Thermal analysis as a tool for traceability monitoring of Greek extra virgin olive oil

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Abstract

In the case of extra virgin olive oil, the implementation of a reliable traceability system is very important, given the nutritional and economic value of this product for the Greek population. Among the parameters that should be recorded in such a system is the varietal and geographical origin of the product. The data of these as well as all parameters of a traceability system should be collected by means of analytical or other methods which must be simple, fast on the course out and the results obtained should be accurate, sensitive and repeatable.

In the present study, the applicability of Differential Scanning Calorimetry (DSC) in the determination of the varietal and geographical origin of extra virgin olive oil was investigated. Samples of extra virgin olive oil were of four different monovarietal categories and originated from four different geographical regions of Greece. The thermal properties of Greek extra virgin olive oils were studied by obtaining the heating and cooling profiles of samples. Heating thermograms exhibited a minor exothermic peak followed by multiple endothermic events, whereas two well distinguishable exothermic peaks were observed in all samples during cooling.

Discriminant analyses of combined results showed that the techniques studied can be effectively used for the determination of varietal and geographical origin of Greek extra virgin olive oil, with a reliability of 91.3% and 76.8% respectively. An attempt to differentiate fourteen monovarietal extra virgin olive oil samples of Koroneiki cultivar from two geographical regions of Greece showed that samples were correctly classified with a reliability of 69%.

***Keywords*:** DSC, Greek extra virgin olive oil, traceability, geographical origin.

1. Introduction

Olive oil represents the main source of dietary fats in countries of the Mediterranean area. In particular, EVOO, which is the highest quality product among olive oils, as it is obtained from olive fruits using only mechanical processing steps or other physical means under conditions that do not lead to oil alteration, is highly appreciated for its natural flavour and aroma, as well as for its health and nutritional properties (Taurino et al., 2002; Chiavaro et al., 2008b). Greece is the third largest producer of olive oils in the world, with about 420.000 tons annually, around 80% of which are extra virgin olive oils (EVOO), thus making Greece the world's largest EVOO producing country.

Traceability according to ISO is defined as "ability to trace the history, application, or location of that which is under consideration" (ISO/DIS 22005). Traceability of EVOO is nowadays of growing interest among producers, since it leads to supply chain optimisation, increase producers' competitiveness and prevention of mislabeling of geographical origin and olive varieties of products, so as to consequently assure correct information to the consumers (Regattieri et al., 2007). The complete farm to fork traceability of olive oil involves the characterisation of the oils obtained from the main cultivars in each producer zone as the chemical composition of EVOO is well known to be influenced by genotype, different agronomic, environmental and technological factors (Torres & Maestri, 2006; Kotti et al., 2009).

Various attempts to confirm the variety and geographical origin of edible oils have been reported, using different analytical methods, such as GC (Luna et al., 2006), GC-MS (Lopez-Feria et al., 2008), UV-Vis (Casale et al., 2007), NIR (Galtier et al., 2007), FT-IR (Lankmayr et al., 2004), HPLC (Stefanoudaki et al., 1997), ICP-MS (Benincasa et al., 2007), NMR (Rezzi et al., 2005) and others. Most of the above mentioned techniques are expensive, time consuming, require analytical expertise and have a high environmental impact. The development of additional analytical techniques as supporting tools for currently used methods will improve EVOO traceability monitoring.

In the present study, the applicability of Differential Scanning Calorimetry (DSC), in the determination of the varietal and geographical origin of Greek EVOO was investigated. This technique, which allows the physical changes that occur upon heating of a sample to be determined, possesses the advantages of being accurate, repeatable, relatively quick and simple to carry out, with minimal sample preparation (Chiavaro et al., 2007). Thermal properties were found to be related to the chemical composition of EVOO, although reported applications of DSC on the traceability of EVOO to date are limited (Reid et al., 2006).

2. Prior Research

The liquid↔solid phase transitions of oils have been particularly studied by DSC, as they are affected by molecular composition changes. Therefore, freezing and melting are promising methods in order to assess oil nature, quality and origin (Gegiou & Georgouli, 1982).

