn, Ca and Mg were observed at least 100-fold of the target analytes during separation and preconcentration. Moreover, the natural compositions of these oils did not have any interfering effect.

Reusability of the sorbent is an important criterion in solid phase extraction studies. Nevertheless, considering the polarity differences in the sample (hydrophobic) and eluent (hydrophilic) solutions which cause a long time requirement for reuse of sorbent, this parameter was not studied. On the other hand, γ-alumina can be modified with fluorescein repeatedly after a basic clean-up procedure. Additionally, elimination of the high organic matrix with only 500 mg of sorbent, makes the developed method quite cheap and accessible.

The improved simple sample preparation strategy for essential oil matrix was found to be accessible, cheap, and useful for eliminating high organic matrix in addition to providing an accurate and precise method with good sensitivity. The practical applicability of the proposed method was tested successfully on various essential oil and fish oil samples for the determination of target analytes and the obtained results were satisfactory enough.

**Author contributions**

Feyzullah TOKAY: Methodology, validation, writing the draft. Refiye GÜNAYDIN: Methodology, validation. Sema BAĞDAT: Methodology, validation, writing the draft, editing.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**References**

[1] J. Richter, I. Schellenberg, Comparison of different extraction methods for the determination of essential oils and related compounds from aromatic plants and optimization of solid-phase microextraction/gas chromatography, Analytical and Bioanalytical Chemistry 387 (2007) 2207-2217. https://doi:10.1007/s00216-006-1045-6

[2] M. Moghaddam, L. Mehdizadeh, Chemistry of Essential Oils and Factors Influencing Their Constituents, Soft Chemistry and Food Fermentation, in: A. M. Grumezescu, A. M. Holban (Eds.), Soft Chemistry and Food Fermentation, Academic Press, London, 2017, pp. 379-419.

[3] B. Ali, N. A. Al-Wabel, S. Shams, A. Ahamad, S. A. Khan, F. Anwar, Essential oils used in aromatherapy: A systemic review, Asian Pasific Journal of Tropical Biomedicine 5 (2015) 601-611. https://doi:10.1016/j.apjtb.2015.05.007

[4] M. M. Won, E. J. Cha, O. K. Yoon, N. S. Kim, K. Kim, D. S. Lee, Use of headspace mulberry paper bag micro solid phase extraction for characterization of volatile aromas of essential oils from Bulgarian rose and Provence lavender, Analytica Chimica Acta 631 (2009) 54-61. https://doi:10.1016/j.aca.2008.10.013

[5] N. F. S. Morsy, Chemical Structure, Quality Indices and Bioactivity of Essential Oil Constituents, in: H. El-Shemy (Eds.), Active Ingredients from Aromatic and Medicinal Plants, InTechOpen, London, 2017, pp. 175-206.

[6] W. Dhifi, S. Bellili, S. Jazi, N. Bahloul, W. Mnif, Essential Oils' Chemical Characterization and Investigation of Some Biological Activities: A Critical Review, Medicines 3 (2016). https://doi:10.3390/medicines3040025

[7] E. C. Luna, I. S. Luna, L. Scotti, A. F. M. Monteiro, M. T. Scotti, R. O. de Moura, R. S. A. de Araujo, K. L. C. Monteiro, T. M. de Aquino, F. F. Ribeiro, F. J. B. M. Junior, Active Essential Oils and Their Components in Use against Neglected Diseases and Arboviruses, Oxidative Medicine and Cellular Longevity (2019) 1-52. https://doi:10.1155/2019/6587150

[8] S. R. Bozhanov, I. B. Karadjova, Determination of Trace Metals in Bulgarian Lavender Oil by Electrothermal Atomic Absorption Spectrometry, Journal of Essential Oil Research 20 (2008) 549-555. https://doi:10.1080/10412905.2008.9700086

[9] S.Bozhanov, I. Karadjova, S. Alexandrov, Determination of trace elements in the Lavender inflorescence(Lavandula angustifolia Mill.)-Lavender oil system, Microchemical Journal 86 (2007) 119-123. https://doi:10.1016/j.microc.2007.01.001

