Research Article / Araştırma Makalesi GU J Sci, Part A, 9(4): 474-481 (2022) https://doi.org/10.54287/gujsa.1190172

Gazi University
Journal of Science
PART A: ENGINEERING AND INNOVATION
http://dergipark.org.tr/gujsa

# Investigation and Development of Polarographic Method for Pb (II) and Cd (II) Analyses in Oils

Şükrü KALAYCI[1*], Sinan Mithat MUHAMMET[1], Bekir Sıtkı ÇEVRİMLİ[1]

[1]*Department of Chemistry, Vocational School of Technical Sciences, Gazi University, 06500, Ankara, Turkey*

**Keywords**

Olive Oil
Analysis
Pb (II)
Cd (II)
Differential Pulse Polarography

**Abstract**

In this study, Differential Pulse Polarography (DPP) method was preferred of Cd (II) and Pb (II) levels, which have toxic effects. This method was applied to determine Cd and Pb levels in cold-pressed olive oil brought from 5 different provinces of Turkey. The samples were dissolved in microwave digestion using concentrated $HNO_3$ and $H_2O_2$. Analyses were carried out in acetate buffer (pH 4) to which EDTA was added. The LOD for Cd and Pb was found as 0.74, 0.52 µg $L^{-1}$ and the LOQ was 0.96, 0.82 µg $L^{-1}$. Additions were made from standard Cd and Pb solutions and the % recovery values were measured as 98 and 99. The relative standard deviation (RSD, %) was found < 5. This method was found to be sensitive to the analyses of two toxic elements in cold pressed olive oil.

**Cite**

Kalaycı, Ş., Muhammet, S. M., & Çevrimli, B. S. (2022). Investigation and development of polarographic method for Pb (II) and Cd (II) analyses in oils. *GU J Sci, Part A, 9*(4), 474-481.

**Author ID (ORCID Number)**

Ş. Kalaycı, 0000-0002-8643-6731
S. M. Muhammet, 0000-0001-6250-9476
B. S. Cevrimli, 0000-0001-9686-7511

**Article Process**

**Submission Date** 16.10.2022
**Revision Date** 13.12.2022
**Accepted Date** 19.12.2022
**Published Date** 31.12.2022

## 1. INTRODUCTION

Fats play an important role among the essential nutrients necessary for people to carry out their life activities. People meet about 25-30% of their daily energy needs from fats. Vegetable oils are obtained from many plant species (Nash et al., 1983). In Turkey, it is produced from olives, sunflowers and hazelnuts. Recently, the tendency of people to consume oil has been increasing. Cold pressed oils are preferred more because of their unique smell, aroma and not using chemicals.

As a result of direct or indirect pollution of air, water and soil, heavy metal contents increase. Excess amounts of heavy metals cause many vital problems and poisonings in living things. Pb, Hg and Cd determinations were made in hair samples taken from various age groups and their effects on child health were investigated (Orun et al., 2011). Therefore, the determination of heavy metals becomes extremely important.

Spectroscopic, chromatographic and electroanalytical methods are used in heavy metal analyses. Metals were determined by using the EAAS method with some organic solvents and appropriate test conditions were investigated (Karadjova et al., 1998; Schiavo et al., 2008). The elements in oils were measured using the GF-AAS method with a THFA atomizer (Canário & Kaskov, 2005). The copper in the samples was enriched with the micro-extraction method. In the naturel sample was carried out with the FAAS method (Menghwar et al., 2019). Other spectroscopic methods (Jiménez et al., 2003; Frazolli et al., 2007) were used for metal analyses in oil. In addition, ion chromatography method of heavy metal determinations in oils was also used (Ramos et al., 2020).

*Corresponding Author, e-mail: skalayci@gazi.edu.tr

It has been used in electroanalytical methods in metal analyses (Kalayci & Somer, 2020; Kalayci, 2021; Kalayci & Muhammet, 2021). It is preferred in the determination of metal levels due to its high sensitivity, absence of interference effects and pre-concentration processes (Somer et al., 2019). The amounts of some metals in oils were determined at the ng level. Toxic elements in various oils were analyzed after the samples were dissolved with a microwave digestion (Kucukkolbasi et al., 2014). Recently, electroanalytical methods with a modified electrode have also been used (Devnani & Satsangee, 2015; Wang & Yue, 2017; Silah et al., 2021).