The DSC technique has been mostly used to study the oxidation processes and deterioration of oils (Tan & Che Man, 1999; Tan & Che Man, 2000; Tan & Che Man, 2002; Vittadini et al., 2003; Kanavouras & Selke, 2004; Ojijo et al., 2004; Besbes et al., 2005; Angiuli et al., 2007; Huang & Sathivel, 2008; Jansen & Birch, 2009). Moreover, it has been applied for the characterization of oils from different vegetables sources (Tan & Che Man, 2000; Tan & Che Man, 2002) or produced with novel processes (Lee et al., 2004), providing a reproducible method for their identification. A data bank with the calorimetric "fingerprints" of the main edible oils has been created (Dyszel & Baish, 1992), as well as an effective protocol for the measurement of olive oil content in olives of varying maturity (Ianotta et al., 2001).

The effects of heating and cooling rate on the melting and freezing thermograms have been studied with DSC (Gegiou & Georgouli, 1982; Tan & Che Man, 2002a; Che Man & Tan, 2002c) and the applicability of calorimetric methods in oil quality control discussed (Tan & Che Man, 2002b).

A good relation was reported between thermal properties and major (triacylglycerols and fatty acids) and minor components (free fatty acids, diacylglycerols, and primary and secondary oxidation products) of monovarietal EVOO samples for both cooling and heating profiles that were deconvoluted into the constituent peaks and related to specific triacylglycerol (TAG) species (Chiavaro et al., 2007; Chiavaro et al., 2008a). DSC application upon cooling and heating also appeared very promising in discriminating among oil samples from olives of different commercial categories, cultivars and/or harvesting periods (Angiuli et al., 2006; Chiavaro et al., 2007; Ferrari et al., 2007; Chiavaro et al., 2008a).

3. Research Methodology

3.1 Materials and Methods

3.1.1 Materials

The samples of EVOO included in this study were kindly supplied by associations of olive oil producers from 4 different geographical regions of Greece (Crete, Peloponnesus, Ionian and Northern Aegean islands). The olives were harvested in the crop period of 2008–2009 and belonged to 4 cultivars (Koroneiki, Lianolia, Thasitiki and Adramitiani). All samples were of known cultivar, geographical origin, method and date of production and were shipped in

amber glass bottles, without headspace. A total of 23 EVOO samples were collected and were stored in the dark at room temperature until the time of analysis, which was no more than 6 months after production.

3.2.1 Methods

EVOO samples (~50ml) were pretreated by gently stirred using a magnetic stirrer, while heating to 50°C for 5 min in a water bath, in order to erase thermal history and improve reproducibility. Three replicates of samples (6–10 mg) were accurately weighed (0.01mg) into hermetic aluminum pans, covers were hermetically sealed into place and analysed with a DSC Q100 (TA Instruments, DE, USA), equipped with a LNCS cooling accessory. Indium (melting temperature 156.6^{o}C, ΔH = 28.45 J/g) was used to calibrate the instrument and an empty pan was used as reference. Prior to analysis of samples, the baseline was obtained with empty, hermetically sealed aluminum pans and was subtracted from all heat flow curves. The two developed protocols of analysis, freezing and melting, involved cooling and heating of EVOO samples, respectively, at a scanning rate of 10°C/min. The freezing protocol involved equilibration at 50°C for 2min and then cooling at -40°C and subsequent holding at -40°C for 10min, while the melting protocol involved an equilibration at -50°C for 10min and then heating at 40°C. Dry nitrogen (99.999% purity) was used as purge gas and flowed at 50 ml/min.

The resulting thermograms were analysed by Universal Analysis Software (Version 4.2E, TA Instruments) to obtain maximum peak temperature Tm or Tf (melting or freezing temperature, ^{o}C), Mon or Fon and Moff or Foff (^{o}C), which represent onset and end (intersection of baseline and tangent at the transition) temperatures of transitions during melting or freezing, respectively, as well as time of transition tf (min), referring only to the freezing protocol. Range of transitions Rm or Rf (^{o}C) were calculated as temperature difference between onset and end temperatures regarding each protocol. Reproducibility of DSC curves was evaluated based on Tm or Tf.

