

# DSC calorimetry of edible oils: the melting curve for a fast authentication of EVOO

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## Subject category:

Composition of Foods  
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## Explanation of the manuscript's significance, including its originality, its contribution to new knowledge in the field...

This paper is submitted as the companion paper of the paper entitled ‘*DSC calorimetry of edible oils: the isothermal freezing curve for assessing olive oil storage history*’ Both the papers deal with calorimetric studies of edible oils and in particular report on: i) oil authentication based on the analysis of the melting curve and ii) detection of oxidative processes induced by light and oxygen from the analysis of the isothermal freezing curve.

The experiments reported in the present paper outline the capability of the calorimetric method in detecting the addition of seed oils to extra virgin olive oil and the possibility of obtaining an identity card of the oil for fast conformity test in the commercial practice.

Calorimetry was suggested in the past for detecting quality and origin of oils but no reliable calorimetric method is, to our knowledge, in use mainly for the intrinsic non-reproducibility of the freezing and melting processes. On the contrary, the method we have developed allows a high reproducibility of the thermograms and is very promising for many applications: from oil authentication to fraud detection. For its simplicity it is surely suitable for utilization in the SMI of edible oil sector.

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# DSC calorimetry of edible oils: the melting curve for a fast authentication of EVOO

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During last year the authors performed explorative measurements to verify the applicability of calorimetry for the authentication of edible oils. The results confirmed that thermodynamics and kinetics of both crystallization and melting of the oils, so strongly related to molecular interactions, supply useful parameters directly correlated to sample composition, therefore to quality and origin of the oil. A suitable calorimetric method for obtaining in a simple and fast way reproducible melting curves against temperature is here described. The curves show heat flow peaks directly correlated to the oil features. In particular we report on the evidence that DSC calorimetry is a powerful technique able: i) to disclose the addition to EVOO of seed oils (refined hazelnut oil included); ii) to detect the presence of refined olive oil, the low cost oil seldom added to EVOOs by defrauders; iii) to obtain a “first glance” genuineness test for EVOO with protected designation of origin; iv) to provide an “identity card” of an oil sample for “conformity test” in the commercial practice.

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**KEYWORDS:** edible oil authentication, calorimetry, phase transitions, olive oil, polymorphism

## INTRODUCTION

Extra Virgin Olive Oil (EVOO) has been obtaining an increasing success in the world market owing to its organoleptic features and benefits for health. In Mediterranean countries, in particular in Italy, Spain and Greece, EVOO is intimately related to culture, traditional cuisine and also to relevant economical activities. Many efforts have been made in these countries for improving EVOO quality and promoting its market. To this end, innovative technologies in each phase of production, from cultivation, fruit harvesting and oil extraction, have been developed. Despite these efforts, the genuineness and quality of extra virgins are sometimes difficult to define and the detection of frauds remain an open challenge. Adulterations are indeed more and more motivated by the increase of EVOO price and market size. The addition of seed oils and/or low cost olive oils is the more diffuse among the possible frauds. The increasing of scientific knowledge and the improvement of the analytical methods can help the defence of the market and the health of the consumers against these frauds, but unfortunately they produce also the growth of defrauder ability (1). Seed oils have triacylglycerol (TAG) composition different from EVOOs (2), so chemical analysis can easily discriminate between olive oil and seed oil, and also put in evidence an addition of seed oil to EVOO (3, 4). Some seed oils, as the hazelnut oil and the high oleic acid sunflower oil, have TAG composition similar to that of EVOO, thus addition of these oils and of refined olive oils is more difficult to detect. For detecting the addition of refined oils in extra virgin olive oil the stigmastadien determination (Reg.CEE 2568/91 all.IV) is used, while the addition of hazelnut and high oleic sunflower oil can be detected by the Delta ECN42 determination (Reg.CEE 2568/91 all.VIII) and sterol esters determination (5, 6). Also the detection of molecular markers in the vapour phase of the oils in some cases (7, 9) is successfully used against frauds. But the refined hazelnut oil has no volatile compound and its presence cannot be detected by headspace sampling, also combined to mass spectrometry (10). There are other techniques, as  $^{13}\text{C}$ -NMR (11),  $^1\text{H}$ -NMR (12), Raman (13, 14) and FT-IR (15) spectroscopy and spectrofluorimetry (16), operating in liquid phase, which can be utilized for detecting hazelnut oil and other adulterant

seed oils, at least above a certain concentration value. Nevertheless it is interesting to develop a new technique that, in addition to common methods, can describe the oil in a glance.

