

**1An optimized approach for sample preparation and elemental analysis of extra-virgin olive oil by  
2inductively coupled plasma mass spectrometry**

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## 11 Abstract

12

13 The accurate determination of trace elements in vegetable edible oils is still an analytical challenge, owing to  
14 their low concentration levels and to the complex matrix of the vegetable oils. The aim of this study is to  
15 develop a fast and simple analytical method to quantify 45 elements in small mass samples (0.5 g) of extra  
16 virgin olive oils by inductively coupled plasma mass spectrometry. To evaluate the best and fastest sample  
17 preparation procedure, ultrasonic extraction and wet digestion methods were compared using oil certified  
18 reference material with different reagent mixtures, reagent volumes and times for sample extraction or  
19 digestion. The selected method using 5 mL acidic mixture [10% HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub>, 2:1 (v/v)] in a water  
20 bath (95 °C, 40 min) was validated performing recovery experiments over three different extra virgin olive  
21 oil samples, obtaining satisfactory results in all cases.

22

23 **Keywords:** Virgin olive oil; metal; sample preparation; ultrasonic extraction; wet digestion;  
24 spectroanalytical technique.

25

## 26 1. Introduction

27

28 Olive oil is a major component of the Mediterranean diet; it is a rich source of antioxidants and  
29 monounsaturated fats, both of which are thought to protect cardiovascular health. However, olive oil can  
30 contain pollutants of various origins, including toxic elements. The presence of trace elements in vegetable  
31 edible oils may be due to soil composition and environmental pollution as well as to contaminations during  
32 the oil production and conservation process (Reyes & Campos, 2006; Benincasa, Lewis, Perri, Sindona, &  
33 Tagarelli, 2007). Trace elements, such as Ca, Co, Cu, Fe, Mg, Mn and Ni are known to have adverse effects  
34 on the flavor and oxidative stability of olive oil (Reyes & Campos, 2006; Lepri et al., 2011), while other  
35 elements, such as As, Cr, Cd and Pb, are very important for their metabolic role and toxicity (Huang &  
36 Jiang, 2001; Anthemidis, Arvanitidis, & Stratis, 2005; Llorent-Martínez, Ortega-Barrales, Fernández-de  
37 Córdova, & Ruiz-Medina, 2011). As quality criteria, the International Olive Council (IOC) has established a  
38 maximum residue level (MRL) for the content of As, Cu, Pb (0.1 mg kg<sup>-1</sup>) and Fe (3 mg kg<sup>-1</sup>) in olive oils

39and olive-pomace oils (International Olive Council, 2009). The maximum levels of Cu and Fe in other  
40vegetable oils have been also legislated (Codex Alimentarius, 2009), varying from 0.1 up to 5 mg kg<sup>-1</sup>.  
41Hence, the chemical quality of olive oils is related to the concentration of trace metals; therefore, the  
42development of analytical procedures for the monitoring and control of their concentrations is very important  
43and of great practical interest (Cabrera Vique, Bouzas, & Oliveras López, 2012).

44Inductively coupled plasma optical emission spectrometry (ICP-OES) (Bakircioglu, Kurtulus, & Yurtsever,  
452013), inductively coupled plasma mass spectrometry (ICP-MS) (Beltrán, Sánchez-Astudillo, Aparicio, &  
46García-González, 2015; Pošćić et al., 2019; Damak, Asano, Baba, Ksibi & Tamura, 2019; Luka & Akun,  
472019) and atomic absorption spectrometry (AAS) (Cassella, Brum, Lima, Caldas, & De Paula, 2011),  
48especially in the electrothermal atomization mode (ETAAS) (Cabrera Vique, Bouzas, & Oliveras López,  
492012; López-García, Vicente-Martínez, & Hernández-Córdoba, 2014), can be considered as suitable  
50analytical techniques for olive oils analysis, due to their wide availability and good sensitivity. Alternative  
51analytical techniques than can be used for the same purpose are electrothermal vaporization ICP-MS (Huang  
52& Jiang, 2001) and direct analysis combining laser ablation with ICP-TOF-MS (Bings, 2002).

53The results obtained with AAS, ICP-OES, and ICP-MS may be affected by matrix and/or spectrum (mass)  
54interferences when the sample solutions contain a high amount of residual carbon compounds (RCC)  
55(Grindlay, Mora, Loos-Vollebregt, & Vanhaecke, 2013). Sample preparation is a crucial and critical step for  
56the analytical procedure. In particular, the elemental content in olive oils is difficult to analyze, since their  
57matrix is complex and characterized by high viscosity and organic content; moreover, some elements are  
58present in olive oils at very low concentration levels (Llorent-Martínez, Ortega-Barrales, Fernández-de  
59Córdoba, & Ruiz-Medina, 2011; Llorent-Martínez, Ortega-Barrales, Fernández-de Córdoba, Domínguez  
60Vidal, & Ruiz-Medina, 2011; Cabrera Vique, Bouzas, & Oliveras López, 2012). Therefore, different sample  
61preparation and extraction techniques have been developed in order to remove the organic content of the  
62edible oil samples before their analysis, including liquid-liquid extraction (Dugo, La Pera, Giuffrida, Salvo,  
63& Lo Turco, 2004), wet or dry ashing, eventually assisted by microwave heating (Brkljača, Giljanović, &  
64Prkić, 2013; Ni, Tang, Liu, Shen, & Mo, 2015), microwave-assisted digestion (MAD) (Llorent-Martínez,  
65Ortega-Barrales, Fernández-de Córdoba, & Ruiz Medina, 2011; Llorent-Martínez, Ortega-Barrales,  
66Fernández-de Córdoba, Domínguez Vidal, & Ruiz-Medina, 2011; Luka, & Akun, 2019; Ni, Chen, Yu,

67Sun, & Tang, 2018), microwave-induced combustion (Pereira et al., 2010), simple dilution with a suitable  
68solvent (Chaves, de Loos Vollebregt, Curtius, & Vanhaecke, 2011; Cabrera Vique, Bouzas, & Oliveras  
69López, 2012), acid extraction in vortexed samples (Ni, Tang, Yu, & Wang, 2016), ultrasonic acid extraction  
70(USE) (Camin et al., 2010; Hill, 2015; Trindade, Dantas, Lima, Ferreira, & Teixeira, 2015; Pošćić et al.,  
712019) and emulsification (He, Chen, Zhou, Wang, & Liu, 2014; Kara, Fisher, & Hill, 2015). Among these,  
72MAD is the most commonly used extraction technique; however, MAD methods are time-consuming and  
73require large amount of reagent (and consequently often use a high final dilution to reduce the acid content)  
74(Lepri et al., 2011, Trindade, Dantas, Lima, Ferreira, & Teixeira, 2015; Damak, Asano, Baba, Ksibi, &  
75Tamura, 2019). On the contrary, ultrasonic acid extraction offers a simple, quick, and sensitive approach for  
76the extraction of elements from edible oils (Pošćić et al., 2019).

77The aim of this work is to evaluate a new fast approach for sample preparation and elemental analysis of  
78extra virgin olive oils (EVOO) by ICP-MS. The method here described reduces acid volume and final  
79dilution as well as the sample transfer steps, in order to prevent sample loss and to minimize volume transfer  
80errors. Method validation was performed using both oil certified reference material (CRM) and recovery  
81experiments over different oil samples.