Overlapping transitions of melting thermograms were deconvoluted into individual constituent peaks using OriginPro software (Version 8.0724, OriginLab Corporation, MA, USA), in order to potentially differentiate multiple lipid fractions of samples. Peak count was calculated as the sum of peaks that were included in the melting transition studied by the melting protocol.

3.1.3 Statistical Analysis

Statistical analysis was conducted using SPSS 15.0 statistical software (SPSS Inc., IL, USA). One-way analysis of variance (ANOVA) and SNK's significant difference test at a 95% confidence level ($p<0.05$) were employed to identify differences among samples.

At a second step, the method of discriminant analysis was applied in order to build a predictive model of cultivar or origin group membership based on the values of an appropriate set of variables. Standard graphical and statistical methods were used in order to verify that the choice of independent variables which were finally suggested, satisfy the necessary conditions (Norusi, 2004).

4. Analysis

In order for calorimetry to be effectively applied to EVOO traceability two requirements must be fulfilled: 1) the homogeneity of liquid samples during melting and a reproducible and complete solidification of samples during freezing 2) the implementation of fast and convenient measuring protocols. In this direction, the pretreatment of samples by stirring in a water bath (at 50°C) for 5min, which allowed sample homogenisation, was shown to produce coincident thermograms for both measuring protocols, thus highly reproducible results. Similarly, for the melting protocol, the initial isothermal freezing of samples at -50°C for 10min was shown to solidify all samples completely. Therefore, the two chosen protocols, freezing and melting, were shown to produce complete Greek EVOO samples' thermal profiles. Similar protocols were chosen by Angiuli et al., (2006), Ferrari et al. (2007) and Chiavaro et al. (2008a), for the study of olive oil's thermal properties.

Regarding the freezing protocol, a temperature–heat flow and a time–heat flow profile of an EVOO sample are shown in Figures 1 and 2, respectively. All samples exhibited multiple transitions. Two well distinguishable exothermic peaks were observed in all samples during cooling from 50 to -40°C. The recorded parameters from the cooling thermograms were Tf, Fon, Foff and Rf, which refer to the first exothermic event occurring in the -27.6 to -17.1^{o}C temperature range. The additional parameter tf refers to the time (in minutes) that the second and largest exothermic event peaked, which was shown to take place between 10.2 to 11.9min.