[10] M. Zeiner, I. J. Cindric, W. Kandler, G. Stingeder, Trace determination of skin-irritating metals in tea tree oil by GFAAS, Microchemical Journal 136 (2018) 101-105. https://doi:10.1016/j.microc.2016.12.016

[11] L. L. Pera, M. Saitta, G. D. Bella, G. Dugo, Simultaneous Determination of Cd(II), Cu(II), Pb(II), and Zn(II) in Citrus Essential Oils by Derivative Potentiometric Stripping Analysis, Journal of Agricultural and Food Chemistry 51 (2003) 1125-1129. https://doi:10.1021/jf020804t

[12] I. Juranovic, P. Breinhoelder, I. Steffan, Determination of trace elements in pumpkin seed oils and pumpkin seeds by ICP-AES, Journal of Analytical Atomic Spectrometry 18 (2003) 54-58. https://doi:10.1039/b209308c

[13] F. Tokay, S. Bağdat, Extraction of nickel from edible oils with a complexing agent prior to determination by FAAS, Food Chemistry 197 (2016) 445-449. https://doi:10.1016/j.foodchem.2015.11.001

[14] I. B. Karadjova, L. Lampugnani, D. L. Tsalev, Electrothermal atomic absorption spectrometric determination of arsenic in essential lavender and rose oils, Talanta 65 (2005) 1015-1021. https://doi:10.1016/j.talanta.2004.08.035

[15] D. Mendil, Ö. D. Uluözlü, M. Tüzen, M. Soylak, Investigation of the levels of some element in edible oil samples produced in Turkey by atomic absorption spectrometry, Journal of Hazardous Materials 165 (2009) 724-728. https:// doi:10.1016/j.jhazmat.2008.10.046

[16] J. S. Almeida, T. A. Anunciaçao, G. C. Brandao, A. F. Dantas, V. A. Lemos, L. S. G. Teixeira, Ultrasound-assisted single-drop microextraction for the determination of cadmium in vegetable oils using high-resolution

continuum source electrothermal atomic absorption spectrometry, Spectrochimica Acta Part B 107 (2015) 159-163. https://doi:10.1016/j.sab.2015.03.002

[17] P. Menghwar, E. Yılmaz, S. T. H. Sherazi, M. Soylak, A sensitive and selective deep eutectic solvent-based ultrasound-assisted liquid phase microextraction procedure for separation-preconcentration and determination of copper in olive oil and water samples, Separation Science and Technology 54 (2019) 2431-2439. https://doi: 10.1080/01496395.2018.1547317

[18] M. Soylak, M. Koksal, Deep eutectic solvent microextraction of lead(II), cobalt(II), nickel(II) and manganese(II) ions for the separation and preconcentration in some oil samples from Turkey prior to their microsampling flame atomic absorption spectrometric determination, Microchemical Journal 147 (2019) 832-837. https://doi.org/ 10.1016/j.microc.2019.04.006

[19] L. S. Nunes, J. T. P. Barbosa, A. P. Fernandes, V. A. Lemos, W. N. L. dos Santos, M. G. A. Korn, L. S. G. Teixeira, Multi-element determination of Cu, Fe, Ni and Zn content in vegetable oils samples by high-resolution continuum source atomic absorption spectrometry and microemulsion sample preparation, Food Chemistry 127 (2011) 780-783. https://doi:10.1016/j.foodchem.2010.12.147

[20] A. Spietelun, L. Marcinkowski, M. de la Guardia, J. Namiesnik, Recent developments and future trends in solid phase microextraction techniques towards green analytical chemistry, Journal of Chromatography A 1321 (2013) 1-13. https://doi:10.1016/j.chroma.2013.10.030

[21] M. Ghaedi, A. Shokrollahi, A. H. Kianfar, A. Pourfarokhi, N. Khanjari, A. S. Mirsadeghi, M. Soylak, Preconcentration and separation of trace amount of heavy metal ions on bis(2-hydroxy acetophenone)ethylendiimine loaded on activated carbon, Journal of Hazardous Materials 162 (2009) 1408-1414. https://doi:10.1016/j.jhazmat.2008.06.057

