Journal of Food Composition and Analysis 112 (2022) 104675

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Determination of $^{87}Sr/^{86}Sr$ isotopic ratio in olive oil and pomace using multicollector-ICPMS: Analysis of pomace residues as a simpler approach for determination of $^{87}Sr/^{86}Sr$ ratio in olive oil with low Sr content

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ARTICLE INFO

Keywords:
Sr isotopic ratio ($^{87}Sr/^{86}Sr$)
Olive oil
Pomace
Multicollector-ICPMS
Liquid-liquid extraction
Traceability
Food origin

ABSTRACT

This study presents an analytical procedure for measuring the $^{87}Sr/^{86}Sr$ isotopic ratio in olive oil and pomace using multicollector-inductively coupled mass spectrometry (MC-ICPMS). The developed method combines liquid-liquid extraction with an acid solution and degradation of organic residues in the extract by dry ashing and oxidation by H_2O_2 and HNO_3. The method enabled $^{87}Sr/^{86}Sr$ ratios to be obtained in olive oil with Sr content as low as 0.2 ng g^{-1}, with a precision of 54 ppm. The method's validity was confirmed by an interlaboratory comparison using NIST SRM 2387, providing the first data on its elemental Sr (2380 ± 230 ng g^{-1}; n = 10), and $^{87}Sr/^{86}Sr$ isotopic composition (0.70908 ± 0.00004; n = 14). The procedure was applied to olive oil and pomace samples, showing that they have an identical $^{87}Sr/^{86}Sr$ ratio, which was consistent with that determined in soils from the same orchards. The results thus revealed that Sr isotopic ratios of olive oil and pomace can both be used in geographical traceability studies of olive oil, which means that, instead of processing large volume of oil, characteristic $^{87}Sr/^{86}Sr$ signatures of olive oil can be more easily obtained by analyzing small quantities of pomace obtained by centrifuging the oil.

1. Introduction

Olive oil is an important ingredient in a well-balanced nutritional Mediterranean diet. Its consumption continues to increase due to its well-known nutritional value, sensory properties and beneficial health effects (Cabrera-Vique et al., 2012; Janin et al., 2014; Kalogiouri et al., 2020). The quality of olive oil depends on its composition, which is determined by factors such as production process, cultivar, climate and soil characteristics (Boskou et al., 2006; Janin et al., 2014). Consequently, the quality of olive oil may differ between various olive orchards and regions, which mean that its market value is often related to its geographical origin. Thus, both consumers and producers demand the labelling of olive oil, which would enable easy recognition of its quality and guarantee its market value. In the European Union, this was achieved through the Regulations (EC) No 29/2012 and No 510/2006, which set specific standards for the marketing of olive oil, including those with Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI). Since coming into force, a great deal of effort has gone into protecting and verifying PDO labelling, but olive oil's high commercial value continues to make it a target of fraud.

Authentication and fraud detection of olive oil is challenging from an analytical point of view because they imply searching for region-specific indicators. Current analytical methodologies are mainly based on determining organoleptic characterization, triglyceride and fatty acid composition, volatile compounds, DNA markers, and ratios of isotopes of light elements (Janin et al., 2014; Medini et al., 2015). In other studies, the distribution pattern of elements has been demonstrated as a potential traceability tool (Benincasa et al., 2007; Camin et al., 2010a;

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https://doi.org/10.1016/j.jfca.2022.104675
Received 2 December 2021; Received in revised form 5 May 2022; Accepted 4 June 2022
Available online 7 June 2022

Zeiner et al., 2005; Damak et al., 2019). The main problem of this approach is that certain elements may be of both natural and anthropogenic origin due to soil contamination, fertilization or contamination during production and storage (Cabrera-Vique et al., 2012; Pošćić et al., 2019). However, all these methods allow only the discrimination of olive oil among various cultivars or adulterated products but they do not provide clear identification of its geographical origin. So far, a reliable protocol for geographical authentication is yet to be adopted, and the authorities are face with the difficult task of verifying PDO labelling. Recently, studies have focused on a more innovative approach such as using the $^{87}Sr/^{86}Sr$ isotopic ratio as a geological tracer that reflects the underlying geology and serves as a reliable region-specific marker (Janin et al., 2014). To date, the $^{87}Sr/^{86}Sr$ methodology has been successfully applied to various food products such as wine (Petrini et al., 2015; Vinciguerra et al., 2016; Durante et al., 2018; Epova et al., 2019), orange juice (Rummel et al., 2010), asparagus (Swoboda et al., 2008), coffee (Techer et al., 2011), ham (Epova et al., 2018), cheese (Fortunato et al., 2004; Stevenson et al., 2015), and rice (Song et al., 2014). Unfortunately, none of these protocols can be applied to olive oil because of significant differences in matrix composition; namely, olive oil is a lipid matrix rich in organic matter, with triacylglycerols accounting for ~ 99% of the whole organic matter (Boskou et al., 2006; Alcaide-Hidalgo et al., 2020). At present, the only protocol developed for determining $^{87}Sr/^{86}Sr$ in olive oil using thermal ionization mass spectrometry (TIMS) (Medini et al., 2015); however, this method is labour-intensive and requires lengthy heating and sample carbonization, and, most importantly, does not apply to olive oils with low Sr concentration (< 1.5 ng g^{-1}), which is often the case. Therefore, a better protocol for obtaining $^{87}Sr/^{86}Sr$ isotopic ratios of olive oils would be a boon for both the scientific community and state laboratories.

Developing a method for measuring the $^{87}Sr/^{86}Sr$ isotopic ratio in olive oil is challenging for several reasons. First, due to its hydrophilic nature, Sr is present in olive oil in very low amounts (< 50 ng g^{-1}) but rarely exceed 0.3 ng g^{-1} (Benincasa et al., 2007; Medini et al., 2015; Damak et al., 2019; Pošćić et al., 2019; Camin et al., 2010b), which means that a large volume sample (up to 1 L) has to be processed to extract a sufficient amount of Sr for isotopic analysis (approximately 50 ng). Consequently, most techniques used for digestion and elemental analysis of olive oil, such as commonly used microwave digestion (MWD), wet digestion or dry ashing, are not suitable pre-treatment methods for $^{87}Sr/^{86}Sr$ analysis because they can only handle 0.5–5 g per analysis. Organic residues remaining in the extract are also problematic because they can amplify or suppress the ICP signal during analysis (Astolfi et al., 2021b), reducing measurement precision (Liu et al., 2016).

In the search for a pre-treatment method that can handle large sample volumes and provide an adequate amount of Sr for $^{87}Sr/^{86}Sr$ analysis, liquid-liquid extraction (LLE) appears to be a technique that could overcome this limitation. Recently, LLE proven to be a simple and sensitive method for extracting elements from olive oil (Pošćić et al., 2019; Astolfi et al., 2021b); however, the critical point is to obtain an extract free of oily residues.

Some olive oils, especially those that do not undergo double-filtration, may contain pomace residues. Pošćić et al. (2019) have shown that these pomace particles, even when present in small quantities (1 g of pomace in 1 kg of oil) can significantly alter not only the concentrations but also the relative proportions of many elements in the oil, including Sr. These particles are rich in Sr and have concentrations that are up to 90,000 times higher compared to those in pure oil (Pošćić et al., 2019). Given this fact, while assuming that both the oil and the pomace have the same $^{87}Sr/^{86}Sr$ isotopic ratios, the specific $^{87}Sr/^{86}Sr$ isotopic signature of olive oil could be more easily determined by analyzing pomace residues rather than processing large quantities of oil, which could significantly simplify the authentication of olive oil with low Sr content.

