Development of method for multielement analysis of olive oil by ICPMS

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Introduction

Multielemental analysis of olive oil can be important tool in evaluation of its geographical traceability, as the elemental composition of soil is reflected in olives and in olive oil. However, whereas determination of elements in soil and plant is an easy task, it is not a case for olive oil, as only minor fraction of elements are transferred to the oil, and concentrations of trace elements are usually very low. An ideal instrumental technique to achieve this goal is inductively coupled plasma mass spectrometry technique (ICPMS), which enable multi-elemental analysis and very low detection limits.

In the present work microwave digestion and the recently proposed ultrasonic extraction method (Camin et al., 2010) for determination of elements in olive oil are compared.

Material and Methods

Preparation of olive oil: Centrifugal oil extraction from olive fruits by Abencor oil mill (mc2, Ingenierias y Sistemas) within 24 h after the harvesting. Six Croatian olive oils were used in the experiments.

Microwave digestion: Digestion of ~0.5 g of olive oil by 6 ml HNO_3 (Trace select, Fluka) in Microwave oven Multiwave GO (Anton Paar) and dilution to 50 ml by Milli-Q® water.

Ultrasonic extraction: Extraction of ~15 g of olive oil with 15 ml of (1 % HNO_3+0.2 % HCl) in the ulrasonic bath; centrifugation, isolation of water layer.

Measurements: HR ICPMS (Element 2, Thermo), Measured elements (47):

LR: ^{7}Li, ^{9}Be, ^{85}Rb, ^{95}Mo, ^{111}Cd, ^{129}Sn, ^{133}Cs, ^{165}Ho, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{238}U

MR: ^{23}Na, ^{24}Mg, ^{27}Al, ^{42}Ca, ^{45}Sc, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{86}Sr, ^{89}Y, ^{90}Zr, ^{121}Sb, ^{138}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{145}Nd, ^{147}Sm, ^{151}Eu, ^{159}Tb, ^{163}Dy, ^{167}Er, ^{169}Tm, ^{171}Yb, ^{175}Lu

HR: ^{39}K, ^{75}As, ^{77}Se, ^{157}Gd

Internal standard: ^{115}In; standard used for recovery experiments: Multi-element II mixture dissolved in oil (100 ppm), Merck, Certipur®

Results and Discussion

Digestion of oil samples in the Multivave GO microwave oven is fast and efficient, but limited to 0.5 g of olive oil due to risk of over-pressure. Recoveries for elements present in oil standard were satisfactory (**Tab. 1**). However, due to the very low concentrations of elements in analysed olive oils, and small quantity of samples, all measured elements, except K and Rb, were below detection limit.

The ultrasonic bath extraction, in which elements are extracted from 15 g of oil, had much lower detection limits, although the concentrations of elements in blank solutions for both methods were similar (**Fig. 1**). Nevertheless, ultrasonic extraction had lower recoveries for some elements than microwave digestion (**Tab. 1**), which may indicate their partial extraction from oil. Due to higher quantity of oil, 34 elements were detectable in analysed oil samples (**Tab. 2**).

Concentrations of K and Rb in olive oils obtained by the two techniques were comparable proving that ultrasonic bath extraction is efficient for these two elements.

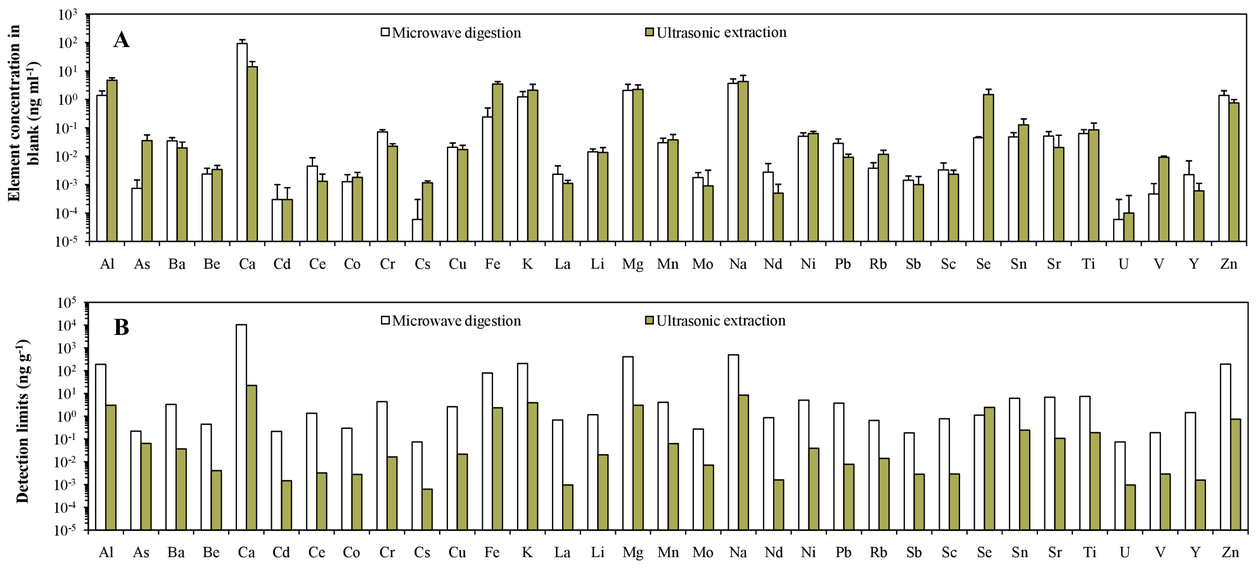

Fig. 1 Mean concentrations of elements in blank (n = 10, bars are SD) (**A**) and detection limits calculated as 3 SD of the blank (**B**) for the two methods.