[22] M. Anastassiades, S. J. Lehotay, D. Stajnbaher, F. J. Schenck, Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce, Journal of AOAC International 86 (2003) 412-431. https://doi:10.1093/jaoac/86.2.412

[23] A. R. Fontana, A. Camargo, L. D. Martinez, J. C. Altamirano, Dispersive solid-phase extraction as a simplified clean-up technique for biological sample extracts. Determination of polybrominated diphenyl ethers by gas chromatography-tandem mass spectrometry, Journal of Chromatography A 1218 (2011) 2490-2496. https://doi:10.1016/j.chroma.2011.02.058

[24] B. Feist, Selective dispersive micro solid-phase extraction using oxidized multiwalled carbon nanotubes modified with 1,10-phenanthroline for preconcentration of lead ions, Food Chemistry 209 (2016) 37-42. https://doi:10.1016/j.foodchem.2016.04.015

[25] M. E. Mahmoud, M. M. Osman, O. F. Hafez, A. H. Hagezi, E. Elmelegy, Removal and preconcentration of lead (II) and other heavy metals from water by alumina adsorbents developed by surface-adsorbed-dithizone, Desalination 251 (2010) 123-130. https://doi:10.1016/j.desal.2009.08.008

[26] S. B. Yaşar, Ş. Güçer, Fractionation analysis of magnesium in olive products by atomic absorption spectrometry, Analytica Chimica Acta 505 (2004) 43-49. https://doi:10.1016/S0003-2670(03)00573-7

[27] N. Limchoowong, P. Sricharoen, S. Techawongstien, S. Chanthai, Using bio-dispersive solution of chitosan for green dispersive liquid- liquid microextraction of trace amounts of Cu(II) in edible oils prior to analysis by ICP-OES, Food Chemistry 230 (2017) 398-404. https://doi:10.1016/j.foodchem.2017.03.070

[28] M. Karimi, S. Dadfarnia, A. M. H. Shabani, F. Tamaddon, D. Azadi, Deep eutectic liquid organic salt as a new solvent for liquid-phase microextraction and its application in ligandless extraction and preconcentraion of lead and cadmium in edible oils, Talanta 144 (2015) 648-654. https://doi:10.1016/j.talanta.2015.07.021

[29] I. Lopez-Garcia, Y. Vicente-Martinez, M. Hernandez-Cordoba, Determination of cadmium and lead in edible oils by electrothermal atomic absorption spectrometry after reverse dispersive liquid-liquid microextraction, Talanta 124 (2014) 106-110. https://doi:10.1016/j.talanta.2014.02.011

[30] A. S. N. Trindade, A. F. Dantas, D. C. Lima, S. L. C. Ferreira, L. S. G. Teixeira, Multivariate optimization of ultrasound-assisted extraction for determination of Cu, Fe, Ni and Zn in vegetable oils by high-resolution continuum source atomic absorption spectrometry, Food Chemistry 185 (2015) 145-150. https://doi:10.1016/j.foodchem.2015.03.118

[31] F. Tokay, S. Bağdat, Extraction of nickel from edible oils with a complexing agent prior to determination by FAAS, Food Chemistry 197 (2016) 445-449. https://doi.org/10.1016/j.foodchem.2015.11.001

[32] F. Tokay, S. Bağdat, Spectrometric determination of iron and copper in vegetable oils after separation with Schiff base impregnated silica gel column: A simple approach for eliminating the high organic matrix, International Journal of Food Science and Technology 50 (2015) 2694-2699. https://doi:10.1111/ijfs.12948

[33] M. Y. Aşçı, A. Efendioğlu, B. Batı, Solid Phase Extraction of Cadmium in Edible Oils Using Zinc Piperazinedithiocarbamate and Its Determination by Flame Atomic Absorption Spectrometry, Turkish Journal of Chemistry 32 (2008) 431-440.