This study developed and validated an analytical procedure to determine the $^{87}Sr/^{86}Sr$ isotopic ratio in olive oil and pomace using multicollector-inductively coupled mass spectrometry (MC-ICPMS). It also tests the hypothesis that olive oil and pertaining pomace have the same $^{87}Sr/^{86}Sr$ ratios, and therefore, both could be used for determining the origin of olive oil. The method's accuracy was evaluated by conducting an interlaboratory comparison using certified reference material NIST SRM 2387 (Peanut butter, NIST, USA). Finally, the method was applied to several olive oil and pomace samples, while its potential applicability in traceability studies was tested by determining the $^{87}Sr/^{86}Sr$ ratio of soils from the corresponding olive orchards.

2. Materials and methods

2.1. Experimental design

The experiment was designed with two critical points in mind: (i) to obtain an adequate amount of Sr from the oil needed for isotopic analysis (≈ 50 ng), and (ii) the purification of the extract before MC-ICPMS analysis. The first step was to define a protocol for extracting Sr from oil and pomace. For this, LLE was chosen, assuming that this method can process large volumes of oil in a single step. The LLE protocol, based on that reported by Pošćić et al. (2019), was tested and optimized, using different types of agitation - mechanical shaking and ultrasound-assisted agitation as well as duration. The results were compared with MWD, which served as a reference method to control the extraction rate of Sr.

In the second step, a protocol for eliminating the remaining organic matter and purifying the digest/extract was established; here, degradation of the organic matter by oxidation with H_2O_2 and HNO_3, MWD and dry ashing of the organic residues were tested. The experimental design is shown in Fig. 1.

2.2. Sample collection

2.2.1. Oil samples

Olive oil samples were obtained from eight olive orchards (S, C1, C2, T1, T2, T3, T4 and T5) originating from three Mediterranean countries: Slovenia, Croatia, and Tunisia (assignment: S, C and T, respectively). All olive oil samples were of "extra virgin" quality and originated from orchards with guaranteed traditional "biological" agricultural practices so the influence of fertilizers could be excluded.

Slovenian olive oil (S), originating from an olive orchard in Izola, was produced by cold pressing and ultra-centrifugation technique in a local mill. This oil has a low content of Sr (Table 1; 0.19 ± 0.04 ng g^{-1} ($n = 12$). Croatian olive oils C1 (Dalmatia) and C2 (Istria) were produced in the laboratory, as described by Pošćić et al. (2019). These oils have very low Sr concentration, below 0.05 ng g^{-1} (Table 1). Such low Sr concentrations were also reported in other studies (Pošćić et al., 2019; Camin et al., 2010a). Tunisian olive oil samples were obtained from five different regions: Sfax (T1), Kairouan (T2), Zarzis (T3), Kasserine (T4), and Jendouba (T5), and were produced using traditional methods. These oils have relatively high Sr concentrations (< 6 ng g^{-1}; Table 1), being few times lower than Sr concentrations in Tunisian olive oils reported by Damak et al. (2019), but comparable to those reported in European olive oils (Nasr et al., 2022; Camin et al., 2010b).

2.2.2. Pomace samples

The pomace samples corresponding to Croatian oils (C1 and C2) represent dried pomace obtained after separating olive oil from the olive paste during the production process in the laboratory (described in Pošćić et al., 2019). Olive pomace from Slovenia and Tunisia represents the dried pomace particles obtained by centrifuging the oil (S, T1, and T2) at 8000 rpm for 10 min.

2.2.3. Soil samples

Soil samples were collected in Slovenian and Croatian olive orchards. Approximately 250 g of soil was collected per site from a depth down to

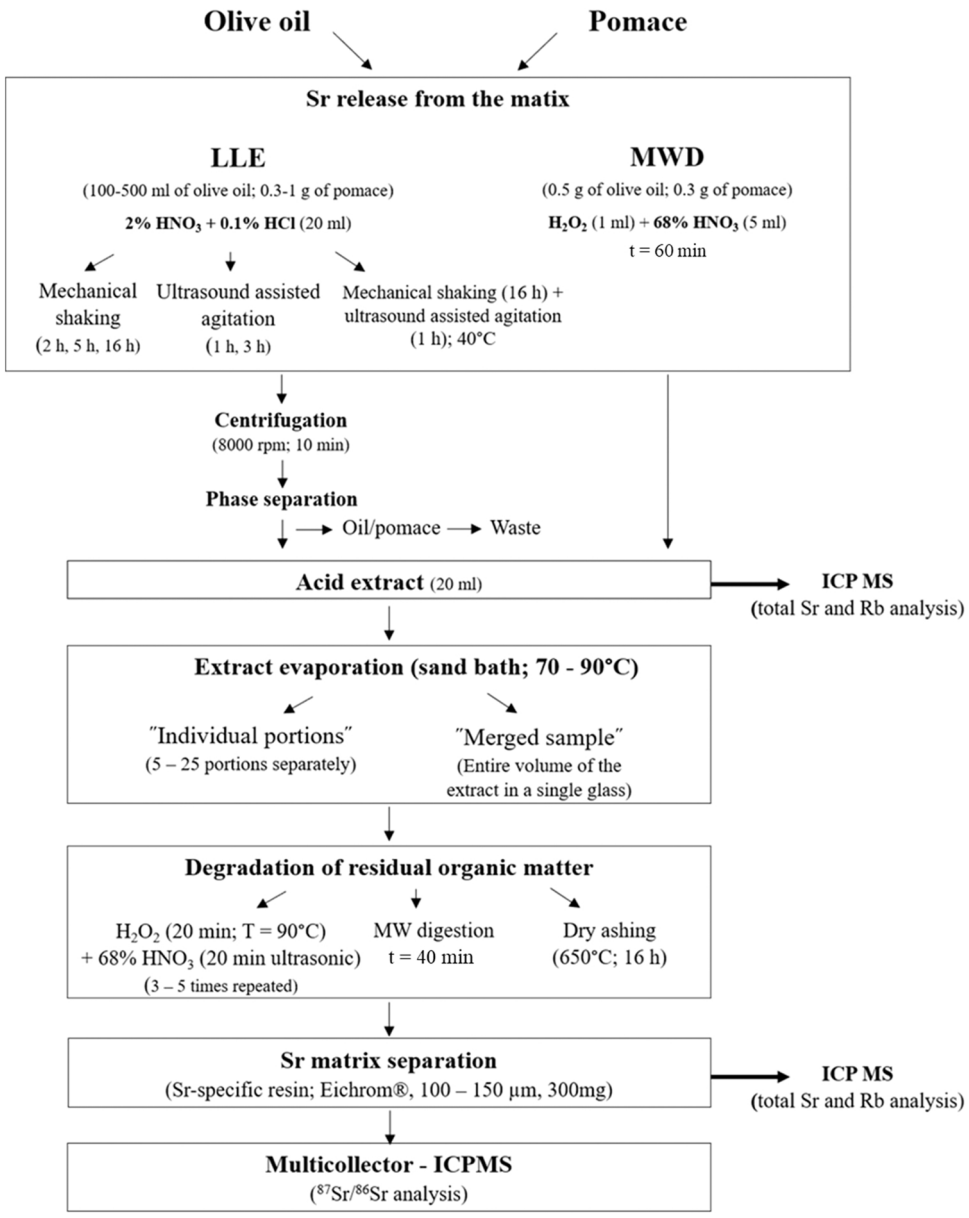

Fig. 1. The scheme of the methods´ development.

