Comparative Assessment of Ni(II) Concentrations in Different Olive Oil Samples from Balıkesir, Türkiye

Feyzullah TOKAY[1,2,*], Enes ALEGÖZ[3], Sema BAĞDAT[1,2]

[1] Chemistry Department, Faculty of Science and Arts, Balıkesir University, Çağış Campus, Balıkesir, 10145, Türkiye

[2] Balıkesir University, Science and Technology Research and Application Center, Çağış Campus, Balıkesir, 10145, Türkiye

[3] Balıkesir University, Institute of Science, Çağış Campus, Balıkesir, 10145, Türkiye

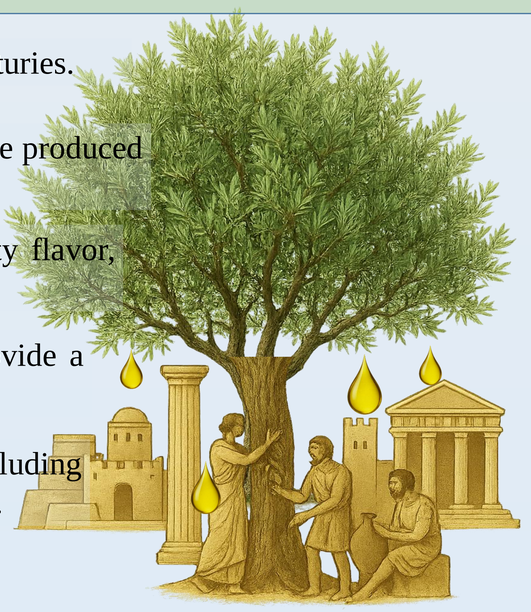
feyzullahtokay@balikesir.edu.tr

ABSTRACT

Humans may be exposed to toxic elements such as Ni(II) mainly from consumption of food and drinking water. Considering the importance of olive oil in Mediterranean diet, ensuring the quality and safety of olive oils is essential for their shelf life, food industry and public health [1]. Herein, assessment of Ni(II) contents of different olive oil samples that obtained from local markets of Balıkesir/Türkiye, were carried out. Additionally, a novel solid phase extraction method was used for preconcentration before determination [2]. The sorbent was synthesized and modified for the aim of Ni(II) sorption. ***Experimentally, the transfer of the analyte ion to the aqueous phase was achieved using a solid phase extraction based methodology with a greenness score of 0.51 that does not require decomposition of oil matrix. The approach involves mixing 19.1 mL of oil sample with 0.22 g of magnetically characterized solid sorbent for 58.3 s in sorption step. After separation of the sorbent with an external magnet, elution of the analytes were achieved vortexing with 6 mL of 0.86 mol L^{-1} HNO_3 solution for 95 s. Finally, eluents were separated using the external magnet and subjected to the detection. A flame atomic absorption spectrometry (FAAS) was utilized for the quantification of Ni(II) content of the eluents equipped with a hallow cathode lamp.*** As the method was specifically developed for the separation and preconcentration of Ni(II) in oil matrix, the instrumental quantification limit did not constitute a limiting factor for its accurate determination. The obtained Ni(II) contents of olive oils were used for calculation of chronic daily intake (CDI), target hazard quotient (THQ) and carcinogenic risk (CR) for assessing the health risks of the analyte.

Olive Oil

- Olive oil has been a cornerstone for the Mediterranean diet for centuries.
- Türkiye produce 14.8% of olive oil in the world. Balıkesir province produced 41,104 ton olive oil in 2023.
- Oilve oil is extracted directly from fresh olives with a rich fruity flavor, colour and texture.
- It has high content of nutrients and bioactive molecules that provide a wide range of health benefits
- Olive oil has beneficial effects on many disorders including cardiovascular diseases, type 2 diabetes, blood pressure, cancer etc.