Tab. 2 Range of elements concentration in six olive oils analysed by ultrasonic extraction method.

Sample	Min (ng g^{-1})	Max (ng g^{-1})
Al	<3	130
Ba	0.045	1.06
Ca	15.3	434
Cd	0.001	0.012
Ce	0.001	0.055
Co	0.001	0.085
Cr	<0.02	0.968
Cs	<0.001	0.005
Cu	0.339	4.08
Dy	<0.001	0.003
Er	<0.001	0.002
Fe	<2.3	101
K	23.0	13337
La	<0.001	0.023
Li	<0.02	0.173
Mg	4.50	361
Mn	<0.06	4.15
Mo	<0.007	0.242
Na	32.0	718
Nd	<0.001	0.020
Ni	<0.04	1.27
Pb	0.095	0.527
Pr	<0.001	0.005
Rb	<0.014	8.47
Sb	<0.003	0.011
Sc	<0.003	0.048
Sm	<0.001	0.005
Sn	<0.05	0.128
Sr	0.02	0.505
Ti	<0.2	0.766
U	<0.001	0.002
V	0.001	0.221
Y	<0.001	0.008
Yb	<0.001	0.007

Tab. 1 Elements recoveries (%) for two methods at 2 ng g^{-1} spiked oil standard.

Method	Ultrasonic extraction	Microwave digestion
Elements	**Mean ± SD**	**Mean ± SD**
Al	13 ± 5	-
Cd	88 ± 1	81 ± 13
Cr	15 ± 1	95 ± 47
Cu	88 ± 0	141 ± 45
Mn	92 ± 0	114 ± 29
Mo	39 ± 0	107 ± 11
Ni	80 ± 2	67 ± 32
Pb	69 ± 1	55 ± 35
Sn	34 ± 1	69 ± 24
Ti	33 ± 1	-
V	54 ± 1	107 ± 8

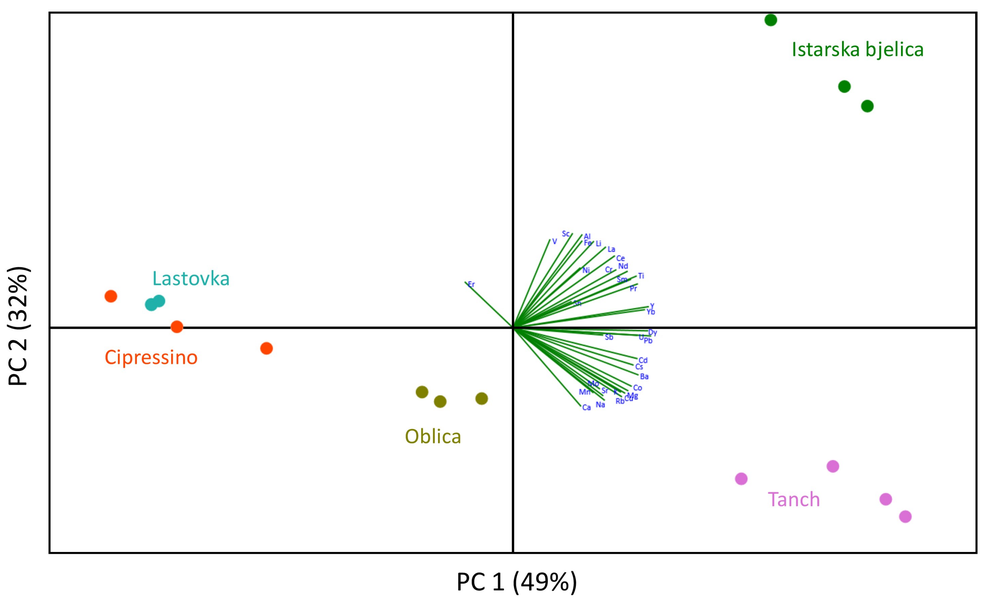

Fig. 2 PCA of analysed olive oils by their multielement composition.

Conclusions

The ultrasonic extraction proposed by Camin et al. (2010) is a promising method for determination of elements in olive oil due to much lower detection limits compared to microwave digestion and good reproducibility. However, for some elements obtained recoveries are not satisfactory and further research on the extraction conditions (acid mitxure, extraction time ect.) is required.

Nevertheless, the 34 elements found in the six olive oils were sufficient to discriminate the samples through Principal Component Analysis (**Fig. 2**) suggesting that multielement composition of olive oils is different enough to be used for traceability of their origin.

Reference

Camin et al. (2010) *Food Chemistry*, 118:901–909 http://dx.doi.org/10.1016/j.foodchem.2008.04.059

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