30 cm. The samples were air-dried and sieved (2 mm).

2.3. Extraction of Sr from the olive oil and pomace

Olive oil samples were centrifuged at 8000 rpm for 10 min to separate pomace particles from the oil. This is important because pomace residues in oil could significantly alter the Sr composition of the oil, as demonstrated by Pošćić et al. (2019). After centrifugation, the supernatant was carefully removed and both (oil and pomace) were used in the further procedure. Notably, no pomace residues were obtained for Tunisian oils (T3, T4, T5).

2.3.1. Microwave digestion (MWD)

Olive oil (0.5 g) and pomace samples (0.3 g) were mineralized in the closed vessel microwave digestion system (MARS6, CEM Corporation, USA) with a mixture of 1 mL of H_2O_2 (30%, *v/v*, *suprapur*, Merck) and 5 mL of HNO_3 (68%, *v/v*, *suprapur*, Carlo Erba Reagents), with a heating program as follows: 20 min of ramp time to 140°, followed by hold time of 5 min, and then ramp time to 210 °C, with a final hold of 25 min at the highest temperature. The samples were kept in the digestion solution overnight before being digested. The digested samples were quantitatively transferred to vials and diluted with Milli-Q water to a final volume of 20 mL. In all samples, the total Sr and Rb concentrations were measured by ICPMS. Special attention was paid to cleaning PTFE vessels between the mineralization cycles, and a blank sample was run during each cycle.

2.3.2. Liquid-liquid extraction (LLE)

2.3.2.1. Olive oil. Each olive oil sample (100–500 mL) was divided into sub-samples of 20 mL. To each sub-sample was added 20 mL of acid solution containing 2 % HNO_3 (68 %, *v/v*, *suprapur*, Carlo Erba Reagents) and 0.1 % HCl (30 %, *v/v*, *suprapur*, Merck). The extraction was performed by (i) mechanical shaking at 300 rpm for 2 h, 5 h and 16 h; (ii) ultrasound-assisted agitation (1100 W, 50 Hz) for 1 h and 3 h, and (iii) mechanical shaking for 16 h, followed by ultrasound-assisted agitation in an ultrasonic bath at 40 °C for 1 h. All mixtures were centrifuged at 8000 rpm for 10 min. The upper oil phase was then

Table 1
Strontium concentrations obtained by LLE (value ± σ) and $^{87}Sr/^{86}Sr$ ratios (value ± 2σ) in olive oil and pomace samples, and Sr recoveries calculated after column separation.

	Origin	Type of sample	Sr concentration (ng g^{-1})	$^{87}Sr/^{86}Sr$	Sr recovery[a] (%)
S	Slovenia, Isola	oil	0.19 ± 0.04	*not performed*[b]	–
		pomace	508 ± 57	0.70840 ± 0.00014	82
		soil	13,200 ± 120	0.70842 ± 0.00007	92
C1	Croatia, Dalmatia	oil	0.033 ± 0.02	*not performed*[b]	–
		pomace	1180 ± 65	0.70834 ± 0.00001	85
		soil	7070 ± 56	0.70850 ± 0.0001	95
C2	Croatia, Istria	oil	0.041 ± 0.02	*not performed*[b]	–
		pomace	1090 ± 13	0.71074 ± 0.00004	85
		soil	1940 ± 29	0.71071 ± 0.00009	95
T1	Tunisia, Sfax	oil	3.10 ± 0.25	0.70872 ± 0.00008	91
		pomace	536 ± 42	0.70860 ± 0.00006	85
T2	Tunisia, Kairouan	oil	0.66 ± 0.09	0.70820 ± 0.00010	94
		pomace	1090 ± 160	0.70820 ± 0.00003	89
T3	Tunisia, Zarzic	oil	5.93 ± 0.02	0.70905 ± 0.00006	90
T4	Tunisia, Kasserine	oil	0.25 ± 0.02	0.70982 ± 0.00008	92
T5	Tunisia, Jendouba	oil	0.14 ± 0.02	0.71057 ± 0.00007	91
Quality Control	SRM NIST 2387	LLE[c]	1560 ± 300	0.70909 ± 0.00003	85
		MWD[c]	2380 ± 230	0.70906 ± 0.00004	91

Note:
[a] Final Sr recovery obtained after the column separation;
[b] $^{87}Sr/^{86}Sr$ analysis could not be performed due to insufficient amount of sample;
[c] Method of sample preparation

carefully removed to a clean vial using a pipette.

2.3.2.2. Pomace. To each pomace sample (0.3–1 g), 10 mL of acid solution (2 % HNO_3 and 0.1 % HCl) was added. The extraction was performed by (i) mechanical shaking at 300 rpm for 16 h, and (ii) ultrasound-assisted agitation (1100 W, 50 Hz) for 1 h. The mixtures were then centrifuged at 8000 rpm for 10 min to precipitate the pomace from the extract. All extracts were filtered using pre-washed syringe cellulose-acetate filters (0.45 μm), previously washed with 10 mL of the extracting solution. In all extracts, the total Sr and Rb concentrations were measured by ICPMS.

2.4. The analytical procedure for organic matter removal from the extract

Obtained acid extracts of oil (100–500 mL) and pomace (10–20 mL) were evaporated to dryness on a sand bath at 70–90 °C. For evaporation of large volumes of olive oil extracts, two procedures were tested: (i) evaporation of separate 20 mL portions (5–25 portions) in PFA vials, which were later combined on the column ('individual portions'), and ii) evaporation of the entire extract volume, combining all portions in a single quartz glass during evaporation ('merged sample'). The residual organic matter, i.e., the yellow/dark brown residue, was subjected to degradation following three different procedures: (i) oxidation with H_2O_2 and HNO_3 on the sand bath, (ii) MWD, and (iii) dry ashing.

2.4.1. Degradation of residual organic matter by oxidation with H_2O_2 and HNO_3

Once the acid had evaporated, 0.5–1.5 mL of H_2O_2 (30 %, *v/v*, *suprapur*, Merck) was added to each PFA vial or quartz glass, and the sample was heated on the sand bath (T = 90 °C) for 25 min. Then, 1–2 mL of HNO_3 (68 %, *v/v*) was added, and the sample was sonicated for 20 min and evaporated again. The whole procedure was repeated 3–5 times until there was no visible precipitate or only a stain of up to 1 mm in size remained. The samples were then dissolved in 0.5–1.5 mL of 8 M HNO_3 to be convenient for subsequent Sr-matrix separation on the Sr-resin (0.5 mL in the case when the extract portions were evaporated separately or 1.5 mL in the case when the entire extract was evaporated in a single quartz glass).