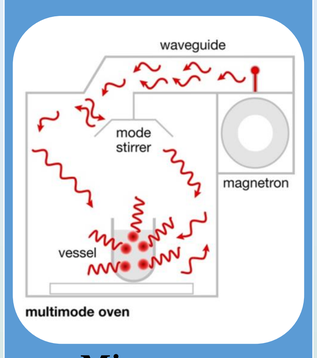
Why metal determination is important in Olive Oil?

- Food Safety
- Public Health
- Nutritional Value
- Quality Control
- Shelf Life
- Trade

What are the problems in metal determination?

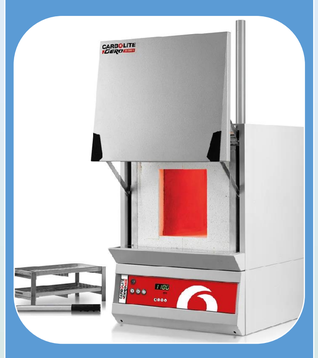
- Viscosity
- Complex organic matrix
- Hydrophobicity
- Emulsification

Sample Preparation Methodologies for Olive Oil



Microwave Assissted Digestion

Based on: Decomposition of whole organic matrix using microwave energy under high pressure
Advantages: Rapid, effective
Disadvantages: Need high energy, high priced equipment, explosion risk, need experienced staff

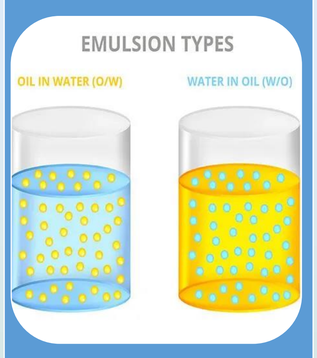


Dry Ashing

Based on: Decomposition of whole organic matrix at high temperature under atmospheric pressure
Advantages: High amount sample usage, effective
Disadvantages: Need high energy, contamination risk, loss of volatile analyte(s)

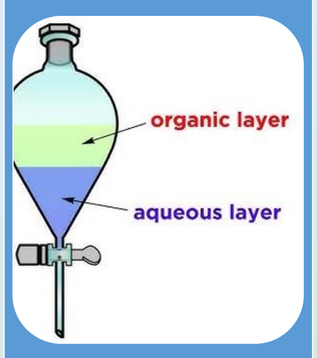
Dilution with organic solvents

Based on: Dilution of original oil matrix with organic solvent (such as MIBK) prior to metal determination
Advantages: No need high energy in sample preparation, rapid
Disadvantages: Need high priced and organic solvent compatible devices, low repeatability, organic solvent consumption, spectral and physical interferences



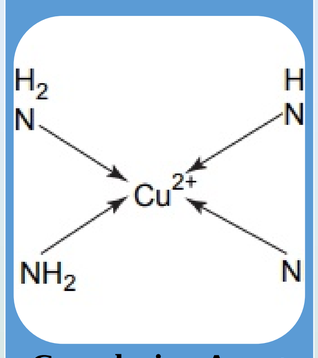
Emulsification

Based on: Emulsification of original oil matrix with surfactants prior to metal determination
Advantages: No need high energy in sample preparation, rapid
Disadvantages: Need high priced and organic solvent compatible devices, low repeatability, organic solvent consumption, spectral and physical interferences



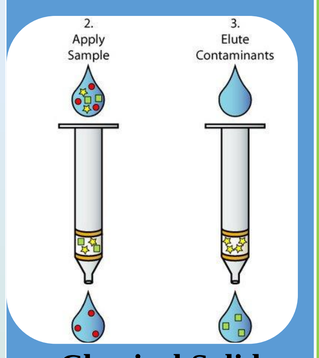
Acid Extraction

Based on: Extraction of analyte(s) from oily phase to aqueous acidic phase
Advantages: No need high energy in sample preparation
Disadvantages: Low repeatability, concantrated acid consumption, time consuming