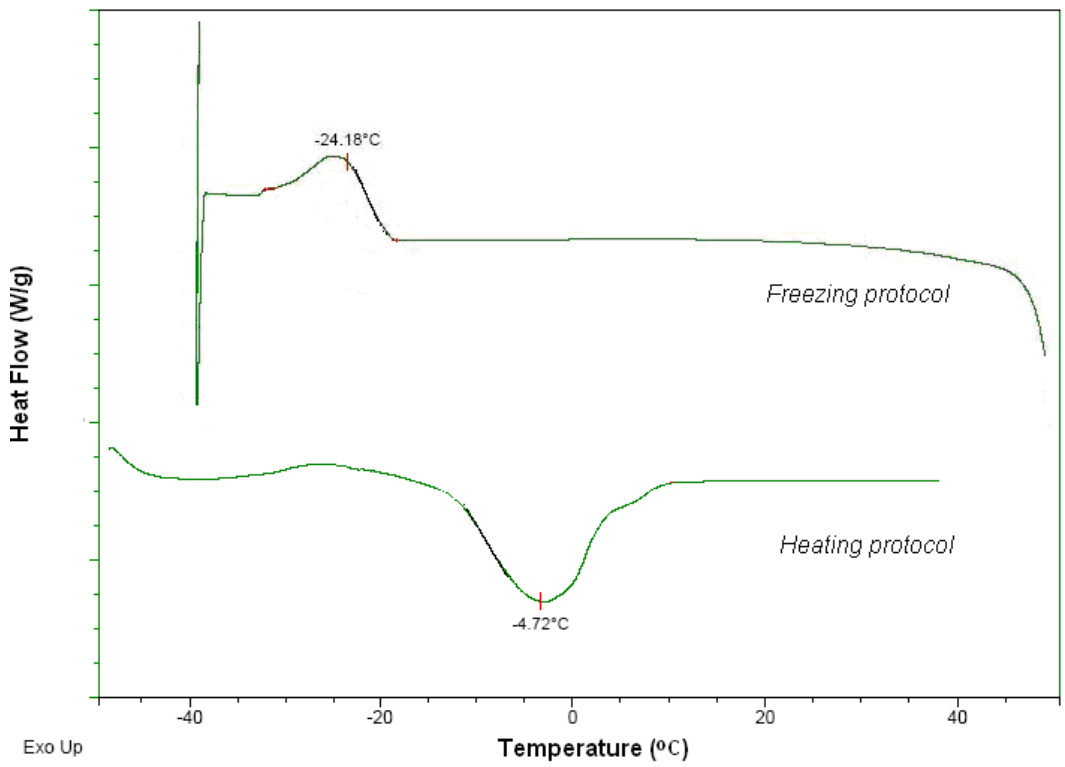

Figure 1. Heating and freezing protocols applied to EVOO and the resulting heat flow curves.

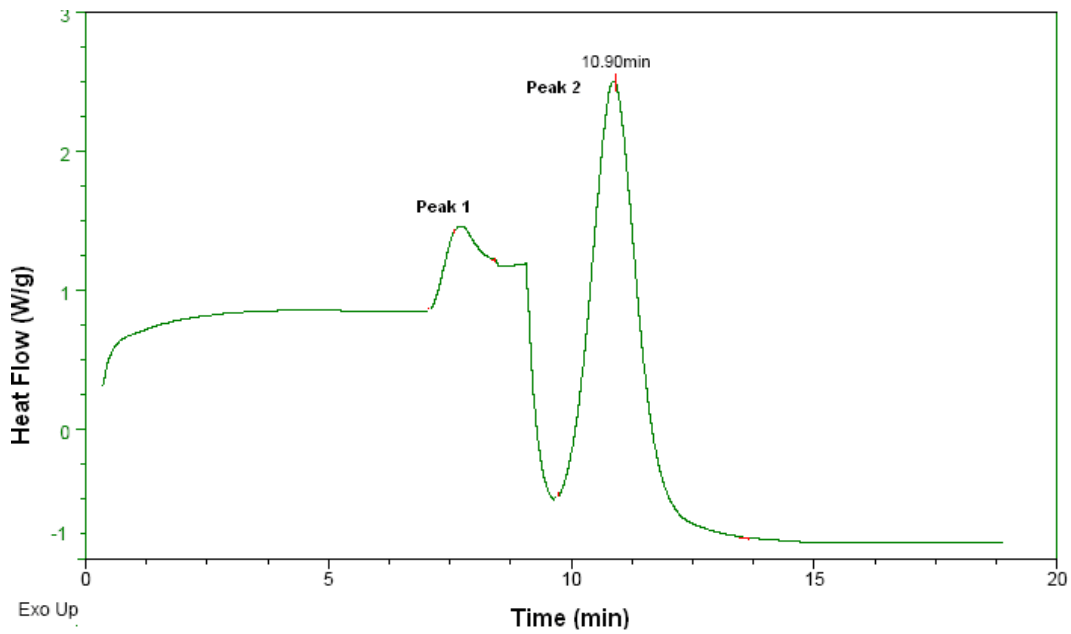

Figure 2. Freezing protocol applied to EVOO and resulting heat flow curve against time of analysis.

A typical thermogram or temperature–heat flow profile of an EVOO sample analysed according to the melting protocol is also shown in Fig. 1. All samples exhibited multiple transitions. Heating thermograms exhibited a minor exothermic peak, occurring in the -38 to -

15°C temperature range, which is attributed to the transition/rearrangement of triacylglycerol polymorphic crystals into more stable forms (Chiavaro et al., 2008a), followed by multiple endothermic events. The recorded parameters from the heating thermograms were Tm, Mon, Moff and Rm, which refer to the largest endothermic event occurring in the -12.2 to -3.6°C temperature range, close to which other minor endothermic events overlap. This endothermic peak was chosen since it is the main fraction that affects thermal properties of EVOO samples and also in order to simplify follow up analysis of thermograms, thus eliminating the need for deconvolution of multiple overlapping peaks. The multiple peak transition during heating of samples can be explained by the presence of mixed glyceride groups with different melting points under the specific experimental conditions (Herrera & Anon, 1991).