2.4.2. Degradation of residual organic matter by microwave digestion

The residual organic matter was degraded using a closed vessel microwave digestion system (Ultrawave Milestone, Italy). First, the evaporated extracts were treated with a small volume (0.3–1 mL) of H_2O_2 (ultra-trace grade, 30 %) and kept at 95 °C for 2 h. Then, 0.5–2 mL of HNO_3 (Ultrex quality, 70 %) were added, and the samples were heated at 95 °C for 30 min. Finally, the samples were quantitatively transferred into a quartz Ultrawave tube. When extracts of the same oil were evaporated separately, the extracts were combined into a single tube. The digestion program was as follows: 20 min of ramp time to 220 °C, followed by a hold time of 20 min. The acid was then evaporated in a sand bath (T = 70–90 °C), and the residues were dissolved in 2 mL of 8 M HNO_3 for subsequent Sr-matrix separation on Sr-spec resin.

2.4.3. Degradation of residual organic matter by dry ashing

The residual organic precipitate was calcined in a muffle furnace (Bosio EUP-K series, Slovenia). The temperature was ramped by 1.5 °C min^{-1} to 650 °C and held there until white ash was obtained. The ash was then dissolved in 5 mL of HNO_3 (68 %, *v/v*) and sonicated for 20 min. The acid was then evaporated in a sand bath (T = 70–90 °C), and the samples were dissolved in 2 mL of 8 M HNO_3 for subsequent Sr-matrix separation on Sr-specific resin.

2.5. Chromatographic Sr-matrix separation

Strontium was isolated from concomitant matrix elements, i.e. to remove potential isobaric interferences, using column chromatography with a Sr-specific resin. The columns were prepared by packing 0.3 g of Sr-spec resin (Eichrom®, 100–150 μm particle size, Triskem International, France) into polypropylene SPE columns with polyethene frits (2 mL, Triskem International, France).

The separation procedure was optimized as follows, with a constant flow of approximately one drop per second: (i) washing the column sequentially with 3 mL of Milli-Q water, 1 mL of 6 M HCl, and 10 mL of Milli-Q water; (ii) activation of the column by eluting with 3 mL of 8 M HNO_3; (iii) loading of the sample in 8 M HNO_3; (iv) elution of Rb and other matrix elements with 3 mL of 8 M HNO_3, and (v) elution of Sr with 10 mL of Milli-Q water. The used resin was not recycled.

After separation, total Sr and Rb were measured using ICPMS to control Sr recovery and check whether Rb was effectively removed. If not, the chromatographic separation was repeated. The calculated Sr recovery represents the ratio between Sr concentrations measured in the eluent after chromatography and the initial extract before evaporation.

If necessary, samples were concentrated by evaporation before analysis.

2.6. Determination of $^{87}Sr/^{86}Sr$ isotopic ratios in soil

The $^{87}Sr/^{86}Sr$ isotopic ratio was determined in the bioavailable fraction of soils following the method described in Hoogewerff et al. (2019). Briefly, Sr was extracted from approximately 1 g of soil with 20 mL of 1 M NH_4NO_3 and mechanical shaking for 2 h. The samples were then centrifuged for 15 min at 8000 rpm, and the supernatant was filtered using a pre-washed (10 mL extracting solution) cellulose-acetate membrane syringe filter (0.45 μm; Sartorius, Germany). An appropriate amount of the supernatant was evaporated on the sand bath (T = 70–90 °C) to dryness before being dissolved in 1 mL of 8 M HNO_3. The samples were then sonicated for 30 min and transferred to a column filled with Sr-specific resin. Extract purification was performed following the same procedure as described in 2.5. Finally, the $^{87}Sr/^{86}Sr$ isotopic ratio in the extracts was measured using MC-ICPMS.

2.7. Determination of total Sr and Rb concentrations using quadrupole ICPMS

Strontium and Rb concentrations were analyzed using a quadrupole ICPMS (7900x, Agilent Technologies, Japan). Typical instrument conditions and measurement parameters used throughout the work are reported elsewhere (Hamzić Gregorčič et al., 2021). Rhodium (Rh) was used as the internal standard (ICP Standard Certipur, Merck), whereas quantification was performed by the external calibration prepared by appropriate dilution of Sr and Rb standard solutions (ICP Standard Certipur, Merck). Quality control was performed by simultaneously analyzing the certified reference material for trace elements in surface water SPS-SW1 (Spectrapure standards, Oslo, Norway). A good agreement between the analyzed and certified concentrations, within their analytical uncertainties, was obtained for both elements (RSD = 10%). The LOD for Sr and Rb were 0.005 and 0.003 ng mL^{-1}, respectively.

2.8. Determination of $^{87}Sr/^{86}Sr$ isotopic ratios using MC-ICPMS

Strontium isotope ratios were measured using MC-ICPMS in two laboratories – at Jožef Stefan Institute (JSI, Slovenia) and Advanced Isotopic Analysis (AIA, France).

2.8.1. JSI (Slovenia)

The Sr isotope ratios were determined on a Nu II MC-ICP-MS (Nu Instruments, Ametek Inc., UK). The sample was introduced using the Aridus desolvation system and PFA nebulizer (100 μL min^{-1}), and nickel plasma cones were used for dry plasma. Typical instrumental conditions, measurement parameters, and all necessary corrections used are reported elsewhere (Zuliani et al., 2020). The isotopic standard reference material NIST SRM 987 (pure $SrCO_3$, NIST, USA) was used for the bracketing standard, with a normalization value of 0.710255 ± 0.000023 (Waight et al., 2002). The operating parameters of the MC-ICPMS were optimized daily using a standard NIST SRM 987 solution with a concentration of 25 μg L^{-1} to achieve the maximum sensitivity and stability for Sr beam. The typical signal for the isotope ^{88}Sr was 12 V. The external reproducibility for Sr isotope ratio measurement was equivalent to 30 ppm (calculated as standard deviation with a 95 % confidence interval of 25 individual measurements of the NIST SRM 987 solution (30 μg L^{-1})). The analysis time per sample was 20 min, whereas the sensitivity was 300 V/ppm ^{88}Sr. To ensure a high precision and accuracy the concentration of Sr in the final extract was not lower than 5 ng mL^{-1}.

2.8.2. AIA (France)

Sr isotope ratios were determined on a Nu Plasma I MC-ICPMS (Nu Instruments Ametek Inc., UK) equipped with a cyclonic spray chamber, a micro-concentric nebulizer (flow rate of 200 μL min^{-1}), and nickel plasma cones (Type A). Typical instrumental conditions, measurement parameters, and all necessary data corrections are reported by Epova et al. (2019). The isotopic standard reference material NIST SRM 987 (pure $SrCO_3$, NIST, USA) was used as the bracketing standard. The average measured value was 0.710255 ± 0.000026, which is in good agreement with the reference value of 0.710255 ± 0.000023 (Waight et al., 2002). The external reproducibility for Sr isotope ratio measurement was equivalent to 37 ppm, calculated as the standard deviation with a 95 % confidence interval of 44 individual measurements of the NIST SRM 987 solution (100 μg L^{-1}) under daily optimized conditions.

3. Results and Discussion

3.1. Development of Sr extraction method for olive oil and pomace

3.1.1. Olive oil

To evaluate the efficiency of LLE, the concentrations of Sr obtained by LLE and MWD were compared. The MDW was here adopted as a reference method because it is an established and commonly used method for elements' determination in oil samples. The measured Sr concentrations in the olive oil S are presented in Fig. 2a. The highest Sr concentration (0.63 ± 0.05 ng g^{-1}) was obtained using MWD. In this case, the high operating pressure and temperature promote the destruction of long-chain aliphatic molecules of fatty acids by oxidation with HNO_3 and H_2O_2, which resulted in a higher release of Sr from the oil matrix.