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## 832. Experimental

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### 852.1. Instrumentation

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87A Bruker (Bremen, Germany) 820-MS quadrupole ICP-MS spectrometer equipped with a collision-reaction  
88interface (CRI) and a glass nebulizer was used for the elemental analysis. Equipment optimization in terms  
89of sensitivity, resolution and mass calibration was performed before each working session by monitoring  
90signals produced by a multi-elemental solution containing 0.005 mg L<sup>-1</sup> Ba, Be, Ce, Co, In, Pb, Mg, Tl, and  
91Th (10.00 ± 0.05 mg L<sup>-1</sup>; Spectro Pure, Ricca Chemical Company, Arlington, TX, USA) in the graphics  
92mode of analysis. The <sup>140</sup>Ce<sup>16</sup>O<sup>+</sup>-<sup>140</sup>Ce<sup>+</sup> ratio was used to check the level of oxide ions in the plasma, which  
93might interfere in the determination of some elements; moreover, instrumental parameters such as RF power

94and carrier gas flow were optimized and the level of doubly charged ion was monitored using the signal  
95 $^{137}\text{Ba}^{2+}/^{137}\text{Ba}^{+}$ .

96A Varian (Victoria, Australia) Vista-MPX CCD Simultaneous ICP-OES with axial view mode was used to  
97determine RCC. Both ICP-MS and ICP-OES analyses were performed following the operating parameters  
98shown in Table 1 and S1, respectively.

99An Arioso (Human Corporation, Seoul, Korea) Power I RO-UP Scholar UV deionizer system was used for  
100the production of analytical reagent-grade water with a resistivity of 18.3 M $\Omega$  cm.

101A temperature-controlled water bath ( $\pm 0.2$  °C), model WB12, furnished by Argo Lab (Modena, Italy) was  
102used for the sample digestion.

103An Ulsonix (Germany) proclean 10.0 ultrasonic cleaner (10 L, ultrasonic power 240 W) was used for the  
104sample extraction.

105A Gibertini Elettronica (Milan, Italy) Europe 60 analytical balance (sensitivity, 0.1 mg) was used to weigh  
106all samples.

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## 1082.2. Reagents

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110All reagents used were of the highest available purity or at least analytical reagent grade.

111A series of element standard solutions were used: multi-element standard solution containing 23 elements  
112( $1000 \pm 5$  mg L $^{-1}$  Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, and  
113Zn) dissolved in 6% HNO $_3$ ; single-element standard solutions containing Dy ( $1001 \pm 7$  mg L $^{-1}$ ), Nd ( $999 \pm 5$   
114mg L $^{-1}$ ), Pr ( $999 \pm 6$  mg L $^{-1}$ ), and Tb ( $999 \pm 4$  mg L $^{-1}$ ) in 2% HNO $_3$  supplied by Merck KGaA (Darmstadt,  
115Germany); and multi-element standard solution containing 40 elements ( $1.000 \pm 0.005$  mg L $^{-1}$  As, Al, Ba,  
116Be, Bi, Cd, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Te, Ti, Tl, U, V, W, and Zr;  $5.00 \pm$   
1170.03 mg L $^{-1}$  Ce and Co;  $10.00 \pm 0.05$  mg L $^{-1}$  Fe and Zn;  $50.00 \pm 0.25$  mg L $^{-1}$  P and Si;  $55.00 \pm 0.25$  mg L $^{-1}$  B  
118and Sr;  $500.0 \pm 2.5$  mg L $^{-1}$  K, Mg, and Na; and  $1000 \pm 5$  mg L $^{-1}$  Ca) in 4% HNO $_3$  purchased from Ultra  
119Scientific/Agilent Technologies (North Kingstown, RI, USA).

120A standard solution of Y (at 0.005 and 0.2 mg L $^{-1}$  from  $1000 \pm 2$  mg L $^{-1}$ ) purchased from Panreac Química  
121(Barcelona, Spain), for both ICP-MS and ICP-OES, and a multi-element standard solution of Sc, Rh, In, and

122Th (at  $0.010 \text{ mg L}^{-1}$  from  $1000 \pm 5 \text{ mg L}^{-1}$ ) from Merck KGaA (Darmstadt, Germany), for ICP-MS only, in  
1231% (v/v)  $\text{HNO}_3$ , were employed as internal standards to control the nebulizer efficiency, as previously  
124reported (Astolfi et al., 2020; Astolfi, Marconi, Protano, & Canepari, 2020).

125Superpure  $\text{HNO}_3$  (67%) was purchased from Carlo Erba Reagents S.r.l. (Milan, Italy),  $\text{HCl}$  (36%) and  $\text{H}_2\text{O}_2$   
126(30%), from Promochem, LGC Standards GmbH (Wesel, Germany), and citric acid anhydrous (99.5%) from  
127Sigma-Aldrich Chemie GmbH (Steinheim, Germany).

128Ar of 99.9995% purity was supplied by SOL Spa (Monza, Italy).

129The oil CRM (Conostan Oil Analysis Standards S-21) was purchased from SCP Science (Baie D'Urfé,  
130Canada).

131Disposable graduated tubes (2.5–5–10 mL in polypropylene) were obtained from Artiglass S.r.l. (Due  
132Carrare, PD, Italy).

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### 1342.3. Sample preparation methods

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136Two types of sample preparation procedures were applied to determine elemental contents in oil CRM  
137samples: wet digestion (WD) and ultrasonic extraction (USE). Both sample treatments were tested with oil  
138CRM masses of around 0.5 g, directly weighed into 10 mL polypropylene tubes subsequently filled with six  
139different reagent mixtures [A, aqua regia; B, 67%  $\text{HNO}_3$ ; C, 67%  $\text{HNO}_3$  and 30%  $\text{H}_2\text{O}_2$  (2:1, v/v); D, 5%  
140 $\text{HNO}_3$ ; E, 30%  $\text{H}_2\text{O}_2$  and F, 10%  $\text{HNO}_3$  and 30%  $\text{H}_2\text{O}_2$  (2:1, v/v)] at different volumes (0.5, 1 and 5 mL). The  
141mixture was thoroughly shaken and then immediately placed in a water bath at  $95 \text{ }^\circ\text{C}$  or in an ultrasonic bath  
142at room temperature ( $19 \text{ }^\circ\text{C}$ ), to extract the elements from the oil CRM to the reagent solution. Both WD and  
143USE methods were performed for 10, 20 and 40 min. Three replicate measurements were carried out for all  
144sample preparation procedures. The solutions obtained from oil CRM sample preparation procedures were  
145diluted to 10 mL deionized water. Then, the upper oil phase was accurately removed by aspiration and 1 mL  
146lower aqueous phase was further diluted (final sample dilution factor of 200x for the Ag, Al, Cd, Cr, Cu, Fe,  
147Mn, Mo, Ni, Pb, Sn, Ti, V and Zn and 10x for the B, Ba, Ca, Mg, Na, P and Si determination) with deionized  
148water before the ICP-MS analysis.

149The vegetable edible oils used for the spike recovery and method validation were obtained from Italian local  
150supermarkets. An aliquot (0.5 g) of each oil sample was directly weighed into a 10 mL polypropylene tube.  
151Then, reagent mixture F (5 mL) was added to each sample before heating in a water bath (95 °C, 40 min).  
152The upper oil phase of digests was accurately removed by aspiration and the lower aqueous phase was  
153analyzed by ICP-MS and ICP-OES (for RCC determination). All samples were analyzed in duplicate.  
154Further details are reported in the following section.

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#### 1562.4. Quality assurance

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158Method validation was performed by evaluating the basic performance criteria: accuracy, precision, and  
159method detection and quantification limits (MDL and MQL, respectively) under repeatable conditions  
160(Konieczka, 2007). Both oil certified material and spiked samples were used to evaluate the analytical  
161performance and quality control. Method blanks, duplicates, and spiked samples were prepared along with  
162every batch of digested and extracted samples. Each digestion/extraction batch contained at least three  
163method blanks to monitor contamination. Standard solutions of all elements were prepared for low and high  
164spikes; 0.05 mL of spike solution was added to appropriate tubes before the addition of reagent mixture and  
165final volumes were adjusted accordingly. The low and high spike concentrations were for all trace elements  
1660.005 and 0.02 mg L<sup>-1</sup> and for major elements (B, Ca, K, Mg, Na, P, Si and Sr) 0.2 and 1 mg L<sup>-1</sup>,  
167respectively. The instrumental detection limit (IDL) and MDL of each element were calculated according to  
168the formula reported in previous work (D'Ilio et al., 2008):  $IDL \text{ or } MDL = 3 SD C_{\text{spike}} / (I_{\text{spike}} - I)$ , where C is  
169the concentration expressed in µg L<sup>-1</sup>, SD is the standard deviation and I is the signal intensity of the  
170element. Six pool method blanks/digested oil and six pool method blanks/digested oil spiked with 0.005 and  
1710.2 mg L<sup>-1</sup> for trace and major elements, respectively, were prepared and analyzed. The method blanks were  
172used for the calculation of IDLs, while digested oil was used for the calculation of MDLs. Final dilution and  
173weight were taken into account to calculate the IDL and MDL final values. MQLs are defined as the lower  
174and upper quantification limit (LQL and UQL, respectively) which are the lowest and highest points of the  
175calibration curve.