**Table Legends**

**Table 1.** The tolerance limits for interferant ions

**Table 2.** The performance characteristics of the method

**Table 3.** Real sample analysis for Mn, Cu, Ni, Cr, Cd and Pb

**Table 4.** Experimental comparison of suggested and conventional procedures

**Table 5.** Comparison of separation and preconcentration procedures

**Table 1**

The tolerance limits for interferant ions

| Coexisting Ion | Coexisting Ion/Analyte (w/w) | | | | | |
|---|---|---|---|---|---|---|
| | Cr | Ni | Cu | Pb | Mn | Cd |
| Zn | >1000 | 100 | >1000 | 10 | >1000 | 100 |
| Ca | 1000 | >5000 | >5000 | 100 | 100 | 100 |
| Mg | 5000 | 100 | >5000 | 100 | 100 | 1000 |
| Fe | >1000 | 100 | >1000 | 100 | >1000 | 100 |

Analyte concentration 30 µg $L^{-1}$

**Table 2**

The performance characteristics of the method

| | Cr | Ni | Pb | Cu | Mn | Cd |
|---|---|---|---|---|---|---|
| Added ($\mu g\ L^{-1}$) | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 |
| Found ($\mu g\ L^{-1}$) | 29.6±1.7 | 29.5±0.8 | 30.3±2.0 | 31.0±1.3 | 29.6±1.2 | 30.7±1.0 |
| Recovery, % | 98.8±5.6 | 98.4±2.6 | 101.1±6.5 | 103.3±4.5 | 98.4±3.6 | 102.0±3.1 |
| RSD, % | 5.7 | 2.6 | 6.4 | 4.3 | 3.6 | 3.0 |
| $t_{experimental}$ | 0.41 | 1.08 | 0.26 | 1.33 | 0.58 | 1.21 |

$t_{theoretical}$= 4.30 for N=3

**Table 3**

Real sample analysis for Mn, Cu, Ni, Cr, Cd and Pb

| Analyte | Added (µg g$^{-1}$) | Apricot Oil | | | | Black Cumin Oil | | | | Pine Turpentine Oil | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Found (µg kg$^{-1}$) | Rec (%) | $\lvert x-\mu \rvert$ | $\frac{ts}{\sqrt{N}}$ | Found (µg kg$^{-1}$) | Rec (%) | $\lvert x-\mu \rvert$ | $\frac{ts}{\sqrt{N}}$ | Found (µg kg$^{-1}$) | Rec (%) | $\lvert x-\mu \rvert$ | $\frac{ts}{\sqrt{N}}$ |
| Mn | 0.0 | 7.1±0.2 | - | - | - | 43.8±1.7 | - | - | - | 2.7±0.2 | - | - | - |
| | 37.5 | 44.4±1.9 | 99.5 | 0.2 | 4.7 | 82.8±2.8 | 104.3 | 1.5 | 7.0 | 40.4±3.1 | 100.5 | 0.2 | 7.7 |
| Cu | 0.0 | 22.7±1.1 | - | - | - | 15.5±4.4 | - | - | - | 16.9±0.4 | - | - | - |
| | 37.5 | 60.5±4.1 | 100.7 | 0.3 | 10.2 | 49.8±3.1 | 91.5 | 3.2 | 7.7 | 55.7±0.9 | 103.6 | 1.3 | 2.2 |
| Ni | 0.0 | 1.2±0.1 | - | - | - | nd | - | - | - | nd | - | - | - |
| | 37.5 | 39.9±1.4 | 103.1 | 1.2 | 3.5 | 35.1±1.2 | 93.6 | 2.4 | 3.0 | 38.4±0.4 | 102.4 | 0.9 | 1.0 |
| Cr | 0.0 | 9.6±2.2 | - | - | - | 4.7±0.4 | - | - | - | 6.9±0.2 | - | - | - |
| | 37.5 | 45.7±4.6 | 96.1 | 1.4 | 11.4 | 42.7±2.6 | 101.2 | 0.5 | 6.4 | 43.5±0.7 | 97.5 | 0.9 | 1.7 |
| Cd | 0.0 | nd | - | - | - | 3.7±0.3 | - | - | - | 6.4±0.3 | - | - | - |
| | 37.5 | 35.8±2.1 | 95.5 | 1.7 | 5.2 | 41.3±1.0 | 100.3 | 0.1 | 2.5 | 44.8±2.9 | 102.4 | 0.9 | 7.2 |
| Pb | 0.0 | nd | - | - | - | nd | - | - | - | 3.9±0.2 | - | - | - |
| | 37.5 | 38.3±2.4 | 102.1 | 0.8 | 6.0 | 38.9±0.8 | 103.6 | 1.4 | 2.0 | 45.1±3.4 | 109.9 | 3.7 | 8.4 |

