MULTI-ELEMENT CONTENT CHARACTERIZATION OF COLD PRESS EDDIBLE OILS PRODUCED FROM TWELVE SUNFLOWER VARIETIES

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INTRODUCTION

The content of the following isotopes of the 36 elements $(Li^7, Be^9, B^{11}, Na^{23}, Mg^{24}, Al^{27}, P^{31}, Ca^{39}, Ti^{48}, V^{51}, Cr^{53}, Mn^{55}, Fe^{56}, Co^{59}, Ni^{60}, Cu^{63}, Zn^{64}, Ga^{71}, Ge^{74}, As^{75}, Se^{77}, Rb^{85}, Sr^{88}, Mo^{95}, Pd^{106}, Ag^{107}, Cd^{111}, In^{115}, Sn^{120}, Sb^{121}, Cs^{133}, Ba^{137}, Tl^{205}, Pb^{206/207/208}$ and Bi^{209}) in EDIBLE OILS produced from TWELVE SUNFLOWER VARIETIES from Republic of Macedonia were determined.

ANALITICAL METHODS



Inductively-coupled plasma-mass spectrometry (ICP-MS) has been used for determination of the elements content, after microwave digestion, employing nitric acid and hydrogen peroxide in this step. The method has been validated using both an oil reference material and recovery experiments over different oil samples, obtaining satisfactory results in both cases. Interday repeatability lower than 10% was observed for all of the analyzed elements in the analyzed oil samples.



Standard addition method: 10 ppb; R (88.1-112%) 50 ppb; R (85.1-102%) 150 ppb; R (92-105%) 1 ppm; R (75.1-114%)

Certified reference material CRM-TMSO (metals in soybean oil) (High-purity standards, Charleston, CS, USA) For: Ag, Ca, Cu, Fe, Mg, Ni, P, Pb, Zn

Recoveries ranges in 87.5-109%

t- test (p=0.005) no-significant differences were found

| | | | NEBULIZATION DESOLVATION VAPO | RIZATION ATOMIZATION IONIZATION | MASS ANALYSIS | INSTRUMENT | (ICP introduction system) | | |
|-----------------|-----------------------------------|---|---|--|----------------------|-----------------------------|----------------------------|--|--|
| | | E F F | Liquid Gaseous Sample | | | Sampler | Cu (standard) | | |
| | | | Aerosol . | ୭ ﷺ ∰ | uille | Skimmer | Ni (standard) | | |
| | B | | -> Particle> Mole | cule ——→ Atom ———> Ion ——— | → Mass Spectrum | Nebulizer | MicroMist (standard) | | |
| _ " | | | Solid Sample | | | Plasma torch | Quartz, 2.5 mm (standard) | | |
| | RF Generator | | Nebulizer (liquid) Spray Laser (solid) Chamber | Plasma | Mass Spectrometer | Integration Time | | | |
| | | | | | | (for all analyzed elements) | 0.3 sec x 1 point | | |
| the | | ON / DEACTTO | 200 | Replication | 3 | | | | |
| | | | Tune parameters | | | | | | |
| d 40 A r 38 A r | ⁵¹ V, ⁵³ Cr | , ⁵⁷ Fe, ⁶⁰ Ni, ⁶ | ³ Cu, ⁶⁶ Zn, ⁶⁹ Ga, ⁷ | ⁷² Ge, ⁷⁵ As, | ⁷⁷ Se | RF power | 1500 W | | |
| | | nterference removal using He mo | de and Kinetic Energy Discrimination (K | ED) | | Sample depth | 8.5 mm | | |
| S | Po | Aystomic Interfering polyatomic ions with | Polystomic Bias voltage rej energy (polyato | ects low mic) ions | | Carrier gas | 0.80 L/min | | |
| | | the same mass | Analyter | | | Makeup gas | 0.23 L/min | | |
| | | | - Analyte | | | Extract lens 1 | -3 V | | |
| | | | - Polyatomic | | | Extract lens 2 | -150 V | | |
| | en | and polyatomic ion regies overlap. Energy I Energy loss from eac read is narrow, due to ShieldTorch System | th collision By cell exit, ion no longer ow polyatomics are using a bias yeld | energies erlap: rejected use "step" | | Energy discriminator | 2 V | | |
| | | polyatomics are big collide more of Cell Distan | per and so (energy discrim Iten. ce Through Cell Cell | ination) | | Reaction gas | He 5.0 mL/min | | |
| | | Entrance | Exit | | | CeO/Ce | 0.58% (ref. value < 0.65%) | | |
| | | | | | | Ce++/Ce | 2.05% ((ref. value <3%) | | |
| UCTF |) INVF | STIGA | TIONS/P | ERS | PE(| CTIVES | | | |