A major difference was observed in the peak count of the melting transition of samples of Adramitiani cultivar, all of which originated from the Northern Aegean islands (specifically Mytilene), in relation to all other samples. In all heat flow curves of samples from Adramitiani cultivar, following the first exothermic event, three overlapping peaks were detected (Figure 3a), while in samples from all other cultivars four overlapping peaks were detected (Figure 3b), even at first-sight analysis.

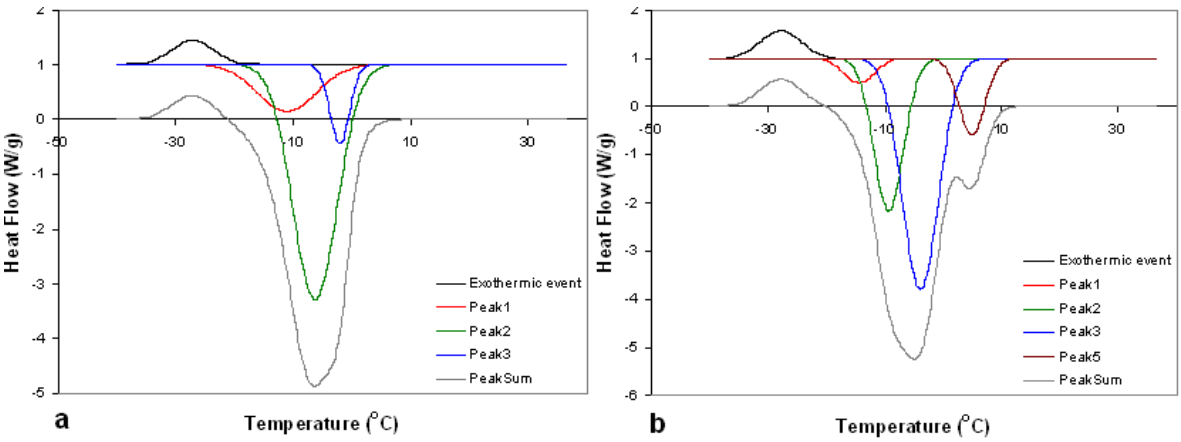

Figure 3. Heat flow curves depicting the deconvoluted and integrated events during heating of samples from different cultivars: a) Adramitiani and b) Koroneiki.

Statistical analysis confirmed the above findings ($p<0.05$). Deconvolution of multiple overlapping peaks produced fitted curves comprising of multi-peaks with a fitting R^2-value higher than 0.99.

Chiavaro et al. (2008a) also identified a clear exothermic event followed by four overlapping peaks during heating of EVOO samples by DSC, after deconvolution of the multiple melting transitions.

EVOO samples were classified into four groups, according to different cultivars and into different four groups, according to different geographical regions of origin. Results of statistical analysis for specific thermal parameters, which were shown to produce better differentiation of samples, by cultivar or geographical origin, are shown in Figures 4 and 5 respectively.