| Analyte | Added (µg g$^{-1}$) | Thyme Oil | | | | Mint Oil | | | | Fish Oil | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Found (µg kg$^{-1}$) | Rec (%) | $\lvert x-\mu \rvert$ | $\frac{ts}{\sqrt{N}}$ | Found (µg kg$^{-1}$) | Rec (%) | $\lvert x-\mu \rvert$ | $\frac{ts}{\sqrt{N}}$ | Found (µg kg$^{-1}$) | Rec (%) | $\lvert x-\mu \rvert$ | $\frac{ts}{\sqrt{N}}$ |
| Mn | 0.0 | 5.7±0.3 | - | - | - | 6.2±0.3 | - | - | - | 2.1±0.3 | - | - | - |
| | 37.5 | 42.8±0.9 | 99.1 | 0.4 | 2.2 | 44.7±0.5 | 102.7 | 1.0 | 1.2 | 35.9±2.7 | 90.2 | 3.7 | 6.7 |
| Cu | 0.0 | 30.8±3.2 | - | - | - | 43.0±0.6 | - | - | - | 15.1±1.2 | - | - | - |
| | 37.5 | 68.5±5.1 | 100.7 | 0.2 | 12.7 | 79.0±0.8 | 94.2 | 1.5 | 2.0 | 54.8±1.6 | 105.7 | 2.2 | 4.0 |
| Ni | 0.0 | nd | - | - | - | nd | - | - | - | nd | - | - | - |
| | 37.5 | 33.3±2.0 | 93.8 | 4.2 | 5.0 | 39.1±0.9 | 104.2 | 1.6 | 2.2 | 37.4±0.7 | 99.8 | 0.1 | 1.7 |
| Cr | 0.0 | 7.3±0.3 | - | - | - | 15.6±0.4 | - | - | - | 5.9±0.6 | - | - | - |
| | 37.5 | 43.8±1.1 | 97.5 | 1.0 | 2.7 | 52.4±0.9 | 98.1 | 0.7 | 2.2 | 44.0±1.5 | 101.7 | 0.6 | 3.7 |
| Cd | 0.0 | 16.2±0.5 | - | - | - | 19.9±1.9 | - | - | - | 7.0±0.2 | - | - | - |
| | 37.5 | 55.8±1.6 | 105.6 | 2.1 | 4.0 | 56.5±1.0 | 97.6 | 0.9 | 2.5 | 45.0±1.9 | 101.4 | 0.5 | 4.7 |
| Pb | 0.0 | nd | - | - | - | nd | - | - | - | nd | - | - | - |
| | 37.5 | 35.7±2.7 | 95.3 | 1.8 | 6.7 | 37.4±0.2 | 99.7 | 0.1 | 0.5 | 35.5±2.4 | 94.7 | 2.0 | 6.0 |