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## 1772.5. Calibration procedure

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179The calibration ranges were selected according to the expected concentrations of the elements of interest in  
180the analyzed oil samples, and all standard solutions were prepared in the same percentage of acid present in  
181the oil digests. The ICP-MS calibration curves, consisting of concentrations between 0.00025-0.05 mg L<sup>-1</sup>  
182and 0.0125 and 5 mg L<sup>-1</sup>, were prepared for all trace and major elements, respectively (Table 2). Citric acid  
183in water was used as solvent to prepare reference solutions of C in the range from 5 to 20 mg L<sup>-1</sup> for the RCC  
184determination through ICP-OES (Astolfi et al., 2018). The correlation coefficient R<sup>2</sup> obtained for the  
185calibration curves of all elements was at least 0.999, excluding Ca, by ICP-MS (R<sup>2</sup> = 0.994) and the linear  
186concentration range was verified by Mandel fitting test. The influence of instrumental drift for the ICP-MS  
187or ICP-OES analysis was corrected using an internal standard solution of In, Rh, Sc, Th and Y or only of Y.  
188During the analysis, check standards and blank samples were analyzed every 20 samples and re-calibration  
189was performed every 100 samples.

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## 1912.6. Interferences study

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193Quantification of some elements (such as As, Cr, Fe, Se, and V) with quadrupole ICP-MS can be affected by  
194the occurrence of the molecular ion interferences (typically 40Ar35Cl) (May, & Wiedmeyer, 1998). This can  
195be solved through the use of CRI with He and H<sub>2</sub> as collision and reaction cell gases, respectively, or using  
196the standard mode analysis with the application of corrective element equations. In this study, different  
197isotopes and both element equations and CRI were used to correct the signal intensity for the presence of  
198spectral interferences. The correction equations are shown below:

$$19951V = 51V - 3.1081 * ?53 + 0.3524 * Cr52;$$

$$20075As = 75As - 3.127 * (?77 - 0.815 * ?82);$$

$$20178Se = 78Se - 0.03043 * Kr83 - 0.1869 * ?76;$$

$$20298Mo = 98Mo - 0.1111 * Ru101$$

203where is used the symbol "?" in place of an element symbol to specify an arbitrary m/z.



204The content of oxides, which potentially interfered with the signal of Cd, was daily kept under control below  
2051% by calculating the oxides percentage on  $CeO^+/Ce^+$  masses. To this end, a standard solution containing  
2060.005 mg L<sup>-1</sup> of Ba, Be, Ce, Co, In, Pb, Mg, Tl, and Th, in 1% HNO<sub>3</sub> was daily measured, and the  
207optimization parameters were adjusted in order to select the best instrument performance, according to the  
208information provided by Bruker (oxide interference  $CeO^+/Ce^+ < 1\%$ ; doubly charged interference:  $Ba^{++}/Ba^+$   
209 $< 3\%$ , and sensitivity:  $^9Be > 25000$  cps,  $^{115}In > 250000$  cps,  $^{232}Th > 100000$  cps).

210The sample matrix and the C content can enhance or suppress the ICP signal and influence the reported  
211concentration of some elements (Astolfi et al., 2018). The RCC in the final digest was  $< 60$  mg kg<sup>-1</sup> and did  
212not significantly interfere with the analysis, in accordance with previously reported results (Astolfi et al.,  
2132018).

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## 2152.7. Statistical analysis

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217SPSS Statistics 25 software (IBM Corp., Armonk, NY, USA) was used for the statistical analyses. Non-  
218parametric tests (Kruskal-Wallis and pairwise post-hoc tests) were used for comparison of different  
219categories of oil samples because of the low and unequal numbers of samples per group and the not always  
220normal distribution (Siegel & Castellan Jr, 1992). A p-value lower than 0.05 was considered statistically  
221significant.

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## 2233. Results and discussion

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225Sample treatment procedures were optimized by reducing all reagent volumes, thus allowing sample  
226preparation and analysis in one 10 mL tube. This prevents sample loss through transfer and reduces sample  
227manipulation and possible contamination from consumables or atmosphere. The reagent mixtures for oil  
228sample treatment commonly used in the literature are concentrated HNO<sub>3</sub> (Benincasa, Lewis, Perri, Sindona,  
229& Tagarelli, 2007; Llorent-Martínez, Ortega-Barrales, Fernández-de Córdova, & Ruiz Medina, 2011;  
230Llorent-Martínez, Ortega-Barrales, Fernández-de Córdova, Domínguez Vidal, & Ruiz-Medina, 2011),  
231HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (Bakircioglu, Kurtulus, & Yurtsever, 2013) and HNO<sub>3</sub>/HCl in different ratios (Bakircioglu,

232Kurtulus, & Yurtsever, 2013; Beltrán, Sánchez-Astudillo, Aparicio, & García-González, 2015). In general,  
233HNO<sub>3</sub> is preferred as reagent because it allows the oxidation of almost all organic compounds and causes  
234minor spectral interferences or problems in ICP-MS compared to other reagents (such as HCl). Moreover,  
235treatment with HNO<sub>3</sub> favors Cl removal as nitrosyl chloride and minimizes the polyatomic interferences in  
236the case of Cr, Ni and As determinations (Cava-Montesinos, Cervera, Pastor, & de la Guardia, 2005). For  
237this reason, the digests obtained with aqua regia were analyzed only with ICP-OES.

238

### 2393.1. Detection and quantification limits (IDL, MDL and MQL)

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241Table 2 shows a summary of the IDL, MDL and MQL for elemental analysis using ICP-MS. The IDL was  
242included for the comparison of instrument capabilities with other instrumentations.

243All of the selected elements in EVOO and peanut oils had concentrations 100% greater than the MDL,  
244except for Ag, As, B, Ba, Bi, Fe, Ga, K, Mo, Nb, Se, Si, Tb, Te and Tl, whose concentrations were in the  
245range 0-92% greater than the MDL (Table 3). In terms of the QL, the results were less satisfactory: only Ca,  
246Cu, Mn, Ni, and Zn were 100% quantifiable in the EVOO samples. For the statistical analyses, we used the  
247original concentrations of all elements, even those with values lower than the UQL, excluding the elements  
248with a percentage of values <MDL greater than 20% (As, B, Bi, Ga, K, Mo, Nb, Se, Si, Te, and Tl), and not  
249completely extracted using the proposed method (Ag, Ba, P, and Sn).

250The obtained MDL values for As, Cu, Fe and Pb were at least 150 times lower than the MRLs established by  
251the IOC for olive and pomace-olive oils, which are 100 µg kg<sup>-1</sup> for As, Cu and Pb and 3000 µg kg<sup>-1</sup> for Fe  
252(International Olive Council, 2009). In the same way, MDLs for Cu and Fe were also 100 times lower than  
253those established in refined vegetable oils, which are 100 and 1500 µg kg<sup>-1</sup>, respectively (Codex  
254Alimentarius, 2009). MDLs for other elements were similar to those reported in other methods using ICP-  
255MS as detection technique (Savio et al. 2014; Llorent-Martínez, Ortega-Barrales, Fernández-de Córdoba,  
256Domínguez Vidal, & Ruiz-Medina, 2011; Damak et al., 2019).