INTERFERENCES in ICP-MS - MOLECULAR (POLYATOMIC) ion at the same nominal mass as the isotope of interest

Quality, assurance

(plasma-based), such as ⁴⁰Ar, ⁴⁰Ar¹⁶O, and ⁴⁰Ar³⁸Ar

(matrix-based), such as ³⁵Cl¹⁶O, and ³²S³²S



Table 1. Basic statistics for elements contents in edible oils

COND

| Element | В | Na | Mg | Si | AI | Р | К | Са | Fe | Cu | Zn | Ni | Ва | Cr | Mn |
|-------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|-------------------------------|-------------------------------|------------------------------|------------------------------|------------------------------|-------------------------------|
| unit | µg/kg | mg/kg | mg/kg | mg/kg | mg/kg | µg/kg | µg/kg |
| Med | 0.12 | 27.1 | 11.5 | 32.7 | 0.45 | 1.64 | 0.27 | 25.2 | 1.32 | 0.22 | 0.22 | 0.29 | 0.19 | 48.4 | 40.8 |
| Min | 0.03 | 4.09 | 0.48 | 26.45 | 0.01 | 0.12 | 0.14 | 0.73 | 0.56 | 0.07 | 0.17 | 0.10 | 0.12 | 30.6 | 9.64 |
| Max | 0.58 | 47.4 | 19.5 | 35.6 | 0.13 | 28.4 | 4.91 | 63.5 | 1.82 | 0.47 | 0.29 | 0.55 | 0.34 | 59.7 | 226 |
| SD | 0.18 | 14.1 | 6.06 | 2.97 | 0.04 | 9.50 | 1.41 | 18.6 | 0.40 | 0.13 | 0.03 | 0.18 | 0.09 | 7.96 | 60.8 |
| CV | 92.9 | 56.5 | 52.6 | 9.37 | 98.9 | 153 | 214 | 72.2 | 31.8 | 55.3 | 14.7 | 71.7 | 65.8 | 17.4 | 102 |
| Element | Ti | V | Ga | Ge | As | Se | Rb | Cd | Со | In | Sn | Sb | Те | ті | Pb |
| unit | µg/kg | ua/ka | ua/ka | ua/ka | ua/ka | ua/L | ua/ka | ua/ka | ua/ka | ua/ka | ua/ka | ua/ka | ua/ka | ua/ka | ua/ka |
| | | 100 | P.9.1.9 | F 3.13 | Maina | P 9/ - | M9/N9 | P.3.1.3 | µg/ng | M9/119 | 1.3.1.3 | P.9 | P9/N9 | μg/ng | 1.2.3 |
| Med | 5.02 | 0.72 | 6.66 | 0.09 | 1.24 | 11.1 | 6.54 | 0.94 | 0.01 | 1.63 | 14.7 | 0.79 | 0.58 | 0.01 | 31.0 |
| Med Min | 5.02 0.50 | 0.72 | 6.66 0.50 | 0.09 | 1.24 0.30 | 11.1 5.60 | 6.54 2.13 | 0.94 | 0.01 0.01 | 1.63 0.36 | 14.7 7.17 | 0.79 | 0.58 0.15 | 0.01 0.09 | 31.0 3.31 |
| Med Min Max | 5.02 0.50 11.3 | 0.72 0.32 8.55 | 6.66 0.50 15.5 | 0.09 0.05 1.21 | 1.24 0.30 5.00 | 11.1 5.60 23.2 | 6.54 2.13 13.5 | 0.94 0.57 1.69 | 0.01 0.01 6.20 | 1.63 0.36 10.83 | 14.7 7.17 24.64 | 0.79 0.49 3.90 | 0.58 0.15 2.11 | 0.01 0.09 0.20 | 31.0 3.31 92.56 |
| Med Min Max SD | 5.02 0.50 11.3 3.21 | 0.72 0.32 8.55 2.47 | 6.66 0.50 15.5 3.99 | 0.09 0.05 1.21 0.33 | 1.24 0.30 5.00 1.45 | 11.1 5.60 23.2 4.48 | 6.54 2.13 13.5 3.48 | 0.94 0.57 1.69 0.30 | 0.01 0.01 6.20 1.86 | 1.63 0.36 10.83 3.57 | 14.7 7.17 24.64 5.85 | 0.79 0.49 3.90 1.25 | 0.58 0.15 2.11 0.54 | 0.01 0.09 0.20 0.06 | 31.0 3.31 92.56 24.7 |



Studying the multi-elements content, in order to detect tendencies in the oil samples between varieties, principal components analysis was used. Promising groupings were observed using a model with two principal components and retaining 82.3% of the variance.

> Principal components analysis





0.64

0.48

0.32

-0.16

-0.32 -

-0.48





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