In our opinion EVOOs, seed oils and all the more reason their mixtures are so complex liquids that they cannot be satisfactorily characterized by a reductionistic picture like that resulting from the quantitative analysis of vapour and/or liquid phase molecular components, as the effects of molecular interactions are not taken into account. A suitable authentication procedure should foresee the integration of vapour phase analytical methods with physical methods able to detect relevant bulk properties of the liquid and solid phase of the oil. In the end, the judgment of a qualified panel of tasters should be added to the instrumental data for a reliable quality certification.

Among the physical methods DSC calorimetry has been already applied to test oil quality by monitoring liquid? solid phase transitions (17-22).

The authors have recently performed explorative measurements in order to test quality and traceability of EVOO by means of different calorimetric modes (23). Some kind of correlation between the measured quantities (induction time of nucleation, enthalpy of crystallization and melting, crystallization and melting temperatures, heat capacity) and the identity of the oil (that is oil organoleptic properties, quality and origin) was expected, as they both are dependent on molecular composition.

Unfortunately, the melting and freezing thermograms are strongly dependent on the temperature-scanning rate (20, 24, 25), and on the time-temperature history of the sample (20). For a successful application of a calorimetric method it was necessary, first of all, to define a suitable time-temperature program and to fulfil some practical conditions. For having reproducible thermograms the program must start from an equilibrium homogeneous liquid phase at the high temperature side of the calorimetric cycle and attain a solid phase at equilibrium at the lowest temperature. For having fast and easy measurement procedure as requested by the oil industry the program must use high temperature scanning rates. To this end we selected the scanning rate at 10°C/min, also by considering that, at this rate, each investigated seed oil shows a melting process ending at  $T = 0^{\circ}\text{C}$ . Only the peanut oil melting goes to completion with a small flat peak extending up to  $+5^{\circ}\text{C}$ . This feature is relevant because EVOO melting curve, at the same rate, shows the last peak just between  $0^{\circ}$  and  $10^{\circ}\text{C}$ . In this interval the melting curve of EVOO should be not affected by the addition of seed oils if the mixtures were ideal solutions. This is not the case and our calorimetric method is based mainly on the analysis of the changes of this peak (height and area) by addition of seed oil and refined olive oil. Preliminary results including mixtures of EVOO-sunflower and EVOO-hazelnut oil were already presented at the Italian CISETA Conference (26).

In the following we will report on the calorimetric protocol and the results of a wider study of the melting curve of edible oils and their mixtures. The analysis of the isothermal freezing curves and their relevance for detecting the effects of light induced oxidation during storage will be reported in the companion paper.

## MATERIALS AND METHODS

### a) *Tuscan and Apulian EVOOs and seed oils.*

The oil samples utilized in the experiments are listed in Tab.1 and Tab. 2. In Tab.1 are the EVOOs with their organoleptic features and chemiometric parameters. The EVOOs were used as received and not submitted to any treatment (filtration, deodorization, etc). The seed oils and refined olive oils in Tab.2 were bought at the market or supplied by other laboratories. The samples were stored in dark at  $20 \pm 2$  °C before each experiment.

### b) *The Calorimeter*

Calorimetric measurements were performed with a Perkin-Elmer DSC7 equipped with an Intracooler II. Dry nitrogen was used as purge gas at a rate of 30 ml/min. The instrument was calibrated in temperature and energy with high purity standards (indium, naphthalene and cyclohexane) at 10 °C/min, according to the procedure for standard DSC. The temperature was known at  $\pm 0.1$ °C; the samples weighted to  $\pm 0.01$ mg. In order to reduce temperature gradients, the sample mass was kept small, approximately equal to 6-8 mg.