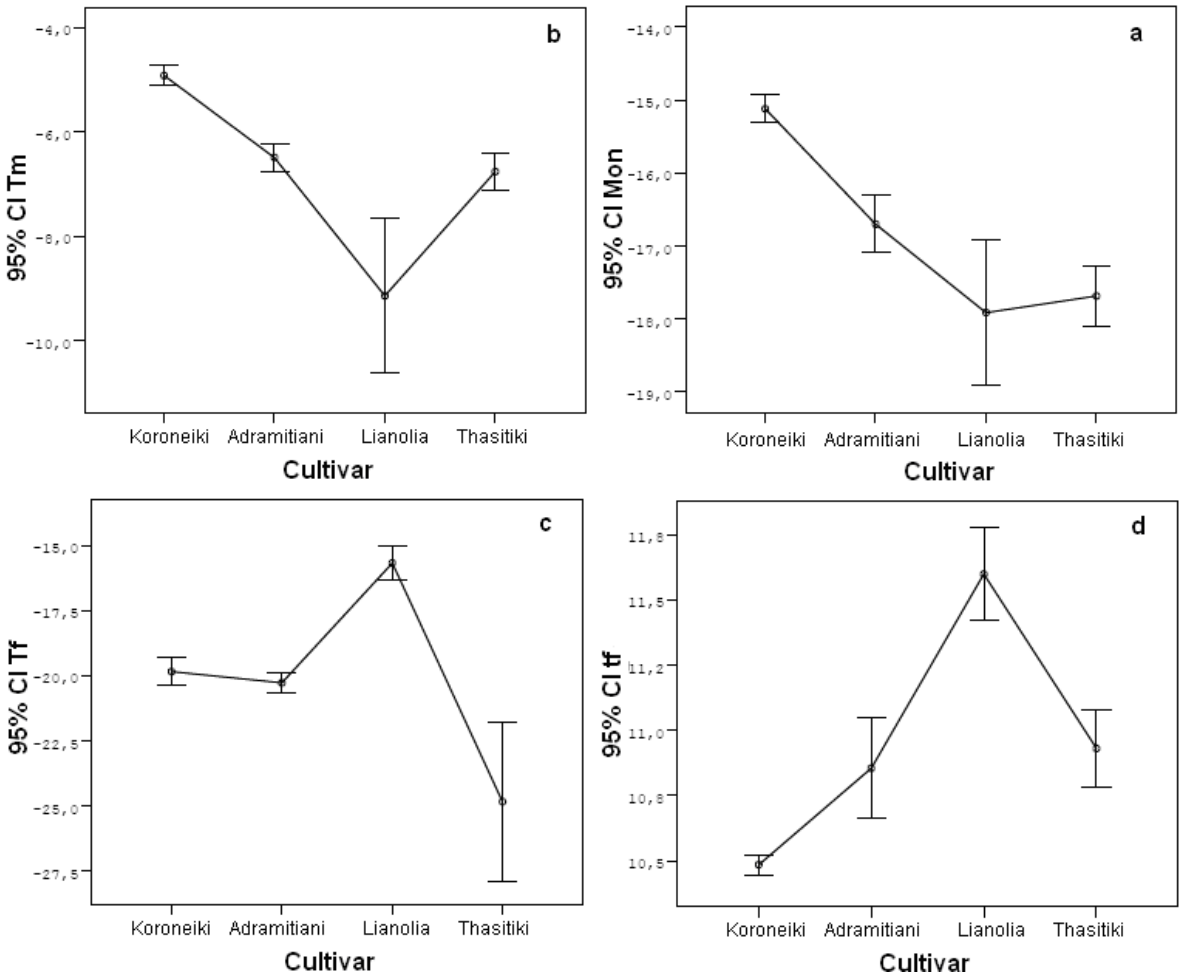

Figure 4. Plots of various thermal parameters of EVOO samples, as affected by olive cultivar (95% confidence intervals with error bars), obtained by the melting protocol: a) Melting onset, Mon as well as b) Melting temperature of major melting transition, Tm, or the freezing protocol: c) Crystallisation temperature of first exothermic event, Tf and d) Time after which the second exothermic event peaked, tf.

Results shown in Figure 4 reveal that three out of four olive cultivars can be correctly differentiated using any of the thermal parameters, such as Tm, Mon, Tf and tf.