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### 2583.2. Accuracy and precision

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260 There are not certified reference materials for each type of selected oil samples. Hence, to validate the  
261 sample procedures here proposed, we used an oil CRM and recovery experiments over three different EVOO  
262 and one peanut oil.

263 The oil CRM containing 21 elements (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn,  
264 Ti, V, and Zn) was analyzed using both WD and USE methods. Various types [A, aqua regia; B, 67% HNO<sub>3</sub>;  
265 C, 67% HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub> (2:1, v/v); D, 5% HNO<sub>3</sub>; E, 30% H<sub>2</sub>O<sub>2</sub>; and F, 10% HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub> (2:1,  
266 v/v)] and volumes (0.5, 1 and 5 mL) of reagent mixtures were prepared and analyzed using both USE and  
267 WD methods for different times (10, 20 and 40 min) in order to determine optimal conditions to be used for  
268 reliable results. All results of the trueness bias percentage (Tbias%) and repeatability (CVR%) for the  
269 certified elements in oil CRM are shown in Tables S2-S10 and Figure 1, while a summary of sample  
270 treatment procedures that gives a Tbias and CVr% within 15% is shown in Table 4. Only P fell outside this  
271 range with Tbias% < -91.3%. Acceptable results for Ag and Sn were only obtained using WD and reagent  
272 mixture A (5 mL; 10, 20 or 40 min), and for Ba using WD and reagent mixture B (5 mL; 40 min). In general,  
273 better accuracy and precision values were obtained as reagent mixture volume, acidity, temperature and  
274 treatment duration increase. However, for some elements (Al, B, Ca, Cd, Cr, Cu, Mg, Mn, Mo, Ni, Si, V, and  
275 Zn), results of Tbias and CVr% within 15% were also obtained only by using H<sub>2</sub>O<sub>2</sub> (reagent mixture E).  
276 Considering these results, the low concentrations in real samples and the not required use of solution F for  
277 sample dilution prior to ICP-MS analysis, we chose to study the recoveries on real samples using the WD  
278 method with 5 mL reagent mixture F for 40 min.

279 Recovery experiments were performed in three EVOO and one peanut oil at two concentration levels  
280 [instrument concentration for all trace elements at 0.005 and 0.02 mg L<sup>-1</sup>, and major elements (B, Ca, K, Mg,  
281 Na, P, Si and Sr) at 0.2 and 1 mg L<sup>-1</sup>, respectively]. The recoveries, shown in Tables 2 and S11-S14, fell  
282 within 20% of the expected value and many of the elements in all the analyzed EVOO (Ag, Al, B, Ba, Be,  
283 Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Ga, La, Li, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sn, Sr, Tb, Te, Ti, Tl, U, V,  
284 and W) recovering within 10%. The obtained recoveries confirmed that no significant element losses  
285 occurred during the WD procedure. Intra-day and inter-day replicate analyses with the proposed method had  
286 good CVr% and reproducibility (CVR%), lower than 15 and 20%, respectively, excluding CVR% of Si at  
287 higher spike level (Tables 2 and S11-S14). Good results obtained by the proposed method indicate that this

288oil sample treatment procedure is satisfactory to release internally bound elements. Moreover, this method  
289was optimized by reducing acidity, volumes, and final dilution, thus allowing sample preparation and  
290analysis in only one vessel. This prevented sample loss, minimized volume transfer errors and reduced the  
291risk of contamination from consumables or atmosphere.

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### 2933.3. Application of the WD method

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295The proposed WD method (5 mL reagent mixture F; 95 °C; 40 min) was applied to the elemental  
296determination in different categories of oils. A total number of 28 samples was analyzed (24 and 4 from  
297EVOO and peanut oils, respectively). Each sample was independently digested and analyzed in duplicate.  
298The concentrations obtained for each oil sample are shown in Table 3. It was not possible to compare the  
299obtained data for Ag, Ba, P and Sn, because these elements were not completely extracted. In general, the  
300presence of elements (such as As, Cu, Fe, and Pb) is undesirable because they can be toxic to customers'  
301health and facilitate oil oxidative degradation, decreasing shelf life. In all cases, the observed concentrations  
302of As, Cu, Fe and Pb were lower than the MRLs allowed (International Olive Council, 2009) and than the  
303maximum levels legislated (Codex Alimentarius, 2009). In particular, As was not detected in any of the  
304analyzed oil samples. The concentrations of elements were very similar for all varieties of the studied oils,  
305except for Be, Cr, Cu, Li, Mg, Na, U, V and Zr, which were significantly higher in EVOO than in peanut  
306oils. The contents of Ti and V in Italian EVOO were significantly higher than in European EVOO, while the  
307concentration of Zr in Italian EVOO was significantly lower than in European EVOO. In biological EVOO,  
308Sb was higher than in non-biological EVOO. Variation in elements was noted across different samples, thus  
309indicating the usefulness of the method for elemental fingerprinting.

310Our results agreed the most with those from studies on Italian olive oils (Benincasa, Lewis, Perri, Sindona, &  
311Tagarelli, 2007; Camin et al., 2010) and Spanish olive oils (Llorent-Martínez, Ortega-Barrales, Fernández-de  
312Córdoba, & Ruiz-Medina, 2011; Llorent-Martínez, Ortega-Barrales, Fernández-de Córdoba, Domínguez  
313Vidal, & Ruiz-Medina, 2011; Cabrera Vique, Bouzas, & Oliveras López, 2012) but for some elements  
314differed from other results in Argentine (Savio et al., 2014) and Tunisian olive oils (Damak et al., 2019). The  
315concentrations of Na found in this study were in the range of 142–315  $\mu\text{g kg}^{-1}$ , which are similar to the

316median value that was found in Italian olive oils (49–280  $\mu\text{g kg}^{-1}$ ) as reported by Camin et al. (2010), but 20  
317times lower than the levels reported in Tunisian olive oils (Damak et al., 2019). The concentrations of Cu  
318and Sb measured in the present study ranged between 2.8 and 17.3  $\mu\text{g kg}^{-1}$ , and 0.07 and 0.45  $\mu\text{g kg}^{-1}$ ,  
319respectively. These values are much lower than those previously reported in Argentine olive oils (Cu = 260–  
3201100  $\mu\text{g kg}^{-1}$ ; and Sb = 1330–2030  $\mu\text{g kg}^{-1}$ ) (Savio et al., 2014), and are in a similar range in the olive oils  
321from Spain (Cu = 3.35–66.47  $\mu\text{g kg}^{-1}$ ) (Cabrera Vique, Bouzas, & Oliveras López, 2012), and Italy (Sb =  
3220.194–0.411  $\mu\text{g kg}^{-1}$ ) (Benincasa, Lewis, Perri, Sindona, & Tagarelli, 2007).

323

### 324**Conclusion**

325

326Sample preparation is a critical stage in the oil analysis. Methods requiring a sample treatment to destroy the  
327organic matrix involve manipulations and the risk of sample contamination and/or analyte loss. Here we  
328reported a rapid analytical method for the determination of 45 elements in EVOO by ICP-MS, useful for  
329routine and control quality analyses as well as for applications such as geographical fingerprinting. Sample  
330preparation of EVOO (0.5 g) was carried out by simply WD oil at 95 °C in 5 mL 10%  $\text{HNO}_3$  and 30%  $\text{H}_2\text{O}_2$   
331(2:1, v/v) for 40 min. The WD method was designed to carry out the sample preparation and instrument  
332analysis from a single tube to prevent sample loss, minimize contamination and reduce both reagent volumes  
333and required dilutions. This method showed good accuracy and precision for all the analyzed elements,  
334excluding Ag, Ba, P, and Sn.