In this study, some cold-pressed olive oils were dissolved in Pb and Cd by microwave digestion method. Samples were analyzed using DPP with a dripping mercury electrode with high reproducibility and sensitivity. Our method determined for the analyses in this study is summarized in Figure 1 below.

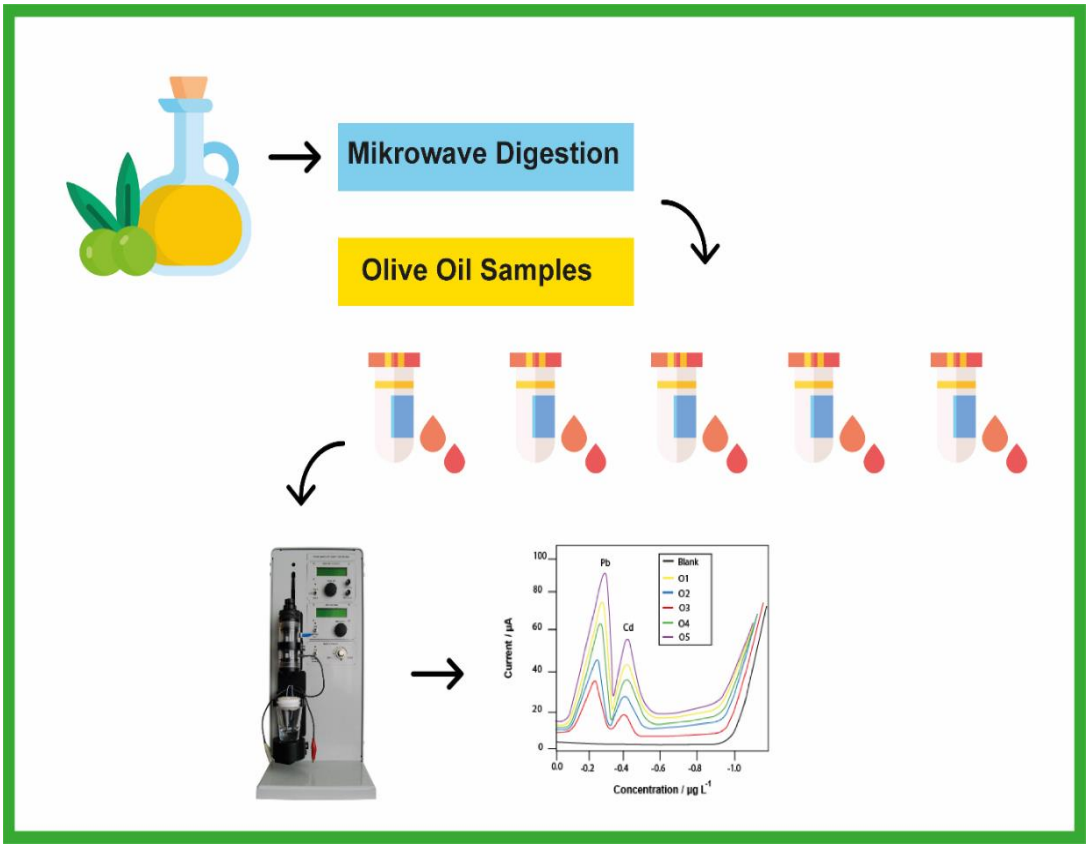


***Figure 1.*** *Summary of method used for Pb and Cd determination in oil*

## 2. MATERIALS

### 2.1. Instruments

These measurements (Figure 2) were made with the Entek brand polarography analyzer with a dripping mercury electrode, Ag/AgCl with Pt electrode and C4 cell. In addition, pure nitrogen gas was used to eliminate the effect of dissolved oxygen in the solution. Milestone microwave digestion device was used to dissolve the oil samples.