**Table 4**

Experimental comparison of suggested and conventional procedures

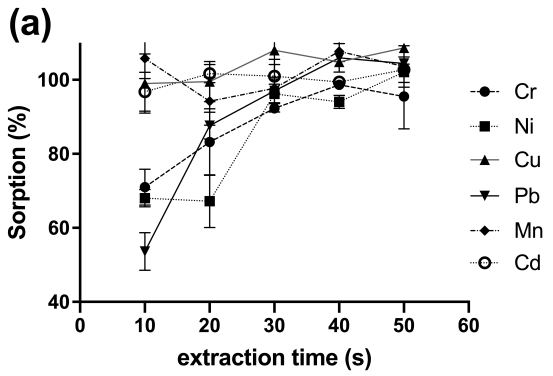
| Oil Sample | Experimental Results (µg $L^{-1}$) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Proposed Procedure | | | | | | Conventional Procedure | | | | | |
| | Mn | Cu | Ni | Cr | Cd | Pb | Mn | Cu | Ni | Cr | Cd | Pb |
| Apricot Oil | 7.1±0.2 | 22.7±1.1 | 1.2±0.1 | 9.6±2.2 | nd | nd | - | 21.6±1.6 | nd | 10.0±0.5 | nd | nd |
| Black Cumin Oil | 43.8±1.7 | 15.5±4.4 | nd | 4.7±0.4 | 3.7±0.3 | nd | - | 14.8±1.0 | nd | 5.1±0.1 | 3.6±0.1 | nd |
| Pine Turpentine Oil | 2.7±0.2 | 16.9±0.4 | nd | 6.9±0.2 | 6.4±0.3 | 3.9±0.2 | 2.3±0.2 | 17.9±2.5 | nd | 6.7±0.4 | 5.9±0.1 | nd |
| Thyme Oil | 5.7±0.3 | 30.8±3.2 | nd | 7.3±0.3 | 16.2±0.5 | nd | 5.5±0.4 | 28.3±1.4 | nd | 7.4±0.2 | 16.6±1.0 | nd |
| Mint Oil | 6.2±0.3 | 43.0±0.6 | nd | 15.6±0.4 | 19.9±1.9 | nd | 6.7±0.1 | 38.7±6.4 | nd | 15.9±0.5 | 18.7±2.0 | nd |
| Fish Oil | 2.1±0.3 | 15.1±1.2 | nd | 5.9±0.6 | 7.0±0.2 | nd | 2.3±0.2 | 13.4±1.1 | nd | 5.2±0.4 | 6.6±0.2 | nd |