335This study is a valuable aid in choosing not only the most appropriate oil pre-treatment method but also the  
336most suitable reagent mixture for the determination of each selected element.

337

### 338**Declaration of interests**

339None declared.

340

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342

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345

#### 346Conflict of interest

347The authors declare no conflict of interest.

348

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515 **Table 1.** Instrumental parameters and operating conditions for the ICP-MS instrument.

516

Radiofrequency power (KW)	1.4
Plasma gas flow (L min <sup>-1</sup> )	18.0
Nebulizer gas flow (L min <sup>-1</sup> )	0.9
Auxiliary gas flow (L min <sup>-1</sup> )	1.8
Sampling depth (mm)	6.5
Sampling and skimmer cones	Ni
Pump rate (rpm)	3
Rinse time (s)	45
Point/peak	1
Scans/replicate	5
Replicates/sample	3
Stabilization delay (s)	50
Dwell time (ms)	50 or 100
Scan mode	Peak hopping

517

518**Table 2.** Isotope, internal standard, IDL ( $\mu\text{g kg}^{-1}$ ), MDL ( $\mu\text{g kg}^{-1}$ ), linearity range ( $\mu\text{g kg}^{-1}$ ), and summary of recovery percentage (R%) and precision [as coefficient of variation (CV%)] for each element in extra virgin olive oils (three different type) by WD with 5 mL reagent mixture F.

521

Isotope	Internal standard	IDL <sup>a</sup>	MDL <sup>b</sup>	Linearity range <sup>c</sup>		Spike - level 1 <sup>d</sup>			Spike - level 2 <sup>e</sup>		
				N	LQL-UQL	R% n = 3	CVr% Intra-day n = 3	CVR% Inter-day n = 9	R% n = 3	CVR% Intra-day n = 3	CVR% Inter-day n = 9
<sup>107</sup> Ag	<sup>115</sup> In	0.04	0.06	6	10–500	94–96	0.1–2.8	1.5–2.5	90–93	1.2–2.4	0.5–2.3
<sup>27</sup> Al	<sup>45</sup> Sc	6	9	4	50–500	108–110	3.8–7	4.3–22	98–106	3.6–5.2	4.9–11
<sup>75</sup> As	<sup>79</sup> Y	0.2	0.3	8	2.5–500	96–97	0.6–1.6	6.4–9.1	87–91	1.0–2.0	1.7–2.3
<sup>11</sup> B	<sup>45</sup> Sc	8	20	6	550–27500	105–110	1.4–3.4	2.6–3.9	95–100	1.4–1.7	2.1–5.2
<sup>137</sup> Ba	<sup>115</sup> In	0.2	0.7	3	100–500	–	–	–	107–113	0.5–2.8	2.7–12
<sup>9</sup> Be	<sup>45</sup> Sc	0.003	0.004	8	2.5–500	98–100	1.8–2.1	1.7–3.1	94–98	0.5–3.5	0.7–4.0
<sup>209</sup> Bi	<sup>232</sup> Th	0.01	0.1	8	2.5–500	100–102	0.2–3.2	1.1–2.9	96–102	1.3–2.4	1.8–5.5
<sup>44</sup> Ca	<sup>79</sup> Y	130	510	3	5000–20000	–	–	–	85–94	2.0–6.1	2.9–17
<sup>112</sup> Cd	<sup>115</sup> In	0.02	0.07	8	2.5–500	92–96	0.4–0.6	1.7–2.9	91–93	0.1–1.6	1.0–2.5
<sup>140</sup> Ce	<sup>115</sup> In	0.03	0.1	8	2.5–500	98–101	0.4–1.4	1.0–3.4	96–96	0.4–1.8	1.4–2.5
<sup>59</sup> Co	<sup>45</sup> Sc	0.01	0.05	8	2.5–500	98–99	1.5–2.4	1.7–5.5	99–102	0.4–3.2	4.3–6.5
<sup>52</sup> Cr	<sup>79</sup> Y	0.2	0.3	8	2.5–500	101–103	1.0–1.9	1.6–6.9	97–101	0.7–2.7	1.9–4.5
<sup>133</sup> Cs	<sup>115</sup> In	0.004	0.007	8	2.5–500	96–102	0.5–1.1	1.2–2.9	94–97	0.2–2.6	2.3–3.9
<sup>65</sup> Cu	<sup>79</sup> Y	0.1	0.6	8	2.5–500	103–108	1.1–1.5	1.4–4.3	97–98	0.0–4.3	1.4–5.1
<sup>163</sup> Dy	<sup>115</sup> In	0.002	0.005	8	2.5–500	93–99	0.7–2.1	1.8–3.4	92–95	0.2–2.4	1.5–3.1
<sup>57</sup> Fe	<sup>79</sup> Y	7	12	5	100–2000	–	–	–	87–112	0.4–14	17–20
<sup>71</sup> Ga	<sup>79</sup> Y	0.002	0.06	8	2.5–500	100–102	0.2–1.4	6.3–8.3	90–91	0.1–3.6	0.9–3.3
<sup>39</sup> K	<sup>45</sup> Sc	24	40	6	1250–50000	91–97	2.9–3.8	2.8–5.6	85–90	0.3–1.4	1.5–3.6
<sup>139</sup> La	<sup>115</sup> In	0.02	0.05	8	2.5–500	98–101	0.5–0.8	1.9–2.7	95–96	0.4–2.7	1.1–2.8
<sup>7</sup> Li	<sup>45</sup> Sc	0.01	0.06	8	2.5–500	105–107	0.2–1.7	1.6–3.7	99–103	0.2–3.6	0.9–3.7
<sup>24</sup> Mg	<sup>45</sup> Sc	7	10	6	1250–50000	96–97	1.3–3.1	5.4–8.6	87–92	0.9–5.5	3.7–4.7
<sup>55</sup> Mn	<sup>79</sup> Y	0.4	0.5	8	2.5–500	105–106	0.1–1.0	0.8–3.1	96–100	0.4–3.7	1.5–3.1
<sup>98</sup> Mo	<sup>103</sup> Rh	0.05	0.3	8	2.5–500	93–96	1.6–4.2	1.8–3.9	92–94	0.3–0.9	1.1–3.5
<sup>23</sup> Na	<sup>45</sup> Sc	7	25	6	1250–50000	93–97	0.5–2.8	7.6–11	90–92	1.2–3.8	6.1–8.5
<sup>93</sup> Nb	<sup>103</sup> Rh	0.1	0.04	8	2.5–500	99–99	0.1–1.3	5.5–7.4	90–91	0.2–2.4	1.7–4.2
<sup>146</sup> Nd	<sup>115</sup> In	0.01	0.03	8	2.5–500	92–98	0.1–1.8	2.2–3.7	92–94	0.8–1.8	1.1–2.7
<sup>60</sup> Ni	<sup>45</sup> Sc	0.1	0.5	8	2.5–500	97–99	0.3–5.1	1.9–6.0	98–112	1.0–3.7	5.0–12
<sup>31</sup> P	<sup>45</sup> Sc	20	60	4	250–25000	97–101	1.1–3.9	3.3–4.0	88–91	0.2–3.1	2.0–3.8
<sup>208</sup> Pb	<sup>232</sup> Th	0.1	0.3	8	2.5–500	100–102	1.2–2.1	1.3–4.1	96–104	1.1–2.1	2.1–6.5
<sup>141</sup> Pr	<sup>115</sup> In	0.004	0.008	8	2.5–500	95–100	0.5–1.8	0.8–3.2	92–94	0.2–1.9	1.6–2.2
<sup>85</sup> Rb	<sup>79</sup> Y	0.02	0.06	8	2.5–500	98–99	0.3–1.2	5.1–7.0	91–92	0.1–2.6	1.0–3.5
<sup>121</sup> Sb	<sup>115</sup> In	0.006	0.02	8	2.5–500	91–96	1.0–1.4	1.3–2.7	91–92	0.8–3.2	0.5–2.9
<sup>76</sup> Se	<sup>79</sup> Y	0.4	0.6	6	10–500	90–98	0.5–3.2	4.4–9.7	88–90	0.1–2.4	2.0–3.3
<sup>28</sup> Si	<sup>45</sup> Sc	65	270	4	2500–25000	115–117	1.8–13	14–28	89–100	3.9–13	20–27
<sup>118</sup> Sn	<sup>115</sup> In	0.04	0.06	8	2.5–500	96–97	1.5–1.8	1.6–3.3	90–93	0.1–3.1	0.5–2.7
<sup>88</sup> Sr	<sup>79</sup> Y	0.7	1	6	550–27500	97–98	0.1–1.6	5.7–8.0	101–106	0.2–2.0	1.6–3.0
<sup>159</sup> Tb	<sup>115</sup> In	0.0005	0.006	8	2.5–500	96–102	1.4–4.0	2.2–5.0	93–96	1.0–2.3	1.7–4.3
<sup>125</sup> Te	<sup>115</sup> In	0.02	0.03	8	2.5–500	92–94	0.9–2.7	2.8–3.6	90–92	0.3–2.5	0.5–2.9
<sup>49</sup> Ti	<sup>45</sup> Sc	0.2	0.4	8	2.5–500	100–103	0.4–2.5	2.3–2.7	95–98	0.4–2.9	0.7–2.7
<sup>205</sup> Tl	<sup>232</sup> Th	0.001	0.06	8	2.5–500	102–104	0.9–2.7	2.3–4.0	98–105	1.2–1.4	1.9–6.5
<sup>238</sup> U	<sup>232</sup> Th	0.001	0.005	8	2.5–500	96–98	0.4–1.4	1.1–4.0	92–98	0.5–2.5	1.9–5.4
<sup>51</sup> V	<sup>79</sup> Y	0.04	0.08	8	2.5–500	101–103	0.7–1.8	0.6–2.3	97–100	0.5–1.1	1.0–2.8
<sup>182</sup> W	<sup>232</sup> Th	0.2	0.3	8	2.5–500	101–105	0.6–2.5	1.4–4.4	96–99	0.6–1.5	1.8–5.5
<sup>66</sup> Zn	<sup>79</sup> Y	8	20	5	50–1000	101–120	6.7–14	15–16	90–95	3.6–15	5.8–16
<sup>90</sup> Zr	<sup>79</sup> Y	0.07	0.1	8	2.5–500	95–98	0.1–1.3	7.2–8.9	85–92	0.5–1.3	0.9–2.6