The best Sr extraction among the three tested LLE protocols was achieved when combining mechanical shaking for 16 h and ultrasonic stirring for 1 h at 40 °C, resulting in 0.35 ± 0.04 ng g^{-1}, which corresponded to 56 % of the Sr released by MWD. The other two LLE protocols

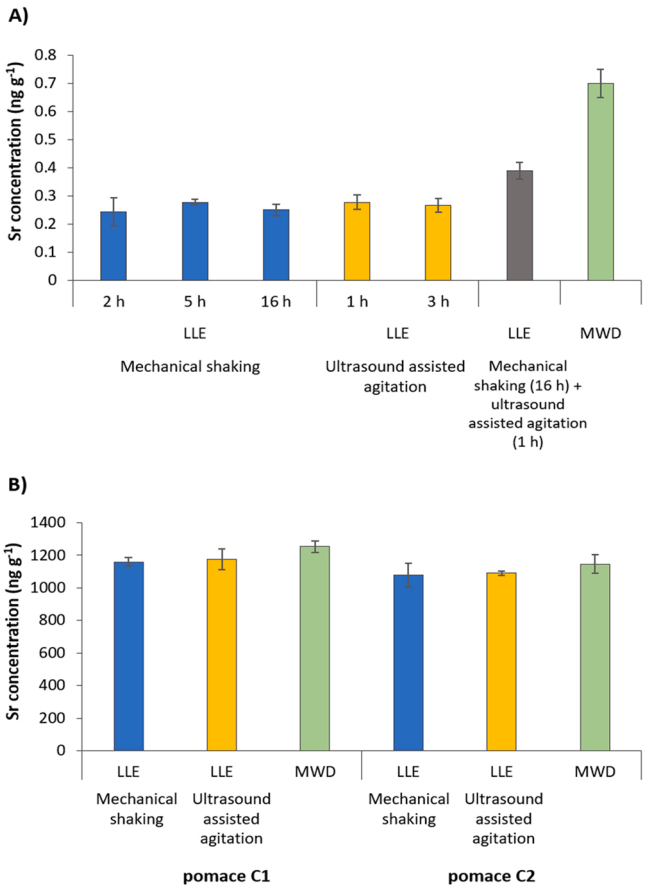

Fig. 2. The Sr concentration in olive oil S (**a**) and pomace C1 and C2 (**b**) obtained by different extraction protocols.

showed lower performance corresponding to Sr levels 35–40 % of that obtained by MWD and were similar regardless of the agitation mode (mechanical or ultrasound) and time (Fig. 2a). However, neither vigorous shaking nor ultrasonic agitation could mix these two immiscible phases sufficiently. The oil droplets were formed and dispersed in an emulsion so that the Sr, which is probably bound to phospholipids that are considered metal scavengers (Boskou et al., 2006), is only partly available for extraction by the acid solution. Nonetheless, Sr extraction was enhanced when both agitation modes were used, and the temperature was increased to 40 °C. The higher temperature reduces the surface tension between liquids (Valasques et al., 2017) and alters the emulsion characteristics, i.e. viscosity and droplet size (Goodarzi and Zendehboudi, 2019), which resulted in better phase mixing and more efficient Sr extraction. Although other studies using similar protocols (i.e. Camin et al., 2010; Pošćić et al., 2019) reported that ion exchange between two phases was completed in less than 30 min, our experiment demonstrated that further optimization of extraction parameters, namely longer extraction time, was needed to assure a high Sr recovery.

To summarize, it was shown that the proposed LLE could be considered as an adequate pre-treatment procedure for $^{87}Sr/^{86}Sr$ analysis of olive oil because it allows the processing of large sample volumes, thereby overcoming the disadvantage of lower Sr recovery and providing a sufficient amount of Sr for analysis.

3.1.2. Pomace

Three different methods were tested for Sr extraction from pomace: MWD, LLE by mechanical shaking for 16 h, and LLE using ultrasonic stirring for 1 h. The measured Sr concentrations ranged from 1160 to 1250 ng g^{-1} for pomace C1, and from 1080 to 1150 ng g^{-1} for pomace C2 (Fig. 2b). The results revealed that all three techniques had similar efficiency, with MWD only slightly better (approximately 5%) than LLE.

3.1.3. Quality control of total Sr analysis

Quality control for elemental analysis of olive oil is problematic because suitable standard reference materials (SRM) for Sr concentrations in edible oil do not exist. However, a similar fatty matrix is NIST SRM 2387 (Peanut butter, NIST, USA), and although Sr is not among the certified elements, it was used to evaluate the performance of LLE. The LLE experiment was performed by mixing different amounts of SRM NIST 2387 (0.0016–0.0400 g) with 5 mL of olive oil with known Sr concentration to reach a total Sr content typical for olive oils (0.5–20 ng g^{-1}). The Sr recoveries obtained by LLE, when compared to values obtained by MWD (2380 ± 230 ng g^{-1}; n = 10), ranged from 63 % to 67 % (n = 4), which is similar to that obtained by analyzing olive oil S where LLE accounted for 56 % of the MWD value (Fig. 2a).

3.2. Purification of the extracts and determination of $^{87}Sr/^{86}Sr$ isotopic ratios

In all olive oil and pomace extracts, regardless of the extraction or evaporation procedures performed, a certain amount of matrix residue, evident as light yellow to dark brown precipitate, was observed. This organic precipitate must be completely degraded before loading on the Sr-resin column; otherwise, the remaining organic compounds can interfere with the chromatography, resulting in the resin's saturation, loss of Sr and the presence of matrix elements in the eluate (Liu et al., 2006). According to Dietz and Jensen (2004), Sr adsorbs onto the resin in the form of $Sr(NO_3)_2$ with the Sr cation residing in the center of the crown-ether ring (4,4′(5′)-di-t-butylcyclohexano-18-crown-6), but organic molecules can obstruct this by participating in complexation and adsorption reactions during the cation exchange process. Improper matrix separation can also result in major elements, e.g. Ca, Na, and K, being present in the eluate, which may cause non-isobaric matrix effects and induce significant isotopic bias during MC-ICPMS analysis, resulting in low precision and reproducibility (Hughes et al., 2011).

3.2.1. Degradation of organic residues in olive oil extracts

The amount of matrix residue in the extracts can be minimized by carefully removing the upper oil phase with a pipette. However, although much effort was made to eliminate traces of oil from the acid extracts, its complete removal could not be achieved. Also, cellulose-acetate membrane syringe filters (0.45 μm) and Amicon Ultra-15 centrifugal filter devices were tested, but neither was effective since both filters leach Sr (~ 0.050 ng mL^{-1}) even after pre-washing with extracting solution (up to 30 mL). Therefore, three alternative protocols were tested: (i) oxidation of organic matter on a hot plate with H_2O_2 and HNO_3 for both "individual portions" and "merged sample", (ii) MWD of "merged sample", and (iii) dry ashing of "merged sample".