### c) *The Calorimetric protocol*

The sample pan was put in the calorimeter and then submitted to the following time-temperature program: 1) heating from room temperature up to 50°C; 2) three minutes at 50°C; 3) cooling at 10°C/min. down to -40°C; 4) six minutes at -40°C; 5) heating at 10°C/min. up to 50°C. The cycle from pt.2) to pt.5) was usually repeated twice in the measurements here reported, even if the reproducibility is so good that the differences between two successive runs could not be appreciated in the normal scale of the thermograms. The solid phase of a crude oil sample is a mixture of polymorphs of TAG, grown in a reproducible way owing to the dominance of heterogeneous nucleation. The thermogram shows the melting of the crystalline fraction of each polymorph and sometimes the occurrence of melt refreezing in other form at higher temperature. When the heterogeneous nuclei are removed by filtering, homogeneous nucleation takes place and the solid composition can be reproduced only under suitable cooling conditions.

The full cycle time is 30 minutes for the first run and 57 minutes for two successive runs. The melting process occurs in the temperature interval  $-30$ °C ?  $+15$ °C, so the measuring time could be reduced to **25.5 minutes**, a time suitable for tests on line during production and fast controls from the mill to the market shelf.

## EXPERIMENTAL RESULT

The melting curves of samples of Tuscan EVOOs (harvesting 2004-2005) from the main production areas (see Table 1) are depicted in Fig.1A. The curves show the following features outlined in Fig.1B: i) a large peak (P2) with the maximum at temperatures between -6°C and -4°C; ii) a smaller peak (P3) with the maximum between 4.5°C and 6.5°C; iii) the value of the ratio of the height of each peak,  $R = P2/P3$ , varies between 2.8 and 3.4; iv) all the curves overlap at  $T < -23$ °C and at  $T > 10$ °C. The resemblance of the melting curves in Fig. 1A supports the possibility of defining a Standard Melting Curve (SMC), calculated as the mean of the melting curves of selected EVOOs, representative of Tuscan production areas. The SMC and the melting curves of two EVOOs from other Italian regions (Apulia and Liguria) and of a IGP Tuscan EVOO are shown in Fig.1B. There are evident differences from the SMC and the curves of the Apulian and Ligurian oils, whereas the IGP Tuscan EVOO agrees very well with the SMC.

A third peak (P1) is present at -20°C in the melting curve of Apulian and Ligurian oils.

In Fig.2 A the melting curves of five seed oils are shown. The differences among them are relevant and their melting process occurs at temperature lower than that of olive oils. The high oleic acid sunflower oil, HOSO, the hazelnut oil and the peanut oil, which have TAG composition similar to that of EVOO, show also similar melting curves (see Fig.2B). For these reasons the detection of their addition to EVOO is more difficult, expensive and time consuming (1, 3, 10, 16).

The melting curves of five ROOs are shown in Fig.3. The common relevant feature is the peak at  $-20^{\circ}\text{C}$  (P1), while the R-value is much higher ( $> 6$ ) than that measured for EVOOs.

For understanding the effects produced by the addition of peanut oil to an Apulian EVOO, a study of the melting process of mixtures of this EVOO with increasing amount of seed oil was performed. The results are in Fig.4. The addition of peanut oil increases the P1 peak (see the insert of the figure) already present in pure Apulian EVOO and decreases the height of peak P3. The effects produced by the addition of HOSO to the same EVOO are depicted in Fig.5. Nothing occurs in the melting curve up to  $-16^{\circ}\text{C}$ . The more relevant effects are the change of height and shape of the P3 peak against the w% of added oil.

The melting curves of mixtures of a Tuscan EVOO and refined hazelnut oil are in Fig.6. The melting curves practically overlap up to the maximum of the P2 peak. By increasing the w% of refined hazelnut oil in the mixture, the P2 peak enlarges more and more and the height of P3 decreases.