522<sup>a</sup> IDL, instrumental detection limit

523<sup>a</sup> LQL, lower limit of quantification; UQL, upper limit of quantification.

524<sup>b</sup> N, number of calibration points.

525 **Table 3.** Comparison of the element contents ( $\mu\text{g kg}^{-1}$ ) in vegetable edible oils available in Italian market and displayed for category.

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Element	EVOO <sup>a</sup> n = 24				Peanut oil n = 4				p-value <sup>b</sup>	Biological EVOO n = 4				Non-biological EVOO n = 20			p-value <sup>c</sup>	Italian EVOO n = 11			European EVOO n = 13			p-value <sup>d</sup>				
	n	>MDL	median	min	max	n	>MDL	median		min	max	n	>MDL	median	min	max		n	>MDL	median	min	max	n		>MDL	median	min	max
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)		(%)	(%)	(%)	(%)	(%)	(%)	(%)		(%)	(%)	(%)	(%)	(%)	(%)		(%)	(%)	(%)	(%)
Ag	0	<0.06	<0.06	<0.06	<0.06	0	<0.06	<0.06	<0.06	-	0	<0.06	<0.06	<0.06	0	<0.06	<0.06	<0.06	-	0	<0.06	<0.06	<0.06	0	<0.06	<0.06	<0.06	-
Al	100	38	22	166	100	42	36	72	ns	100	38	34	65	100	38	22	166	ns	100	38	29	166	100	38	22	65	ns	
As	0	<0.3	<0.3	<0.3	0	<0.3	<0.3	<0.3	-	0	<0.3	<0.3	<0.3	0	<0.3	<0.3	<0.3	-	0	<0.3	<0.3	<0.3	0	<0.3	<0.3	<0.3	-	
B	0	<20	<20	<20	0	<20	<20	<20	-	0	<20	<20	<20	0	<20	<20	<20	-	0	<20	<20	<20	0	<20	<20	<20	-	
Ba	92	1.2	<0.7	2.2	75	1.6	<0.7	3.3	-	100	1.6	1.2	2.1	90	1.0	<0.7	2.2	-	100	1.1	<0.7	2.1	85	1.4	<0.7	2.2	-	
Be	100	<b>0.054</b>	<b>0.019</b>	<b>0.126</b>	100	<b>0.029</b>	<b>0.019</b>	<b>0.047</b>	***	100	0.051	0.033	0.101	100	0.054	0.019	0.126	ns	100	0.046	0.019	0.097	100	0.058	0.027	0.126	ns	
Bi	42	0.1	0.1	0.3	75	0.2	0.1	0.2	-	50	0.1	0.1	0.2	40	0.1	0.1	0.3	-	54	0.2	0.1	0.3	38	0.1	0.1	0.3	-	
Ca	100	10164	9661	11503	100	10089	9765	10719	ns	100	10413	9830	10879	100	10161	9661	11503	ns	100	10149	9661	11503	100	10172	9765	11489	ns	
Cd	100	0.41	0.34	0.79	100	0.40	0.33	0.43	ns	100	0.42	0.36	0.79	100	0.41	0.34	0.71	ns	100	0.40	0.34	0.48	100	0.42	0.35	0.79	ns	
Ce	100	0.3	0.1	0.8	100	0.2	0.2	0.4	ns	100	0.2	0.2	0.4	100	0.3	0.1	0.8	ns	100	0.3	0.1	0.4	100	0.3	0.2	0.8	ns	
Co	100	0.12	0.06	0.39	100	0.11	0.06	0.12	ns	100	0.17	0.09	0.39	100	0.12	0.06	0.39	ns	100	0.12	0.09	0.23	100	0.11	0.06	0.39	ns	
Cr	100	<b>2.9</b>	<b>1.7</b>	<b>7.2</b>	100	<b>1.7</b>	<b>1.2</b>	<b>2.4</b>	***	100	3.0	2.6	7.2	100	2.9	1.7	6.4	ns	100	3.0	1.7	7.2	100	2.7	2.1	6.4	ns	
Cs	100	0.028	0.011	0.072	100	0.031	0.010	0.058	ns	100	0.027	0.025	0.043	100	0.029	0.011	0.072	ns	100	0.029	0.011	0.052	100	0.028	0.011	0.072	ns	
Cu	100	<b>3.7</b>	<b>2.8</b>	<b>17.3</b>	100	<b>3.0</b>	<b>2.5</b>	<b>3.5</b>	**	100	3.9	2.8	6.1	100	3.6	2.9	17.3	ns	100	3.7	2.8	17.3	100	3.7	2.9	6.1	ns	
Dy	100	0.026	0.013	0.042	100	0.026	0.011	0.033	ns	100	0.025	0.021	0.033	100	0.026	0.013	0.042	ns	100	0.027	0.013	0.032	100	0.026	0.016	0.042	ns	
Fe	75	42	<12	262	100	49	22	126	ns	75	39	<12	96	75	48	<12	262	ns	54	23	<12	262	92	46	<12	154	ns	
Ga	54	0.07	<0.06	0.44	75	0.10	<0.06	0.11	ns	50	0.06	<0.06	0.11	55	0.07	<0.06	0.44	ns	77	0.10	0.03	0.14	38	<0.06	<0.06	0.44	ns	
K	8	<40	<40	48	0	<40	<40	<40	-	0	<40	<40	<40	10	<40	<40	48	-	18	<40	<40	48	0	<40	<40	<40	-	
La	100	0.15	0.09	0.48	100	0.14	0.12	1.22	ns	100	0.14	0.11	0.21	100	0.16	0.09	0.48	ns	100	0.14	0.09	0.28	100	0.16	0.12	0.48	ns	
Li	100	<b>0.17</b>	<b>0.10</b>	<b>0.46</b>	100	<b>0.13</b>	<b>0.08</b>	<b>0.15</b>	**	100	0.19	0.12	0.36	100	0.16	0.10	0.46	ns	100	0.15	0.10	0.36	100	0.18	0.11	0.46	ns	
Mg	100	<b>218</b>	<b>198</b>	<b>431</b>	100	<b>207</b>	<b>204</b>	<b>224</b>	*	100	223	203	431	100	217	198	291	ns	100	221	203	431	100	217	198	286	ns	
Mn	100	3.5	2.9	11.6	100	3.3	2.9	3.7	ns	100	3.5	3.2	6.3	100	3.5	2.9	11.6	ns	100	3.5	2.9	6.3	100	3.5	3.0	11.6	ns	
Mo	46	0.3	<0.3	0.9	100	0.3	0.3	0.4	-	50	<0.3	<0.3	0.5	55	0.3	<0.3	0.9	-	64	0.3	<0.3	0.5	23	0.3	<0.3	0.9	-	
Na	100	<b>182</b>	<b>142</b>	<b>315</b>	100	<b>160</b>	<b>139</b>	<b>301</b>	*	100	194	166	315	100	177	142	311	ns	100	181	142	311	100	189	153	315	ns	
Nb	0	<0.04	<0.04	0.05	0	<0.04	<0.04	<0.04	-	0	<0.04	<0.04	0.03	0	<0.04	<0.04	0.05	-	0	<0.04	<0.04	<0.04	15	<0.04	<0.04	0.05	-	
Nd	100	0.10	0.06	1.60	100	0.09	0.07	0.14	ns	100	0.09	0.08	0.13	100	0.10	0.06	1.60	ns	100	0.10	0.06	1.60	100	0.10	0.07	0.21	ns	