### 2.2. Reagents

Deionized water system was used as solvent in solutions and samples (Heal Force, Smart RO30, Chinese), the resistivity measured after this treatment was not less than 10 MΩ cm. Certain volumes of nitric acid (63%, w/w) and hydrogen peroxide (35%, w/w) were used for sample dissolution. For element determination, 1 mol $L^{-1}$ solution was prepared from acetic acid (100%, w/w) and ammonia (17%, w/w) as electrolytes. As the working electrode, metallic mercury and the salts of the elements to be used in the analyses (Merck) have analytical purity.

### 2.3. Solubilization of Oil Samples

Cold pressed oil samples brought from 5 different parts of Turkey were named O1 (Bursa), O2 (Manisa), O3 (Muğla), O4 (Denizli) and O5 (Kilis), respectively. The samples weighed about 0.500 g. In the process of solubilization of the samples, it was carried out with a microwave digestion device by applying high heat and pressure. The solubilization of oils was done with a microwave digestion device. The samples were placed in Teflon containers and to them, a mixture of acid was added according to the procedure. These were resolved by applying the parameters for 15 minutes at 200 psi and 10 minutes at 170 °C. This oil samples were cooled at 25°Cm, filtered and diluted to 25 ml in volume.

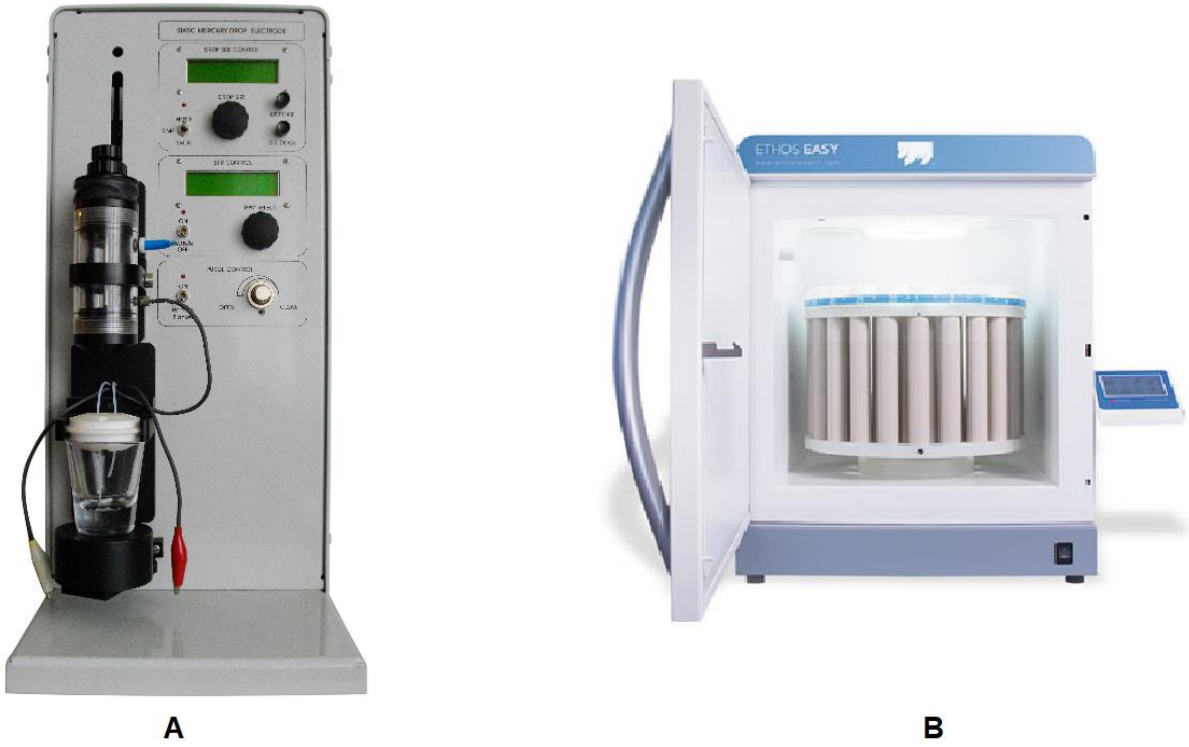


***Figure 2. A)*** *Polarography and* ***B)*** *microwave digestion device used during analyses*

## 3. RESULTS AND DISCUSSION

### 3.1. Polarographic Behavior of Elements

Qualitative analyses of elements are carried out according to their potential. The potentials of the elements differ according to the electrolytes. (Locatelli & Melucci, 2013). Electrolyte medium with high sensitivity should be chosen in elemental analyses. The polarograms of Pb and Cd in olive oils were examined in various electrolytes. These peak potentials are given in Table 1. From this, electrolytes suitable for the quantitation of each element were determined. EDTA added acetate buffer was used for the measurements of the elements.