For a first quantitative analysis of the thermograms in Figs. 4, 5, 6, the values of the area under the peak P3 (a quantity proportional to the enthalpy variation of the involved melting process) and the height of the peak against the w% of the seed oil added to the EVOO were measured. The data are shown in Fig.7A and 7B.

In Fig.8 are the melting curves of mixtures of ROO and increasing amounts of EVOO, to mimic the composition of commercial Olive Oil (OO).

The addition of EVOO to ROO affects mainly the P3 peak. The P1 peak decreases, even if slowly (see the insert of the figure). The two effects can be observed in Fig.9, where the value of the area under P1 and P3 are shown against the w% of added EVOO.

Fig.10 shows the melting curves of the same EVOO sample (harvesting 2005-2006), recorded weekly during 11 weeks from the production day for studying the maturation process of fresh oil. The P2 peak shifts towards higher temperature of about  $2^{\circ}\text{C}$  while the height of P3 remains constant. The curve does not change at least qualitatively during this period.

## DISCUSSION

The melting of a solid EVOO is a process more complex than the fusion of a mixture of different crystalline structures of a single component sample owing to the numerous TAGs in the oil composition, the possible polymorph modifications and the kinetics of conversion among their main modifications. Moreover the minor components of EVOO affect the nucleation and growth kinetics of the crystalline phases, that is the crystalline composition of the solid sample. In this scenario a thermodynamic description of the freezing and melting of the oil is practically impossible (27, 28), but the observed high sensitivity of the thermograms to small changes of the oil composition can be understood.

In an explorative work on virgin olive oils it was shown that at least nine parameters for oil characterization could be obtained from calorimetry by using the melting, the freezing and the isothermal freezing curves (23). We are confident that the whole set of data, or a selected part of them, and a proper analysis, or better a combined analysis of calorimetric data with data from an artificial nose will be the way for testing quality, origin and defects of EVOOs. Indeed calorimetry gives information on the composition dependent properties of the bulk, whereas the artificial nose is sensitive to the molecular components of the vapour phase. Here we are proposing a fast calorimetric method, based on a simple analysis of the melting curve, able to give: i) relevant

information for commercial practice, as: a “first glance” test of EVOO quality, an “identity card” for conformity test of the oil if the reference melting curve of the oil has been monitored at the origin; ii) a first-level test of the quality declared on the label, for detecting the main frauds in the EVOO market.

It is undoubtedly necessary an enlargement of the statistics to include also mono-cultivar EVOOs (the Tuscan EVOOs here considered are blends) for further support and increase of the confidence in SMC utilization. Moreover SMC is expected changing from year to year. The amount of this change remains an open question and the refinements of the here-proposed analysis are tasks of a future investigation.

Having clear the limits of the present data, for discussing the potentiality of the calorimetric method let us assume that genuine Tuscan EVOOs are those having melting curve qualitatively identical and quantitatively inside an “acceptance band” around the SMC. The width,  $\Delta$ , of this band could be defined in order to contain the curves of the reference EVOOs, representative of the main production areas of Tuscany. The quality of an unknown sample could be certified with the following criteria: i) a Tuscan EVOO is expected to have its melting curve, obtained following the calorimetric protocol, wholly inside the acceptance band around the SMC; ii) a too large R value marks the adulteration with seed oils and/or ROO or a different origin; iii) the presence of a peak at  $-20^{\circ}\text{C}$  in the melting curve indicates the addition of ROO or of peanut oil or both or a different origin.

To verify this procedure we applied the calorimetric analysis to six Tuscan EVOOs, 4 from private productions and 2, with PDO declaration, bought at the market. They all fulfilled the conditions of genuineness, while 5 commercial EVOOs, so declared on the battle label but not having Tuscan origin, showed a peak at  $-20^{\circ}\text{C}$  and a value of  $R > 5$  or only a too large R value.

The sensitivity limit for checking addition of seed oil to a known EVOO is about 2% (see Fig.7). In the assumed authentication procedure the sensitivity reduces to about 10%, owing to the ignorance of the reference melting curve of the original (that is before adulteration) EVOO. This limit comes from the assumption of SMC as the reference curve of the sample. Indeed the uncertainty in the P3 peak area due to the acceptance band around the SMC corresponds to the effects provoked by the addition of about 10 w% of seed oil.