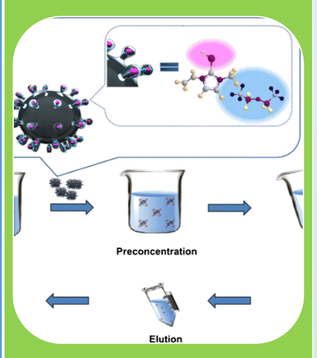
Complexing Agent Extraction

Based on: Extraction of analyte(s) from oily phase to complexing reagent containing aqueous phase
Advantages: No need high energy in sample preparation, relatively high repeatablity
Disadvantages: Time consuming



Classical Solid Phase Extraction

Based on: Sorption of analyte(s) from oily phase onto a solid sorbent and then, stripping with an eluent
Advantages: Relatively rapid, high repeatability, automation
Disadvantages: Blockage of cartridge,



Magnetic Dispersive Solid Phase Extraction

Based on: Sorption of analyte(s) from oily phase onto a solid sorbent and then, stripping with an eluent, separation with n external magnet
Advantages: Quite rapid, high repeatability, no cartridge, cheap, miniaturized
Disadvantages: -

Analysis Results for Olive Oil Samples

Experimentally, above mentioned vortex assissted magnetic dispersive solid phase extraction method was used to prepare olive oil samples prior to Ni(II) determination by FAAS. Analysis results for 8 olive oil samples that obtained commercially from Balıkesir province. Additionally, regarding the obtained concentrations, chronic daily intake (CDI), target hazard quotient (THQ) and carcinogenic risk (CR) were calculated with equations given below for assessing the health risks.

Olive Oil	Ni(II) concentration (mg/kg)	Chronic Daily Intake (CDI)	Target Hazard Quotient (THQ)	Carginogenic Risk (CR)
1	3.56±0.51	$1.0x10^{-3}$	0.05	$8.6x10^{-4}$
2	2.82±0.17	$8.1x10^{-4}$	0.04	$6.8x10^{-4}$
3	2.22±0.22	$6.4x10^{-4}$	0.03	$5.4x10^{-4}$
4	1.88±0.04	$5.4x10^{-4}$	0.03	$4.6x10^{-4}$
5	7.02±0.28	$2.0x10^{-3}$	0.10	$1.7x10^{-3}$
6	0.69±0.18	$2.0x10^{-4}$	0.01	$1.7x10^{-4}$
7	<0.12	-	-	
8	<0.12	-	-	

The analysis results showed that Ni(II) concentration of the investigated samples were between 1.46±0.18 – 4.67±0.51 mg kg^{-1}. In literaure, Ni(II) content of olive oil samples were reported between 0.07 – 6.40 mg kg^{-1}. The results shows that Ni(II) concentrations of the investigated samples are in agreement with the ones reported in the literatures. The differences in detected levels of analyte in the analyzed oil samples may be attributed to the natural background of Ni(II) in sources or manufacturing processes.

$$CDI = \frac{C \times IR \times ED \times EF}{BW \times AT} \qquad THQ = \frac{CDI}{RfD} \qquad CR = CDI \times CSF$$

C: Metal concentration of the detected in virgin olive oil (mg/kg).
IR: daily intake (kg/day), set at 0.03 kg (30 g) for adults
ED: Exposure duration: 70 years for adults.
EF: Exposure frequency, estimated at 300 days per year.
BW: Average body weight, (Adults:80 kg)
AT: Average time, 27375 days for risks of cancer/non-cancer in Adults
RfD: Oral reference dosage (0,02 for Ni(II))
CSF: Carsinogenic slope factor (0,84 for Ni(II))

The calculated THQ values demonstrated that results below 1.00 indicate no health risks associated with Ni(II) exposure from the analyzed samples. On the other hand, calculated CR values were found about the reference value ($1x10^{-4}$).

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Tokay F, Bağdat S. Extraction of nickel from edible oils with a complexing agent prior to determination by FAAS. *Food Chemistry*. 2016 Apr 15;197(A):445–449. doi:10.1016/j.foodchem.2015.10.133.

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