The $^{87}Sr/^{86}Sr$ ratios in the purified extracts of the olive oil T3 prepared using the tested protocols (Fig. 3a) ranged from 0.70900 ± 0.00006–0.70923 ± 0.00007, with three out of four values being within the limit of analytical uncertainty of 0.0001 (± 2σ). Namely, the extract evaporated as "individual portions" followed by oxidation with H_2O_2 and HNO_3, and the extract merged during evaporation (i.e. "merged sample") subjected to MWD and dry ashing, had the same Sr isotopic composition. The high Sr recoveries (> 90%) obtained after the column separation after dry ashing of "merged sample" and H_2O_2/HNO_3 treatment of the "individual portions" further confirmed the validity of these two protocols. For the MWD of organic residue in "merged sample", the Sr recovery was slightly lower (> 70 %), but this result showed that 30 % loss of Sr during sample treatment does not result in isotope fractionation.

On the contrary, the treatment of "merged sample" with H_2O_2 and HNO_3 exhibited a higher $^{87}Sr/^{86}Sr$ ratio and lower Sr recovery (50–60 %) than the three other procedures, and therefore this procedure was considered inappropriate. This result could be explained by the incomplete degradation of a substantial amount of residual organic material remaining after evaporating large extract volumes in a single glass. Apparently, the presence of organic material caused the isotopic fractionation of Sr during chromatography since higher isotope ratios were obtained.

3.2.2. Degradation of organic residues in the pomace extracts

The extracts of pomace samples C1 and C2 obtained by three different extraction techniques (LLE with mechanical shaking, LLE with ultrasound-assisted agitation, and MWD) were treated with H_2O_2 and HNO_3 on a hot plate to remove any organic precipitate remaining after the evaporation. After the separation of Sr from the sample matrix, all tested procedures produced equivalent $^{87}Sr/^{86}Sr$ isotopic ratios within the analytical uncertainty of 0.0001 (± 2σ) for both samples (Fig. 3b); the average values were 0.70834 ± 0.00009 and 0.71074 ± 0.00004 for pomace samples C1and C2, respectively. Meanwhile, Sr recoveries calculated after column chromatography were greater than 85%, demonstrating that no significant loss of Sr occurred using any of the tested protocols. These results, therefore, demonstrate the applicability of all three protocols for determining $^{87}Sr/^{86}Sr$ ratios in pomace.

3.3. Quality control of $^{87}Sr/^{86}Sr$ analysis

Even though the two tested protocols proved to be equally efficient for obtaining $^{87}Sr/^{86}Sr$ ratios in olive oil (Fig. 3a), due to its greater simplicity, the final procedure was defined as follows: LLE extraction with an acid solution (2 % HNO_3 and 0.1 % HCl) and mechanical shaking for 16 h, followed by ultrasonic agitation for 1 h at 40 °C. Any residues remaining after the evaporation were then calcined at 650 °C for 16 h. The validity of this method is supported by high Sr recovery after the column chromatography (> 90%) and high precision (6.0×10^{-5}) expressed as the analytical uncertainty (2σ) of 3 independent analyses.

For pomace, all tested procedures proved to be equally efficient (Fig. 3b); however, the following method was selected: extraction with 2 % HNO_3 and 0.1 % HCl and ultrasonic agitation for 1 h. Any matrix

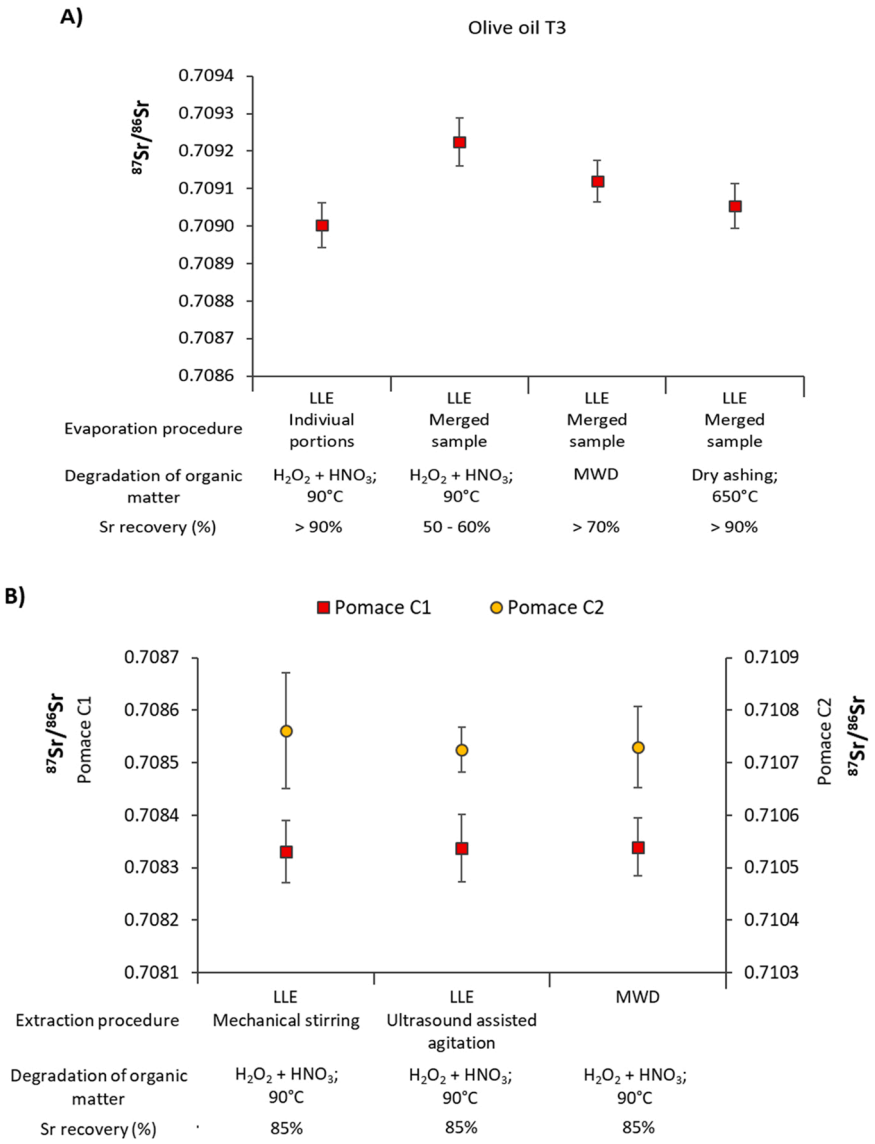

Fig. 3. The $^{87}Sr/^{86}Sr$ values in olive oil (**a**) and pomace (**b**) obtained using different sample treatment protocols. (Note: "merged sample" - the entire volume of extract (100–500 mL) was merged and evaporated in a single glass; "individual portions" - evaporation of individual portions (20 mL) of the same sample separately, which were later merged on the column.).

residues were removed by repeated cycles (3–5 times) of oxidation with H_2O_2 and HNO_3 on a sand bath. The Sr recovery after purification was satisfactory (> 85%), and analytical uncertainty was 1.0×10^{-4} (2σ from 3 repeats).