A more complex analysis should be necessary for identifying the added adulterant oil. The task becomes more difficult if the added oils are more than one. To this end a systematic study of mixtures of EVOO with two or more seed oils is in progress, together with an investigation on the molecular origin of the main thermogram features.

A specific calorimetric study is indeed promising for the identification of the melting processes under the peaks P1, P2 and P3 (29). To gain information on the crystalline structures in the solid sample the best experimental method is surely combined calorimetry and synchrotron X-ray diffraction, a technique developed by Michel Ollivon and co-workers and successfully applied to the study of the polymorphism of fats (30, 31).

During an experiment for studying the maturation process of fresh EVOO, we have observed a high reproducibility of the melting curve of samples of the same EVOO, also after many weeks of storage in dark. The minor changes observed in the weekly-recorded curves (see Fig.10) could be related to the sample aging, however this evidence support the use of the melting curve as the “identity card” of the sample. The effects of longer storage in dark will be reported and discussed in the companion paper, together with the calorimetric detection of the oxidative processes induced by exposition to ambient light (32).

In conclusion, the melting curve of the samples here considered, through a simple analysis, gives information useful for: i) the detection of some commercial frauds; ii) a “first glance” genuineness test for Tuscan EVOO with Protected Designation of Origin; iii) an “identity card” for fast and low cost conformity test in the commercial practice. In other words, if the curve of the oil under test is like the SMC or the curve of the reference EVOO at the origin, the oil is very likely the same EVOO or an EVOO of the same quality.

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## FIGURE CAPTION

Fig.1

A -The melting thermograms of six extra virgin olive oils (EVOO) from Tuscany. The samples and their characteristics are listed in Tab.1. B -The Reference Melting Curve (SMC), calculated as the mean of the melting curves in Fig.1A, compared with the curves of two Italian EVOOs from different regions: one from Apulia and one from Liguria. The curve of a commercial IGP EVOO from Tuscany is also shown. The numbers refer to samples listed in Tab.2.

Fig.2

A - The melting thermograms of some seed oils; B - The thermograms of the three seed oils with acidic composition similar to that of EVOO. The numbers refer to samples listed in Tab.2.

Fig.3

The melting thermograms of refined olive oils. The numbers refer to samples listed in Tab.1.

Fig.4

The melting thermograms of mixtures obtained by adding increasing amounts (w%) of peanut oil (sample n° 17 in Tab.2) to Apulian EVOO (sample n°20 in Tab.2)

Fig.5

The melting thermograms of mixtures obtained by adding increasing amounts (w%) of high oleic sunflower oil (sample n° 23 in Tab.2) to Apulian EVOO (sample n°20 in Tab.2).

Fig.6

The melting thermograms of mixtures obtained by adding increasing amounts (w%) of refined hazelnut oil (sample n° 21 in Tab.2) to Tuscan EVOO (sample n°25 in Tab.2).

Fig.7

The values of the area and the height of the peak P3 calculated from the curves of Figs. 4, 5, 6 against the w% of added seed oil. To obtain the enthalpy variation value of the melting processes under the peak P3 in unit [J/g], it is necessary to divide the area by the temperature-scanning rate (1/6 °C/s).

Fig.8 The melting thermograms of mixtures obtained by adding increasing amounts (w%) of Apulian EVOO (sample n°20 in Tab.2) to refined olive oil (sample n° 24 in Tab.2).

Fig.9

The values of the area of the peaks P1 and P3 calculated from the curves of Fig. 8 against the w% of added EVOO. To obtain the enthalpy variation value of the melting processes under the peaks P1 and P3 in unit [J/g], it is necessary to divide the areas by the temperature-scanning rate ( $1/6$  °C/s).

Fig.10

The melting curves of a EVOO sample (n°25 in Tab.2) recorded at increasing aging time. The label on each curve indicates the number of weeks passed since the production of the oil.