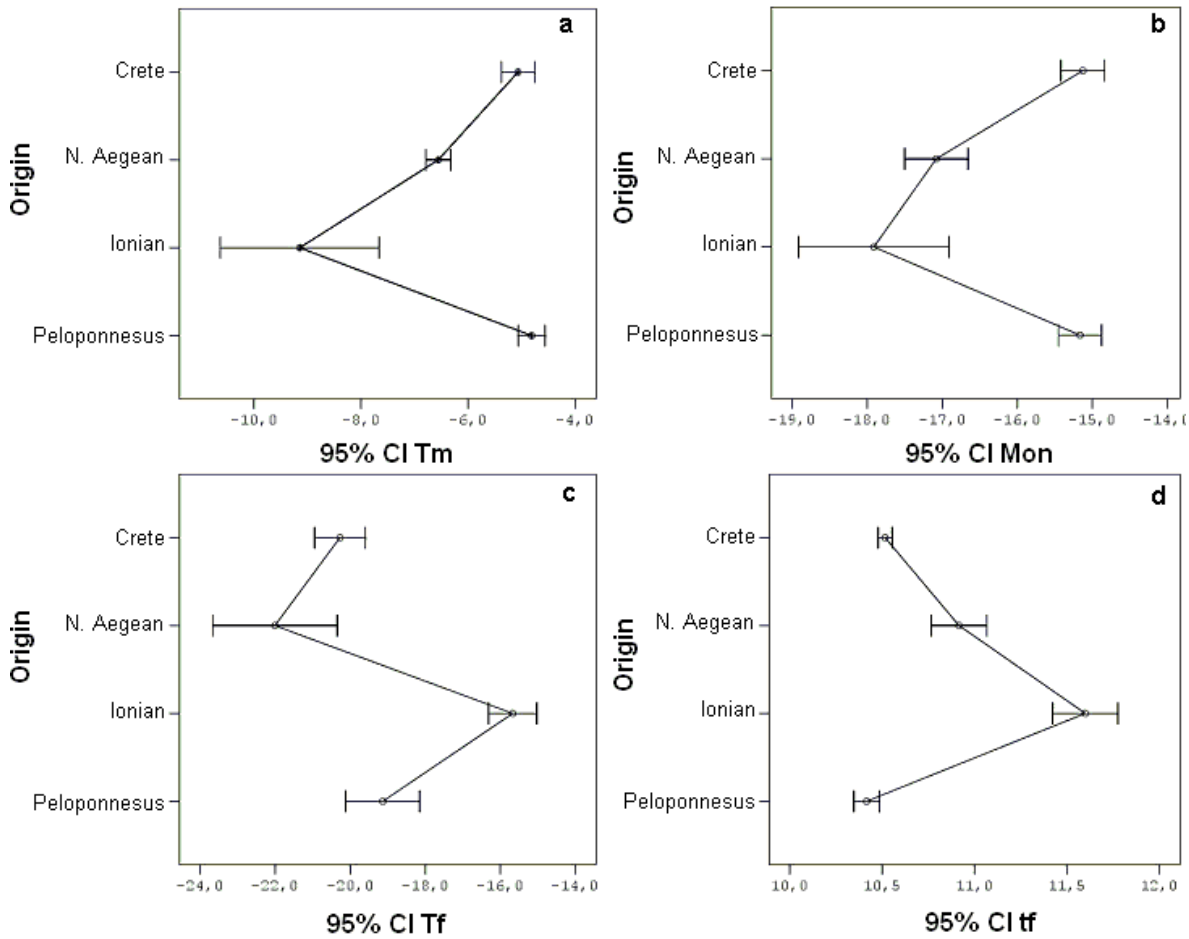

Figure 5. Plots of various thermal parameters of EVOO samples, as affected by geographical origin of olives (95% confidence intervals with error bars), obtained by the melting protocol (a, b) or the freezing protocol (c, d). Thermal parameters shown are as detailed in Fig. 4.

Results shown in Figure 5 reveal that three out of four groups of EVOO samples from different geographical origin can be correctly differentiated using any of the thermal parameters, such as Tm, Tf and tf.

In order to improve sample differentiation, all thermal parameters were examined with the help of linear discriminant analysis so as to decide which single or combination of these would produce an appreciable EVOO sample differentiation and correct classification. Furthermore, peak count was included in the discriminant analysis as a thermal parameter valuable for differentiating EVOO samples.