3.3.1. Sr isotopic composition of NIST SRM 2387 – Interlaboratory comparison study

The validity of the proposed method was further evaluated by conducting an interlaboratory comparison of $^{87}Sr/^{86}Sr$ analyses using NIST SRM 2387. Given that LLE could extract only ~ 60 % of Sr compared to that released by MWD (Fig. 1a), the method was verified by proving that Sr isotopic composition was unaffected by incomplete extraction of Sr from the matrix. This was accomplished by comparing $^{87}Sr/^{86}Sr$ isotopic ratios in the NIST SRM 2387 obtained by both methods (MWD and LLE) in two laboratories - IJS, Slovenia and AIA, France.

The results showed that both methods gave similar $^{87}Sr/^{86}Sr$ ratios in both laboratories (Fig. 4), i.e. the $^{87}Sr/^{86}Sr$ isotopic ratios obtained by MWD was 0.70909 ± 0.00003 for AIA (confidence interval at 95%, calculated as 2σ from individual mineralizations, n = 8; external reproducibility is 37 ppm calculated as 2RSD), and 0.70909 ± 0.00003

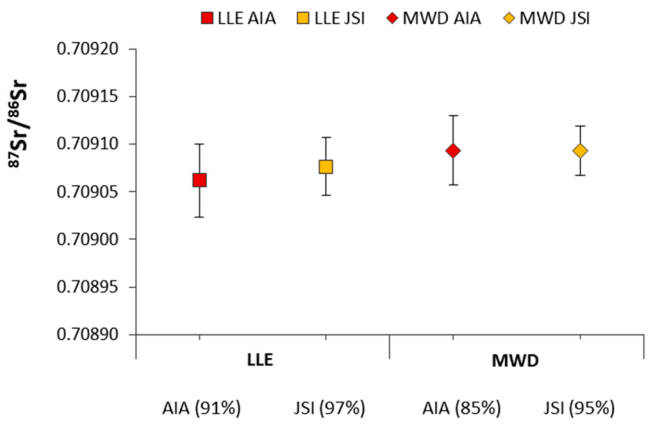

Fig. 4. The interlaboratory comparison of $^{87}Sr/^{86}Sr$ analysis of NIST SRM 2387.
Note: "AIA" - Advanced Isotopic Analysis (France); JSI - Josef Stefan Institute (Slovenia). Sr recoveries are given in brackets.

for IJS (confidence interval at 95%, calculated as 2σ from individual mineralizations, n = 6; external reproducibility is 43 ppm calculated as 2RSD). The $^{87}Sr/^{86}Sr$ isotopic ratios obtained by LLE were 0.70906 ± 0.00004 for AIA (confidence interval at 95%, calculated as 2σ from individual extractions, n = 6; external reproducibility is 54 ppm calculated as 2RSD) and 0.70908 ± 0.00003 for IJS (confidence interval at 95%, calculated as 2σ from individual extractions, n = 6; external reproducibility is 50 ppm calculated as 2RSD). The results were not statistically different when comparing methods or laboratories, confirming that incomplete Sr extraction during LLE extraction does not enrich one Sr isotope relative to another. Moreover, the results obtained are the first established data on the $^{87}Sr/^{86}Sr$ isotopic ratio in NIST SRM 2387, and this data (0.70908 ± 0.00004, n = 14 individual preparations) could be used as a reference value for the quality control of $^{87}Sr/^{86}Sr$ analysis of olive oil and pomace.

3.4. The application of the developed method for $^{87}Sr/^{86}Sr$ determination in olive oil and pomace

The proposed method was applied to olive oil and pomace samples from eight olive orchards in Tunisia, Slovenia and Croatia. The results of the Sr isotopic analyses are presented in Fig. 5, while the concentrations of total Sr extracted from the samples and the final Sr recovery obtained after column separation are given in Table 1.

The $^{87}Sr/^{86}Sr$ ratios in Tunisian olive oils T1, T2, T3, T4 and T5 ranged from 0.70820 ± 0.00005–0.71057 ± 0.00007. Unfortunately, given the quantity of sample that was available (<0.5 kg), the content of Sr in olive oil S (Slovenia) and C1 and C2 (Croatia) was too low (0.033–0.194 ng g^{-1}, Table 1) to perform $^{87}Sr/^{86}Sr$ analysis, but the $^{87}Sr/^{86}Sr$ ratios were determined in the pomace obtained by centrifugation of these olive oils.

The measured $^{87}Sr/^{86}Sr$ ratio in pomace samples S, C1, C2, T1 and T2 ranged from 0.70820 ± 0.0003 (T2) to 0.71074 ± 0.00004 (C2). The measured values for pomace T1 and T2 were similar within the analytical uncertainty of 2σ to those measured in the corresponding oil samples (Fig. 5), which showed that olive oil and pomace obtained by oil centrifugation have the same Sr isotopic composition. This result reveals that Sr isotopes do not fractionate during olive oil production and also confirms that olive oil's Sr isotopic composition could be determined by analyzing the corresponding pomace residues if they are present in the oil. This finding significantly simplifies $^{87}Sr/^{86}Sr$ analysis of oil, particularly those with trace levels of Sr, because it is showed that, instead of processing large volumes of oil, the $^{87}Sr/^{86}Sr$ isotopic ratio can be more easily measured in small amounts of pomace obtained by centrifuging the oil.

3.5. The preliminary application of the developed method in provenance studies - the link between the olive oil, pomace and the geology of the production area

The method's applicability for determining the provenance of olive oil was tested by exploring the link between olive oil and soil from the same orchard (S, C1 and C2). The $^{87}Sr/^{86}Sr$ ratios measured in soils (Fig. 5) are within the range predicted by Hoogewerff et al. (2019), who present a baseline map of $^{87}Sr/^{86}Sr$ distribution in the bioavailable fraction of soils from the corresponding regions. The results presented in Fig. 5 show that the measured $^{87}Sr/^{86}Sr$ ratios in pomace and soil from the same orchards (S, C1, C2) are similar within the analytical uncertainty (2σ) of 0.0001, which means that $^{87}Sr/^{86}Sr$ ratio in pomace reflects the characteristic isotopic signature of soil. Considering that oil and pomace have identical $^{87}Sr/^{86}Sr$ isotopic ratios (as demonstrated for the samples T1 and T2; Fig. 5), the presented results confirm that $^{87}Sr/^{86}Sr$ ratio in the oil reflects that of the soil and therefore both could be used as a geological tracer in traceability of olive oil.