***Table 1.*** *Peak potentials of elements in oil samples*

| **Analyte** | **pH 4 (1M AcOH + 0.1 M EDTA)** | **pH 7 (1M AcOH + 0.1 M EDTA)** | **pH 10 (1M $NH_3$)** |
|---|---|---|---|
| Pb | -0.20 | -0.30 | -0.40 |
| Cd | -0.40 | -0.41 | -0.55 |

### 3.2. Method Evaluation

The analytical parameters of the applied method were examined. For this, the sensitivity, linear range, LOD and LOQ of the method were measured (Kalayci, 2022). These parameters are shown in Table 2.

***Table 2.*** *Performance values of the applied method*

| Analyte | LOD, $\mu gL^{-1}$ | LOQ, $\mu gL^{-1}$ | $R^2$ | Linear range, $\mu gL^{-1}$ |
|---|---|---|---|---|
| Pb | 0.52 | 1.82 | 0.9975 | 5-50 |
| Cd | 0.74 | 2.36 | 0.9956 | 5-50 |

### 3.3. Samples Analyses

Olive oil is produced from olives in the early harvest period. Olive oil is a healthy oil on its own. However, especially cold-pressed olive oil is a very healthy type of oil. Olive oils are produced by cold press method in two-phase systems under 22°C. With this production method, the values of vitamin E, phenolic components and antioxidant substances that are beneficial for health are at high levels (Matthäus & Brühl, 2003).

Differential pulse polarography method, which can determine high and low concentrations with sensitivity, reproducibility, has been used in metal analyses in many samples. Standard addition method was preferred for content of Cd and Pb in olive oils. This type of calibration was chosen to minimize the error rate in metal analyses in oil types. The polarograms of the samples are given in Figure 3 and calibration graphics obtained by adding standard solutions are given in Figure 4. Analyses of Pb and Cd levels in 5 olive oils are shown in Table 3.