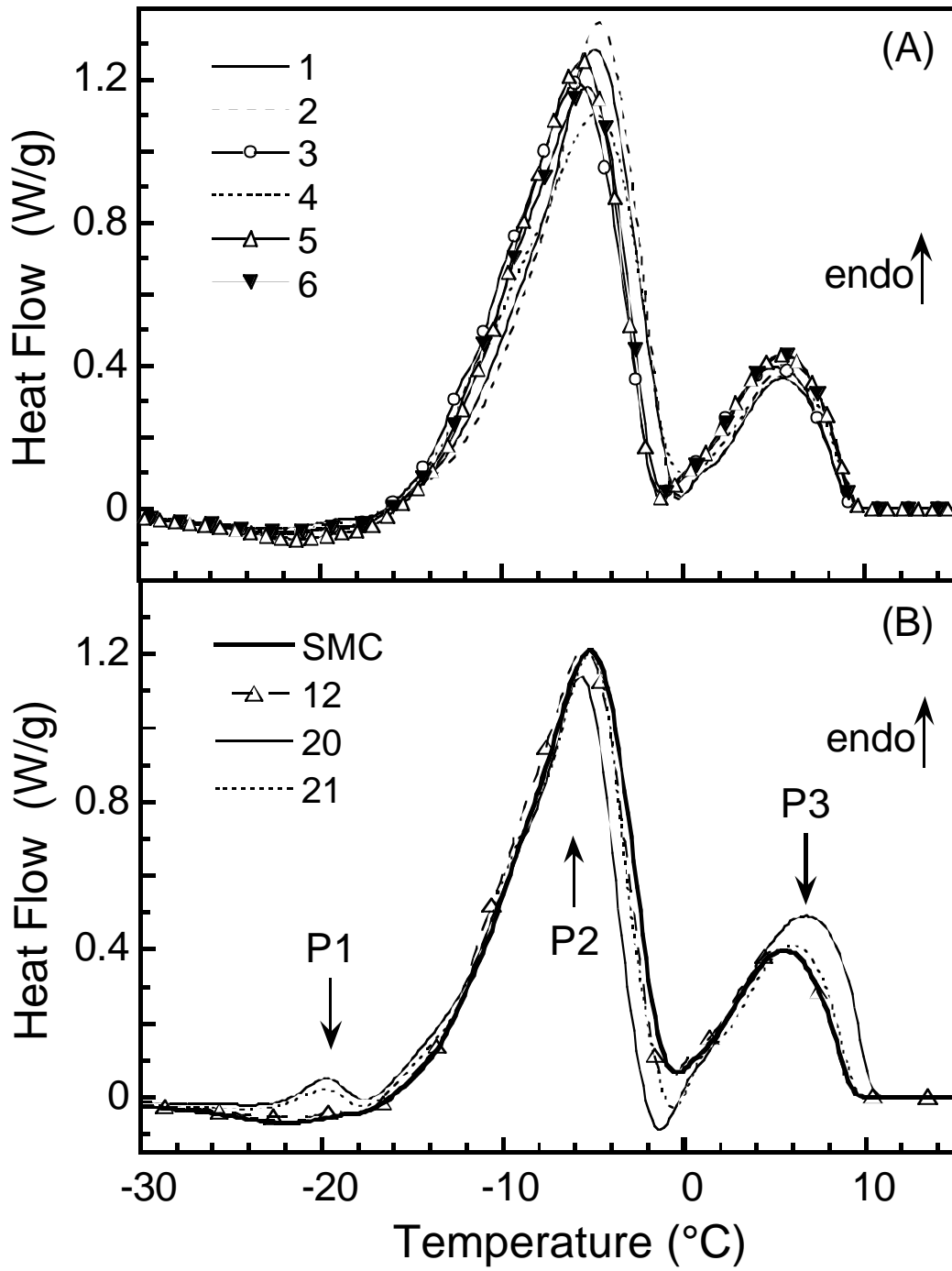


Figure 1. "Fast authentication of .....", G. Salvetti et al.