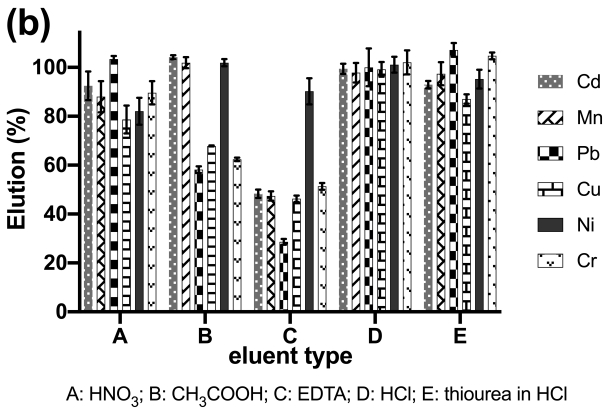
**Table 5**

Comparison of separation and preconcentration procedures

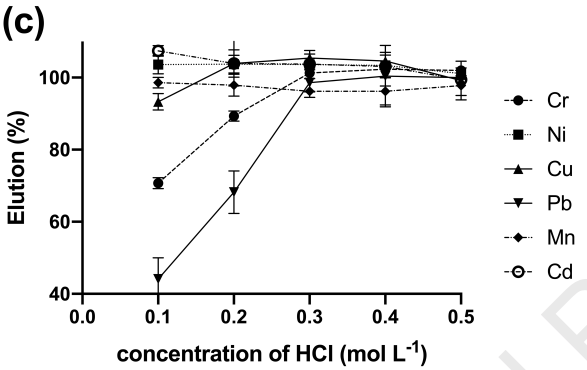
| Separation/Preconcentration | Sample Matrix | Detection Technique | Analyte (LOD, µg $kg^{-1}$; [a] ng $kg^{-1}$; [b] µg $L^{-1}$; [c] mg $kg^{-1}$) | RSD (%) | Sample Frequency ($h^{-1}$) | initial oil amount/final solution volume | Reference |
|---|---|---|---|---|---|---|---|
| Ultrasound assisted acid micro extraction | Vegetable oils | HR-CS ETAAS | Cd (2)[a] | 3.0 | 4* | 50 mL / 50 µL | [16] |
| Dispersive Liquid-liquid micro extraction | Vegetable oils | ICP-OES | Cu (2.1)[b] | 6.4 | 120* | 1 mL / 4.5 mL | [27] |
| Deep eutectic solvent-liquid phase micro extraction | Vegetable oils | ETAAS | Pb(8)[a], Cd(0.2)[a] | 3.5-4.5 | 6* | 28 g / 200 µL | [28] |
| Dispersive Liquid-liquid micro extraction | Vegetable oils | ETAAS | Pb(10)[a], Cd(0.6)[a] | 3.5-4.0 | 3.33* | 10 g / 67µL | [29] |
| Ultrasound assisted Liquid-liquid extraction | Vegetable oils | HR-CS FAAS | Cu(41), Fe(61), Ni(63), Zn(12) | 1.4-3.6 | 9.50* | 50 mL / 10 mL | [30] |
| Liquid-liquid extraction | Vegetable oils | FAAS | Ni(0.06)[c] | 4.2 | 3.90* | 10 g / 9.7 mL | [31] |
| Solid phase extraction | Vegetable oils | FAAS | Fe(22.8), Cu(13.9) | 0.1-1.5 | 3.69* | 20 g / 5 mL | [32] |
| Solid phase extraction | Vegetable oils | FAAS | Cd(2.8) | 0.7 | 0.67* | 20 g / 2 mL | [33] |
| *Dispersive solid phase extraction* | *Essential oils* | *ICP-OES* | *Mn(0.7), Cu(4.1), Ni(1.0), Cr(1.6), Cd(0.7), Pb(1.0)* | *2.6-6.4* | *11.25* | *8 g / 5 mL* | *This work* |

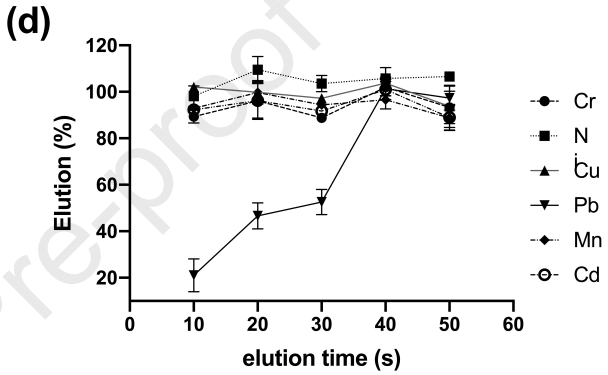
*not declared, calculated by the reported sample preparation cycle