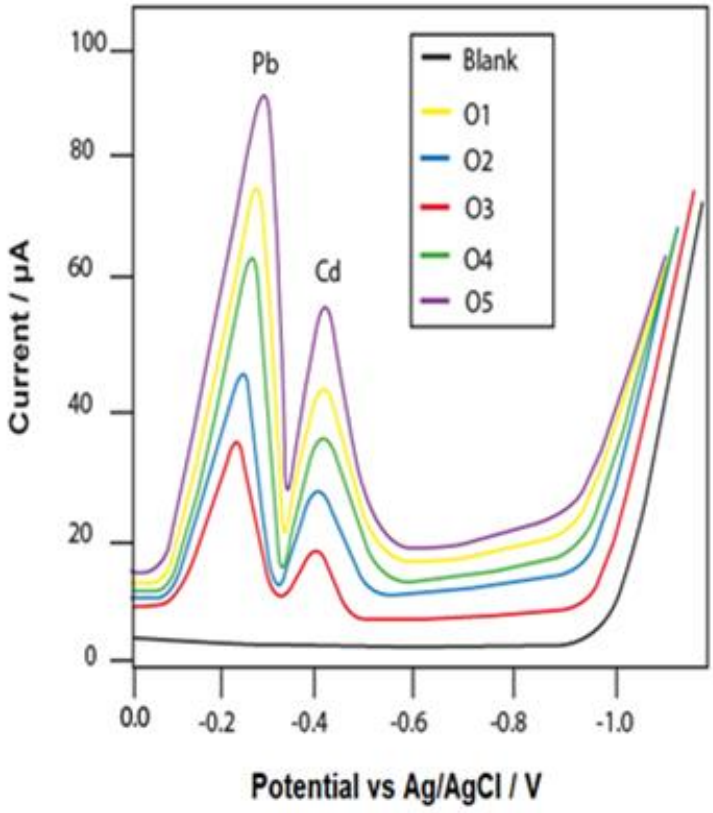


***Figure 3.*** *Polarograms obtained from analytical curves of standard solutions Pb and Cd.*

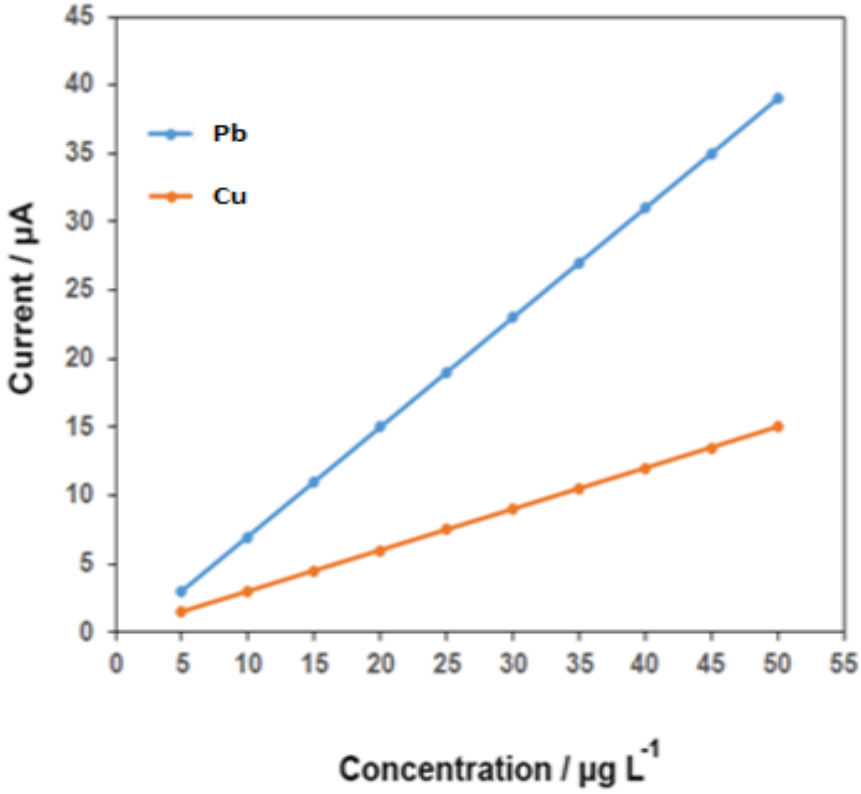


***Figure 4.*** *Analytical signals versus Pb and Cu concentrations*

***Table 3.*** *Pb and Cd amounts in 5 different cold pressed oil samples (CL 95%, N=4)*

| Sample | Concentration, µg $L^{-1}$ ($x \pm \frac{txS}{\sqrt{N}}$) | |
|---|---|---|
| | Pb | Cd |
| O1 | 18.23 ± 2.74 | 4.52 ± 0.27 |
| O2 | 16.85 ± 1.95 | 3.23 ± 0.22 |
| O3 | 14.46 ± 1.37 | 2.89 ± 0.18 |
| O4 | 17.23 ± 2.22 | 4.05 ± 0.24 |
| O5 | 19.23 ± 3.12 | 4.86 ± 0.33 |

In addition, the amount and recovery values found against the amount of analyte added to the cell were examined and these parameters are given in Table 4.

***Table 4.*** *The recovery versus standard additions in O1(Bursa) sample*

| Sample | Analyte | Added µg $L^{-1}$ | Found µg $L^{-1}$ | Recovery, % |
|---|---|---|---|---|
| O1 | Pb | 0 | ULQ | --- |
| | | 1.50 | 1.48 ± 0.15 | 99 |
| | | 3.25 | 3.23 ± 0.26 | 99 |
| | Cd | 0 | ULQ | --- |
| | | 1.00 | 0.97 ± 0.04 | 97 |
| | | 2.00 | 1.96 ± 0.13 | 98 |
| ULQ: Under the limit of quantification | | | | |

### 3.4. Comparation of Electroanalytical and Other Methods

The comparison of Pb and Cd values in oil samples with electroanalytical methods given in the literature is shown in Table 5. The name of each method was given the detection limit. In Pb and Cd analyses, it was determined that the most suitable method among the compared methods was electroanalytical methods.