Regarding the varietal differentiation of Greek EVOO samples, single thermal parameters, obtained either from melting or cooling protocols, such as Mon and tf, were shown to correctly classify 79.7% and 82.6% of samples, respectively. Furthermore, the integration of a second thermal parameter, such as peak count deriving from peak deconvolution of the

melting transitions, combined with tf, improved EVOO sample classification to 91.3%. The best resulting Fischer's linear discriminant functions are shown in Table 1.

Table 1. Classification function coefficients for thermal parameters peak count and tf, in relation to olive cultivar.

Thermal parameters	**Cultivar**			
	Koroneiki	*Adramitiani*	*Lianolia*	*Thasitiki*
Peak count	110.249	62.398	102.764	84.722
tf	255.748	274.063	286.091	271.397
Constant	–1561.089	–1589.389	–1866.002	–1632.836

An example of the analysis from Table 1 is that by inserting the derived thermal parameters peak count and tf to the derived equations, the exact olive cultivar can be given from the equation that produces the highest value. Linear discrimination equations shown in Table 1 are:

Koroneiki = 110.249 x Peak count + 255.748 x tf – 1561.089

Adramitiani = 62.398 x Peak count + 274.063 x tf – 1589.389

Lianolia = 102.764 x Peak count + 286.091 x tf – 1866.002

Thasitiki = 84.722 x Peak count + 271.397 x tf – 1632.836

However, EVOO samples of Thasitiki cultivar appeared not to be correctly classified by the above analysis. As seen from Fig. 4c, Thasitiki cultivar can be effectively differentiated by the thermal parameter Tf (ranging from -27.9 to -21.8^{o}C), since it is clearly different from all other samples (ranging from -19.6 to -18.5^{o}C) (p<0.05). Therefore, a combination of the derived thermal parameters from DSC, such as Tf, peak count and tf, will correctly classify all the analysed Greek EVOO cultivars.

Regarding the differentiation of geographical origin of Greek EVOO samples, best classification of samples was derived by incorporating peak count combined with tf into the analysis. Thus, 76.8% of EVOO samples were correctly classified. The resulting Fischer's linear discriminant functions are shown in Table 2, where all classification equations are presented.

Table 2. Classification function coefficients for thermal parameters peak count and tf, in relation to olive geographical origin.

Thermal parameters	**Origin**			
	Peloponnesus	*Ionian islands*	*N. Aegean islands*	*Crete*
Peak count	61.523	55.83	36.786	61.040
tf	271.366	304.368	289.161	274.164
Constant	–1537.645	–1878.128	–1638.391	–1564.997

Furthermore, from all analysed EVOO samples in the present study, the only monovarietal samples originating from more than one geographical origin were those of Koroneiki cultivar, since it is the major EVOO producing cultivar in Greece. An attempt to classify samples from Crete and Peloponnesus (8 and 6 samples, respectively), a produced 69% correct classification was achieved by using only one thermal parameter, tf, derived from the freezing protocol. Fischer's linear discriminant functions are shown in Table 3, where both classification equations are presented.

Table 2. Classification function coefficients for thermal parameters peak count and tf of Koroneiki cultivar, in relation to olive geographical origin.

Thermal parameter	**Origin**	
	Crete	*Peloponnesus*
tf	271.366	304.368
Constant	–1537.645	–1878.128

5. Conclusions

Melting and freezing curves obtained by DSC analysis of Greek EVOO samples could be correlated with cultivar and origin of the samples in a fast and simple way, suitable for oil industry and market traceability systems. Our observations strengthen the premise that DSC is an efficient and accurate method for characterizing EVOO samples.

In particular, the present study revealed that the fastest and most accurate method for screening differences among Greek EVOO samples was by crystallisation, using the proposed freezing protocol. Additional and valuable information obtained by the melting protocol was shown to correctly classify almost all samples under analyses, according to their varietal

origin. These two proposed protocols of analysis were shown to be ideal for studying the thermal properties of EVOO samples, originating from Greece.

Furthermore, DSC can be a valuable technique, suitable for obtaining a specific sample's thermal "fingerprint", which can be accurately used in conformity tests by EVOO manufacturers, standardisation centres and other members of EVOO handling supply chains in Greece.

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