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Ni	100	4.8	4.2	9.8	100	4.7	4.4	5.3	ns	100	4.9	4.4	7.1	100	4.8	4.2	9.8	ns	100	4.8	4.3	9.8	100	4.8	4.2	8.4	ns
P	100	275	188	2224	100	263	252	275	-	100	271	234	2224	100	275	188	495	-	100	280	234	2224	100	272	188	347	-
Pb	100	1.6	1.3	5.5	100	1.5	1.4	1.7	ns	100	1.7	1.5	5.5	100	1.6	1.3	2.6	ns	100	1.6	1.4	2.3	100	1.7	1.3	5.5	ns
Pr	100	0.036	0.017	0.364	100	0.035	0.019	0.048	ns	100	0.034	0.030	0.050	100	0.038	0.017	0.364	ns	100	0.038	0.017	0.364	100	0.035	0.024	0.070	ns
Rb	100	0.28	0.20	4.20	100	0.27	0.22	0.50	ns	100	0.31	0.20	4.20	100	0.28	0.20	1.15	ns	100	0.29	0.20	4.20	100	0.27	0.20	0.64	ns
Sb	100	0.11	0.07	0.45	100	0.12	0.07	0.14	ns	100	<b>0.15</b>	<b>0.08</b>	<b>0.45</b>	100	<b>0.11</b>	<b>0.07</b>	<b>0.44</b>	*	100	0.11	0.07	0.45	100	0.11	0.07	0.44	ns
Se	42	1.4	<0.6	4.7	50	1.0	<0.6	3.2	-	25	1.5	<0.6	2.4	50	1.4	<0.6	4.7	-	45	1.3	0.3	3.2	31	1.5	<0.6	4.7	-
Si	0	<270	<270	<270	0	<270	<270	<270	-	0	<270	<270	<270	0	<270	<270	<270	-	0	<270	<270	<270	<270	<270	<270	-	-
Sn	100	0.19	0.12	0.85	100	0.15	0.11	0.25	-	100	0.19	0.13	0.44	100	0.20	0.12	0.85	-	100	0.18	0.12	0.85	100	0.20	0.12	0.70	-
Sr	100	7.0	5.4	10.0	100	6.9	6.4	7.5	ns	100	8	7	8	100	7	5	10	ns	100	7	6	9	100	7	5	10	ns
Tb	92	0.018	<0.006	0.035	75	0.020	<0.006	0.021	ns	100	0.017	0.014	0.020	90	0.018	<0.006	0.035	ns	91	0.019	<0.006	0.025	91	0.017	<0.006	0.035	ns
Te	54	0.05	<0.03	0.14	75	0.03	<0.03	0.08	-	50	0.05	<0.03	0.09	60	0.06	<0.03	0.14	-	36	0.06	<0.03	0.12	77	0.05	<0.03	0.14	-
Ti	100	1.6	1.1	4.2	100	1.8	1.3	2.8	ns	100	1.6	1.1	2.4	100	1.6	1.1	4.2	ns	100	<b>1.5</b>	<b>1.1</b>	<b>2.1</b>	100	<b>1.7</b>	<b>1.3</b>	<b>4.2</b>	*
Tl	54	0.06	<0.06	0.15	75	0.07	<0.06	0.08	-	50	<0.06	<0.06	0.08	55	0.06	<0.06	0.15	-	73	0.08	<0.06	0.10	38	<0.06	<0.06	0.15	-
U	100	<b>0.029</b>	<b>0.019</b>	<b>0.156</b>	100	<b>0.021</b>	<b>0.008</b>	<b>0.025</b>	**	100	0.026	0.019	0.141	100	0.029	0.019	0.156	ns	100	0.027	0.019	0.068	100	0.030	0.019	0.156	ns
V	100	<b>0.53</b>	<b>0.35</b>	<b>1.37</b>	100	<b>0.23</b>	<b>&lt;0.08</b>	<b>0.34</b>	***	100	0.49	0.40	0.57	100	0.55	0.35	1.37	ns	100	<b>0.52</b>	<b>0.35</b>	<b>0.68</b>	100	<b>0.56</b>	<b>0.40</b>	<b>1.37</b>	*
W	100	1.1	0.9	2.4	100	1.0	0.9	3.6	ns	100	1.1	0.9	1.8	100	1.0	0.9	2.4	ns	100	1.1	0.9	1.8	100	1.1	0.9	2.4	ns
Zn	100	445	417	492	100	446	432	462	ns	100	451	433	488	100	442	417	492	ns	100	436	430	492	100	448	417	483	ns
Zr	100	<b>0.2</b>	<b>0.1</b>	<b>1.5</b>	100	<b>0.1</b>	<b>0.1</b>	<b>0.2</b>	*	100	0.2	0.1	1.5	100	0.2	0.1	0.7	ns	100	<b>0.1</b>	<b>0.1</b>	<b>0.5</b>	100	<b>0.2</b>	<b>0.1</b>	<b>1.5</b>	*

527<sup>a</sup> EVOO, extra virgin olive oils.

528<sup>b, c, d</sup> Non-parametric Mann Whitney test was applied: ns = not significant at  $p > 0.05$ ; \* =  $p < 0.05$ ; \*\* =  $p < 0.01$ ; \*\*\* =  $p < 0.001$ . Numbers in bold in the same row indicate significant differences ( $p < 0.05$ ).

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530**Table 4.** Summary of sample treatment procedures that give a repeatability and trueness bias percentage for  
531the certified elements in oil CRM within 15%.