Although the measured $^{87}Sr/^{86}Sr$ ratios confirmed a link between the olive oil and the local geology, the discrimination of the investigated olive oils according to the country of origin could not be obtained on the basis of such a small amount of data. Indeed, $^{87}Sr/^{86}Sr$ isotopic ratio, as a

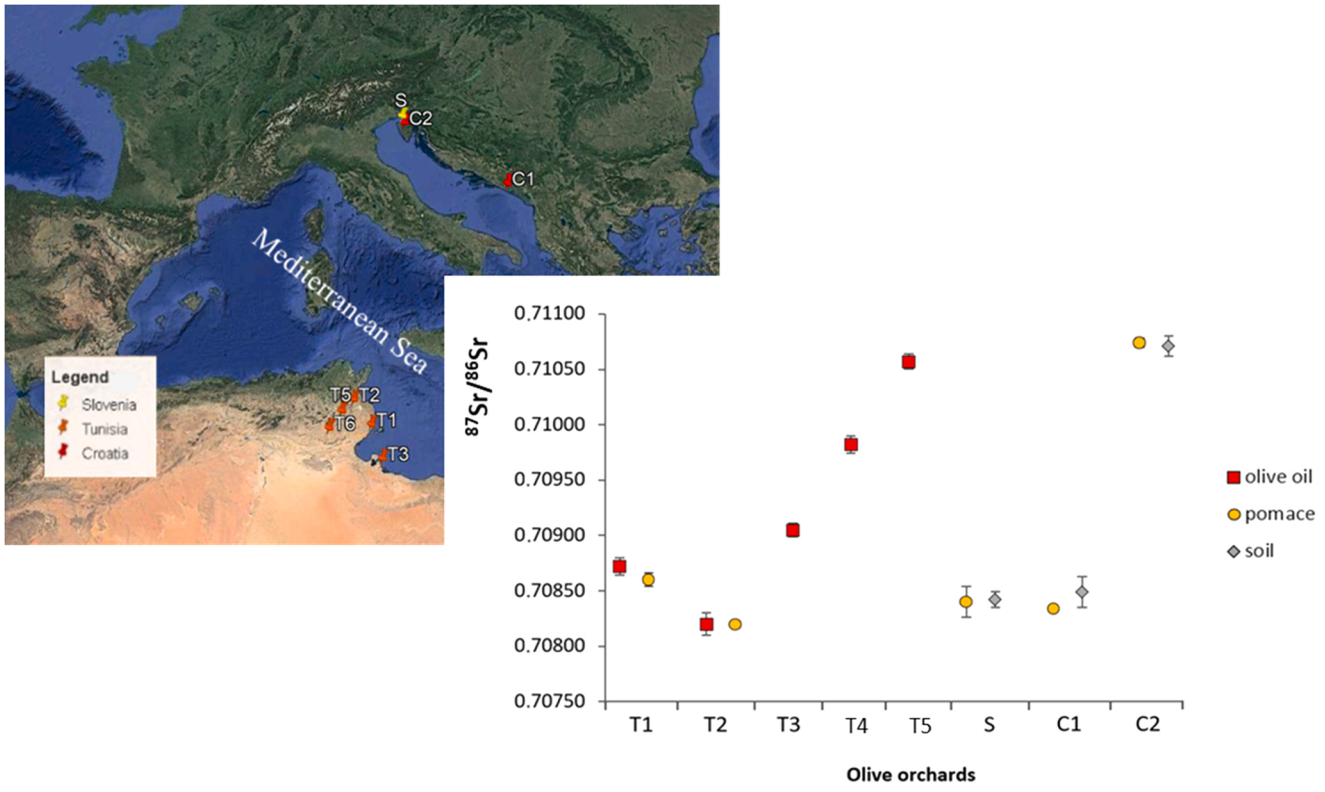

Fig. 5. A comparison of $^{87}Sr/^{86}Sr$ values determined in olive oil, pomace and soil from different olive orchards in Tunisia (T1, T2, T3 T4, T4), Slovenia (S1, S2) and Croatia (C1, C2).

geological tracer, reflects the underlying geology which may be different within a country, but may also be similar in different countries (as shown for European soils in Hoogewerff et al., 2019). Consequently, the use of $^{87}Sr/^{86}Sr$ approach in traceability studies should be interpreted in terms of the background geology, which means that the use of this approach solely could not always discriminate the oil, as well as other foods, according to country of origin.

The different background geology explains the different $^{87}Sr/^{86}Sr$ ratios determined in two olive oils from Croatia. The more radiogenic soil and higher ratios of pomace in orchard C2 ($^{87}Sr/^{86}Sr = 0.7107$) are consistent with the Lower Cretaceous limestones associated with the Istrian region (Croatia), while lower ratios ($^{87}Sr/^{86}Sr = 0.7085$) in the orchard C1 located in the southern Dalmatia (Croatia) are consistent with Upper Cretaceous dolomites. The different underlying geology also explains why the isotopic signature of samples from the Slovenian orchard S ($^{87}Sr/^{86}Sr = 0.7084$) is different to that of the nearby Istrian region (C2); S corresponds to abundance of younger Paleocene-Eocene foraminiferal limestones and is, therefore, more similar isotopically to the samples from orchard C1. However, to verify the origin of foods, including olive oil, various markers for tracing the geographical origin should be combined, i.e. Sr isotopic signature should be used together with geochemical fingerprints, stable isotope (H, C, O) signatures and physico-chemical characteristics of the oil.

4. Conclusion

This study contributes significantly to advances in the $^{87}Sr/^{86}Sr$ analysis of olive oil and its implication in investigating its origin because of several findings. The first is that the developed methodology based on MC-ICPMS enables the precise measurement of $^{87}Sr/^{86}Sr$ isotopic ratios in olive oil, even in those with Sr content as low as 0.2–6 ng g^{-1}, with a precision of 54 ppm. The second is that olive oil and corresponding pomace have an identical $^{87}Sr/^{86}Sr$ isotopic signature, which means that accurate $^{87}Sr/^{86}Sr$ ratio in olive oil can be obtained by analyzing only the pomace residues obtained by centrifuging the oil, thereby avoiding the need to extract large amounts of oil. This finding could be crucial for the $^{87}Sr/^{86}Sr$ analysis of olive oil with very low Sr content.

This method's validity was confirmed by conducting an interlaboratory comparison study, which provides the first data on Sr concentration (2380 ± 230 ng g^{-1}) and $^{87}Sr/^{86}Sr$ isotopic ratio (0.70908 ± 0.00004) of NIST SRM 2387. Finally, a link between the $^{87}Sr/^{86}Sr$ of the oil and that of the soil, i.e. local geology, was confirmed, indicating that $^{87}Sr/^{86}Sr$ ratio could be used as a reliable indicator in verification of olive oil origin. However, for a reliable determination of the geographical origin, a study on traceability should be carried out using a larger data set and multi-elemental and multi-isotopic approaches.

Funding

The work was financially supported by the Croatian Ministry of Science and Education and Unity through Knowledge Fund Project No. 23/15 "Role of soil properties and environmental conditions in the elemental and isotopic composition of the olive: basis for oil geographic traceability", the Slovenian Research Agency ARRS Programme P1-0143, the project MARSS (Mass Spectrometry for Reactivity and Speciation Sciences), the project MASSTWIN - Spreading excellence and widening participation in support of mass spectrometry and related techniques in health, environment and food analysis (H2020, GA no. 692241), TUNTWIN - Twinning towards advanced analytical strategies for capacity building and innovation for the Tunisian economy: application to three industrial key sectors in Tunisia (H2020, GA no. 952306), and ERA Chair ISO-FOOD for isotope techniques in food quality, safety, and traceability (H2020, GA No. 621329).

CRediT authorship contribution statement

All: All authors made substantial intellectual contribution, reviewed the manuscript, and approved the final version of the manuscript. **T.Z., M. F.T., E.N.E.:** Conceptualization, Methodology. **T.Z., M.F.T., E.N.E., F.P., E.N., J.B.:** Data curation, Writing – original draft preparation. **M.F. T., T.Z.:** Visualization, Investigation. **O.F.X.D.,.Z.:** Supervision. **M.F.T., T.Z.:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank dr. David Heath for editing the manuscript and all those who participated in sampling and preparing pomace and oil samples. We would like to thank the anonymous reviewers for their constructive comments.

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