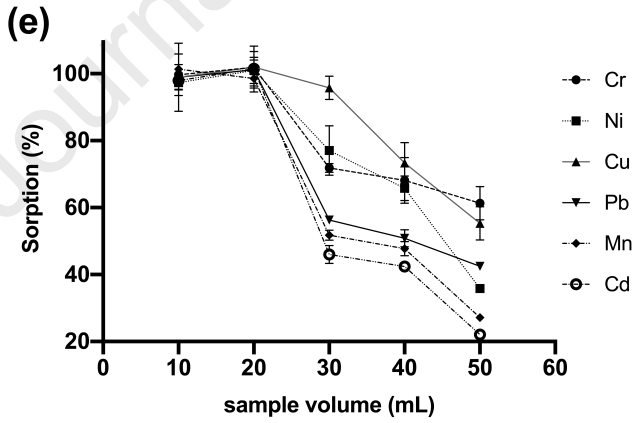


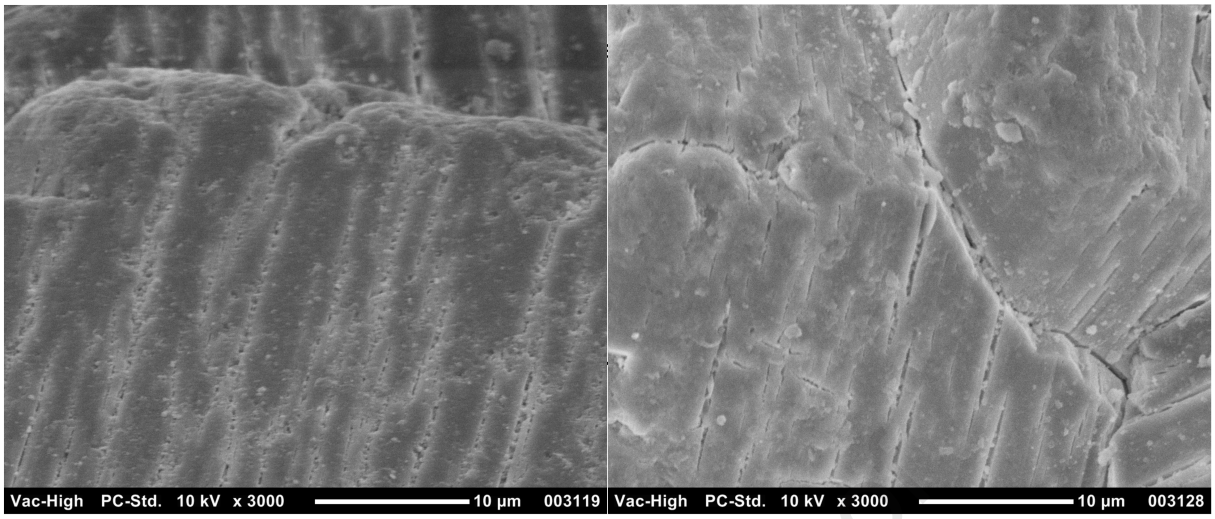




A: $HNO_3$; B: $CH_3COOH$; C: EDTA; D: HCl; E: thiourea in HCl

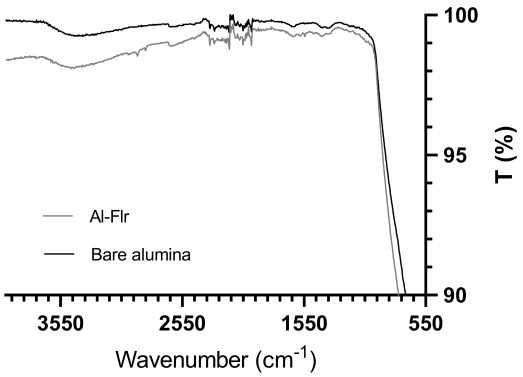


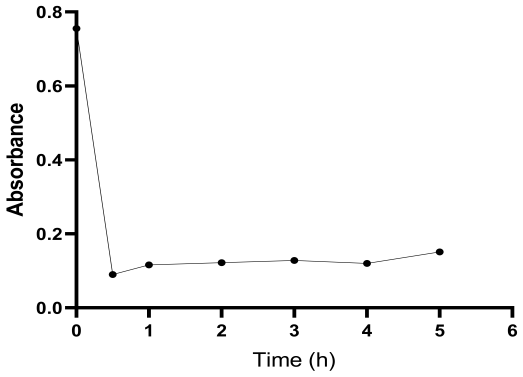






(a) (b)




(a)




(b)

**Highlights**

- Fluorescein functionalized γ-$Al_2O_3$ was synthesized and characterized.
- Vortex assisted separation and preconcentration of Mn, Cu, Ni, Cr, Cd and Pb were achieved simultaneously from oily matrix to aqueous solution in short time with 11.25 $h^{-1}$ sample frequency and followed by ICP-OES measurement.
- Besides being simple, fast and selective, presented greener approach do not need of mineralization pretreatment of organic matrix.
- The developed method was successfully applied for the analysis of apricot, black cumin, pine turpentine, thyme, mint essential oils and fish oil samples.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.