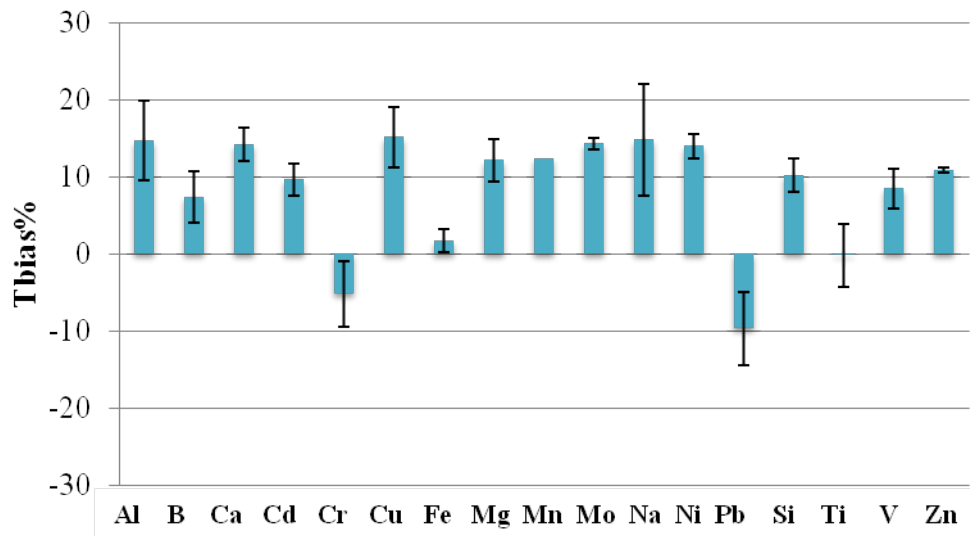
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Elemen t	WD (95 °C)			USE (19 °C)		
	10 min	20 min	40 min	10 min	20 min	40 min
<b>Ag</b>	5 mL A	5 mL A	5 mL A	–	–	–
<b>Al</b>	0.5 mL B; 1 mL B or F; 5 mL A, B, E and F	1 mL A, B and F; 5 mL A or B	0.5 mL A, B, E and F, 1 mL A, B and F; 5 mL A or F	1 mL B, C and F; 5 mL B	0.5 mL B; 1 mL A, B and C, F; 5 mL B	0.5 mL A or B; 1 mL A, C and F; 5 mL A or B
<b>B</b>	0.5 mL or 1 mL B and F; 5 mL A, B, E and F	0.5 mL B; 1 mL F; 5 mL A, B, E and F	0.5 mL B, E and F; 1 mL A, B and F; 5 mL A, B, E and F	1 mL B or F; 5 mL B	0.5 mL B; 1 mL A or F; 5 mL A or B	0.5 mL B; 1 mL B, C and F; 5 mL A or B
<b>Ba</b>	–	–	5 mL B	–	–	–
<b>Ca</b>	0.5 mL or 1 mL B and F; 5 mL A, B, E and F	0.5 mL B or F; 1 mL A or F; 5 mL A, B, E and F	0.5 mL B or F; 1 mL or 5 mL A, B and F	1 mL F	0.5 mL B; 1 mL A or F; 5 mL A, B and E	0.5 mL or 1 mL B and F; 5 mL B
<b>Cd</b>	0.5 mL B; 1 mL B or F; 5 mL A, B, E and F	0.5 mL B and F or 1 mL F; 5 mL A, B, E and F	0.5 or 1 mL B and F; 5 mL A, B, E and F	1 mL B or F; 5 mL B	0.5 mL A or B; 1 mL A, B and F; 5 mL B	0.5 mL A or B; 1 mL B or F; 5 mL A or B
<b>Cr</b>	5 mL A, B and E	5 mL A, B, E and F	1 mL B; 5 mL A, B, E and F	–	–	–
<b>Cu</b>	0.5 or 1 mL B and F; 5 mL A, B, E and F	0.5 mL B or F; 1 mL B, E and F; 5 mL A, B, E and F	0.5 mL or 1 mL B and F; 5 mL A, B, E and F	1 mL A, B, C and F; 5 mL B	0.5 mL B; 1 mL A, B, C and F; 5 mL B	0.5 mL or 1 mL B and F; 5 mL A and B
<b>Fe</b>	0.5 or 1 mL B; 5 mL A or B	0.5 or 1 mL B; 5 mL A, B and F	0.5 mL or 1 mL B; 5 mL A, B and F	5 mL B	5 mL B	0.5 mL B; 1 mL or 5 mL A and B
<b>Mg</b>	0.5 or 1 mL B and F; 5 mL A, B, E and F	0.5 mL B or F; 1 mL B; 5 mL A, B, E and F	0.5 mL or 1 mL B; 5 mL A, B, E and F	1 mL B or F; 5 mL B	0.5 mL A or B; 1 mL B or F; 5 mL B	0.5 mL or 1 mL A, B and F; 5 mL A and B
<b>Mn</b>	0.5 mL or 1 mL B and F; 5 mL A, B, E and F	0.5 mL B or F; 1 mL A, B and F; 5 mL A, B, E and F	0.5 mL B or F; 1 mL A, B and F; 5 mL A, B, E and F	1 mL B or F; 5 mL B	0.5 mL B; 1 mL A, B and F; 5 mL B	0.5 mL or 1 mL B or F; 5 mL A or B
<b>Mo</b>	0.5 mL B or E; 1 mL B, E and F; 5 mL A, B, E and F	0.5 mL B; 1 mL E or F; 5 mL A, B, E and F	0.5 mL B or E; 1 mL B, E and F; 5 mL A, B, E and F	1 mL B or F; 5 mL B	0.5 mL B; 1 mL F; 5 mL A or B	0.5 mL B or F; 1 mL F; 5 mL A or B
<b>Na</b>	0.5 mL F; 1 mL B or F; 5 mL A	0.5 mL F; 5 mL B	0.5 mL F; 1 mL B or F; 5 mL A, B and F	1 mL B or F; 5 mL B	1 mL A, B and F	0.5 mL B or F; 1 mL A, B and F; 5 mL B
<b>Ni</b>	0.5 mL or 1 mL B and F; 5 mL A, E and F	0.5 mL or 1 mL B and F; 5 mL A, B, E and F	0.5 mL or 1 mL B and F; 5 mL A, B, E and F	1 mL B or F; 5 mL B	0.5 mL A or B; 1 mL A, B and F; 5 mL B	0.5 mL A, B and F; 1 mL B or F; 5 mL A or B
<b>P</b>	–	–	–	–	–	–
<b>Pb</b>	5 mL A or B	1 mL A; 5 mL A or B	1 mL A or B; 5 mL B or F	–	5 mL A	1 mL C or F; 5 mL A or B
<b>Si</b>	5 mL B, C, D, E and F	5 mL A, B, E and F	5 mL A, B, C, E and F	5 mL A, B, C, D, E and F	5 mL A, B, C, E and F	5 mL A, B, C, D, E and F
<b>Sn</b>	5 mL A	5 mL A	5 mL A	–	–	–
<b>Ti</b>	5 mL A or B	5 mL A, B and F	1 mL F; 5 mL A, B and F	–	–	1 mL F; 5 mL A
<b>V</b>	0.5 mL B; 1 mL B, E and F; 5 mL A, B, E and F	0.5 mL B; 1 mL A, E and F; 5 mL A, B, E and F	0.5 mL B, E and F; 1 mL A, B and F; 5 mL A, B, E and F	1 mL B or F; 5 mL B	0.5 mL B; 1 mL C or F; 5 mL A or B	0.5 mL B or F; 1 mL C or F; 5 mL A or B
<b>Zn</b>	0.5 or 1 mL B and F; 5 mL A, B, E and F	0.5 mL B or F; 1 mL F; 5 mL A, B, E and F	0.5 mL or 1 mL B and F; 5 mL A, B, E and F	1 mL B or F; 5 mL B	0.5 or 5 mL B; 1 mL F	0.5 mL B or F; 1 mL C or F; 5 mL A or B

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536**Figure 1.** Trueness bias percentage with standard deviation for the certified elements in oil CRM by WD (5  
537mL reagent mixture F; 95 °C; 40 min).