***Table 5.*** *The comparation of methods for Pb and Cd contents in oils samples in literature*

| Analytes | Sample | Methods | Detection limits | Reference |
|---|---|---|---|---|
| Cd, Pb | Edible oil | ASV | Cd:0.3; Pb:0.5 ng $g^{-1}$ | Kucukkolbasi et al., 2014 |
| Cd, Pb | Vegetable oil | SWASV | Cd:0.006; Pb: 0.01 µg $kg^{-1}$ | Shishov et al., 2022 |
| Cd, Pb | Olive oil | DPP | Cd: 0.96; Pb:0.82 µg $L^{-1}$ | This work |

The O1 (Bursa) oil sample was analyzed by atomic absorption spectroscopy and ICP-OES, respectively, and the results were compared with the results obtained by differential pulse polarography. The t-test was applied to the obtained results. These values are given in Table 6. The results were found to be compatible with each other.

***Table 6.*** *Comparison of Pb and Cd amounts of AAS, ICP-OES and Differential pulse polarography, (CL 95%, N=4)*

| Methods | Pb (II): µg $L^{-1}$ | Cd (II): µg $L^{-1}$ |
|---|---|---|
| AAS | 20.11 ± 3.54 | 4.79 ± 0.315 |
| ICP-OES | 18.41 ± 2.89 | 4.55 ± 0.285 |
| Differential pulse polarography | 18.23 ± 2.74 | 4.52 ± 0.268 |
| t-test ($t_{Critical}$=3.18) | 2.03 | 2.61 |

## 4. CONCLUSION

For Cd and Pb analyses in cold pressed olive oil brought from 5 different regions of Turkey, measurements were made by differential pulse polarography method. The detection limits were between 0.82-0.92 µg $L^{-1}$ and allowed the determination of two toxic metal levels in 5 samples. The recovery values obtained against the added Pb and Cd amounts show that this method is suitable for analyses in the samples. Differential pulse polarography method was found to be suitable because of its high reproducibility, no need for pre-concentration processes, no interference effects, and low detection limit. It was also determined that the measured Pb and Cd values were not in the range to cause toxic effects.

## ACKNOWLEDGEMENT

Every stage of this study was conducted in Gazi University Chemistry Research Laboratory.

## CONFLICT OF INTEREST

The authors declare that they have no competing interests.

## REFERENCES

Canário, C. M., & Kaskov, D. A. (2005). Direct determination of Cd and Pb in edible oils by atomic absorption spectrometry with transverse heated filter atomizer. *Journal of Analytical Atomic Spectrometry*, *20*(12), 1386-1388. doi:10.1039/B506627C

Devnani, H., & Satsangee, S. P. (2015). Green gold nanoparticle modified anthocyanin-based carbon paste electrode for voltammetric determination of heavy metals. *International Journal Environmental Science Technology*, *12*(4), 1269-1282. doi:10.1007/s13762-014-0497-z

Frazolli, C., D`llio, S., & Bocca, B. (2007). Determination cadmium and lead in honey by SF-ICP-MS: validation figures and uncertainly of results. *Analytical Letters*, *40*(10), 1992-2004. doi:10.1080/00032710701484525

Jiménez, M. S., Velarte, R., & Castillo, J. R. (2003). On-line emulsions of olive oil samples and ICP-MS multi-elemental determination. *Journal of Analytical Atomic Spectrometry*, *18*(9), 1154-1162. doi:10.1039/B303131D

Kalayci, S. (2021). High Sensitivity Sulphite Membrane Selective Electrode and its Application. *Journal of the Chemical Society of Pakistan*, *43*(4), 451-455. doi:10.52568/000590/JCSP/43.04.2021

Kalayci, S. (2022). Investigation of Arsenic Content in Field Pesticides using inductively coupled plasma optical emission spectroscopy (ICP-OES). *GU. J Sci, Part A, 9(2)*, 96-103. doi:10.54287/gujsa.1100870

Kalayci, S., & Muhammet, S. (2021). Analysis of trace elements in Turkish raki by differential pulse polarography. *International Journal of Electrochemical Science*, *16*, 210932. doi:10.20964/2021.09.43

Kalayci, S., & Somer, G. (2020). Differential Pulse Polarography Method for the Determination of Trace Fe, Ni, Pb, Zn, Se and Cu in Black Tea Leaves. *Chemical Science International Journal*, *29*(4), 15-23. doi:10.9734/CSJI/2020/v29i430171

Karadjova, I., Zachariadis, G., Boskou, G., & Stratis, J. (1998). Electrothermal atomic absorption spectrometric determination of aluminum, cadmium, chromium, copper, iron, manganese, nickel and lead in olive oil. *Journal of Analytical Atomic Spectrometry*, *13*(3), 201-204. doi:10.1039/A707256B

Kucukkolbasi, S., Temur, O., Kara, H., & Khaskheli, A. R. (2014). Monitoring of Zn (II), Cd (II), Pb (II) and Cu (II) during refining of some vegetable oils using differential pulse anodic stripping voltammetry. *Food Analytical Methods*, *7*(4), 872-878. doi:10.1007/s12161-013-9694-5

Locatelli, C., & Melucci, D. (2013). Voltammetric method for ultra-trace determination of total mercury and toxic metals in vegetables. Comparison with spectroscopy. *Open Chemistry*, *11*(5), 790-800. doi:10.2478/s11532-013-0221-8

Matthäus, B., & Brühl, L. (2003). Quality of cold-pressed edible rapeseed oil in Germany. *Nahrung/Food*, *47*(6), 413-419. doi:10.1002/food.200390092

Menghwar, P., Yilmaz, E., Sherazi, S. T. H., & Soylak, M. (2019). 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*(15), 2431-2439. doi:10.1080/01496395.2018.1547317

Nash, A. M., Mounts, T. L., & Kwolek, W. F. (1983). Determination of ultratrace metals in hydrogenated, vegetable oils and fats. *Journal of American Oil Chemists' Society*, *60*(4), 811-814. doi:10.1007/BF02787433

Orun, E., Yalcin, S. S., Aykut, O., Orhan, G., Morgil, G. K., Yurdakok, K., & Uzun, R. (2011). Breast milk lead and cadmium levels from suburban areas of Ankara. *Science of the Total Environment*, *409*(13), 2467-2472. doi:10.1016/j.scitotenv.2011.02.035

Ramos, A. C. O. P., Caldeira, G. R. F., Nunes, C. R. O., Terra, W. S., & Souza, M. O. (2020). Optimization of extraction induced by emulsion breaking variables for subsequent determination of crude oil salinity by ion chromatography. *Brazilian Journal of Analytical Chemistry*, *7*(27), 31-39. doi:10.30744/brjac.2179-3425.AR-15-2020

Schiavo, D., Neira, J. Y., Nóbrega, J. A. (2008). Direct determination of cadmium, copper and lead in wines and grape juices by thermo spray flame furnace atomic absorption spectrometry. *Talanta*, *76*(5), 1113-1118. doi:10.1016/j.talanta.2008.05.010

Shishov, A., Volodina, N., Semenova, E., Navolotskaya, D., Ermakov, S., & Bulatov, A. (2022). Reversed-phase dispersive liquid-liquid microextraction based on decomposition of deep eutectic solvent for the determination of lead and cadmium in vegetable oil. *Food Chemistry*, *373*(Part B), 131456. doi:10.1016/j.foodchem.2021.131456

Silah, H., Erkmen, C., Demir, E., & Uslu, B. (2021). Modified indium tin oxide electrodes: Electrochemical applications in pharmaceutical, biological, environmental and food analysis. *TrAC Trends in Analytical Chemistry*, *141*, 116289. doi:10.1016/j.trac.2021.116289

Somer, G., Kalayci, S., & Yılmaz, U. (2019). Determination of Sulfite in Wine Using Differential Pulse Polarography. *Russian Journal of Electrochemistry*, *55*(12), 1360-1365. doi:10.1134/S1023193519020101

Wang, T., & Yue, W. (2017). Carbon nanotubes heavy metal detection with stripping voltammetry: a review paper. *Electroanalysis*, *29*(10), 2178-2189. doi:10.1002/elan.201700276