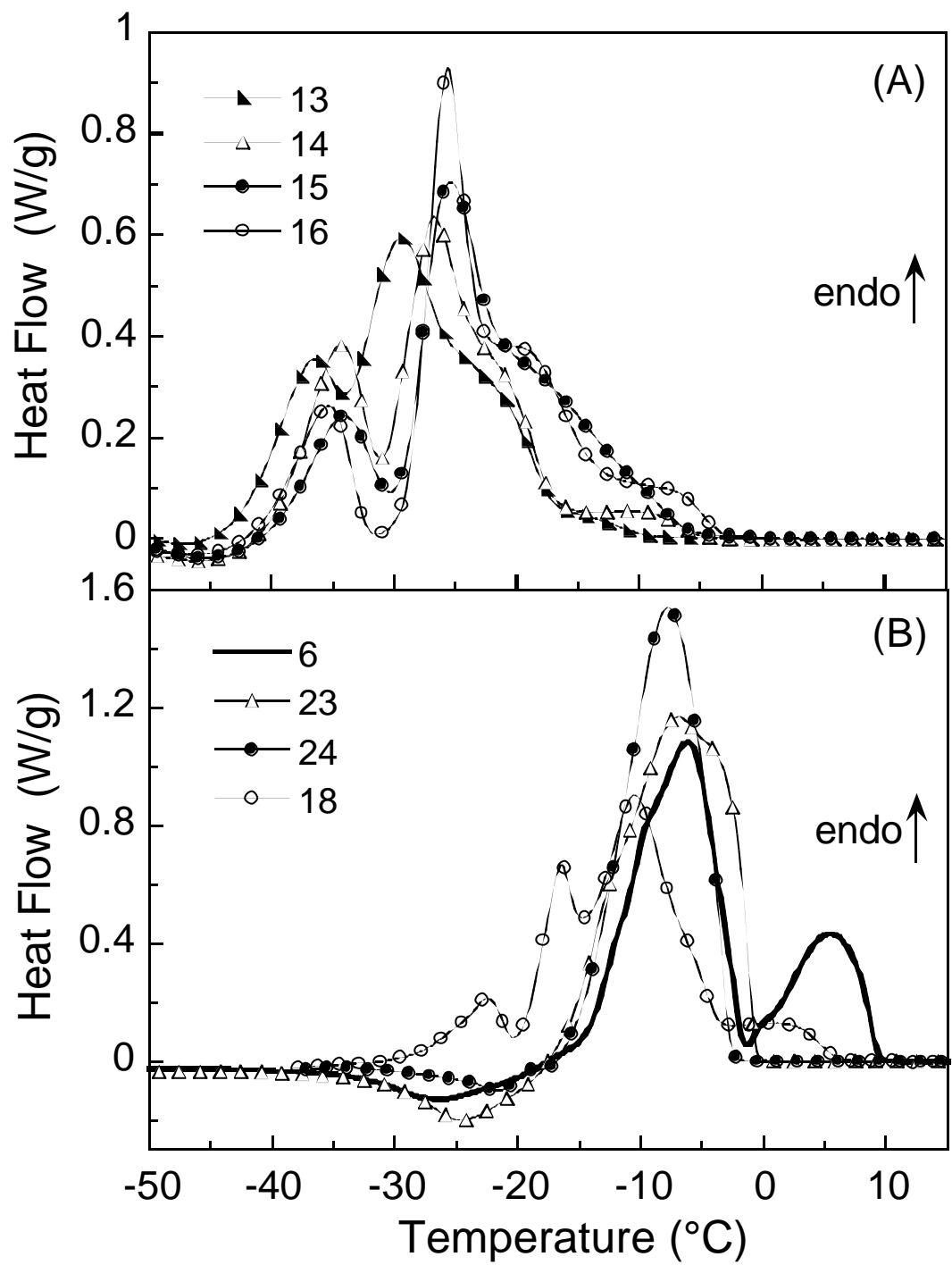


Figure 2. "Fast authentication of .....", G. Salvetti et al.

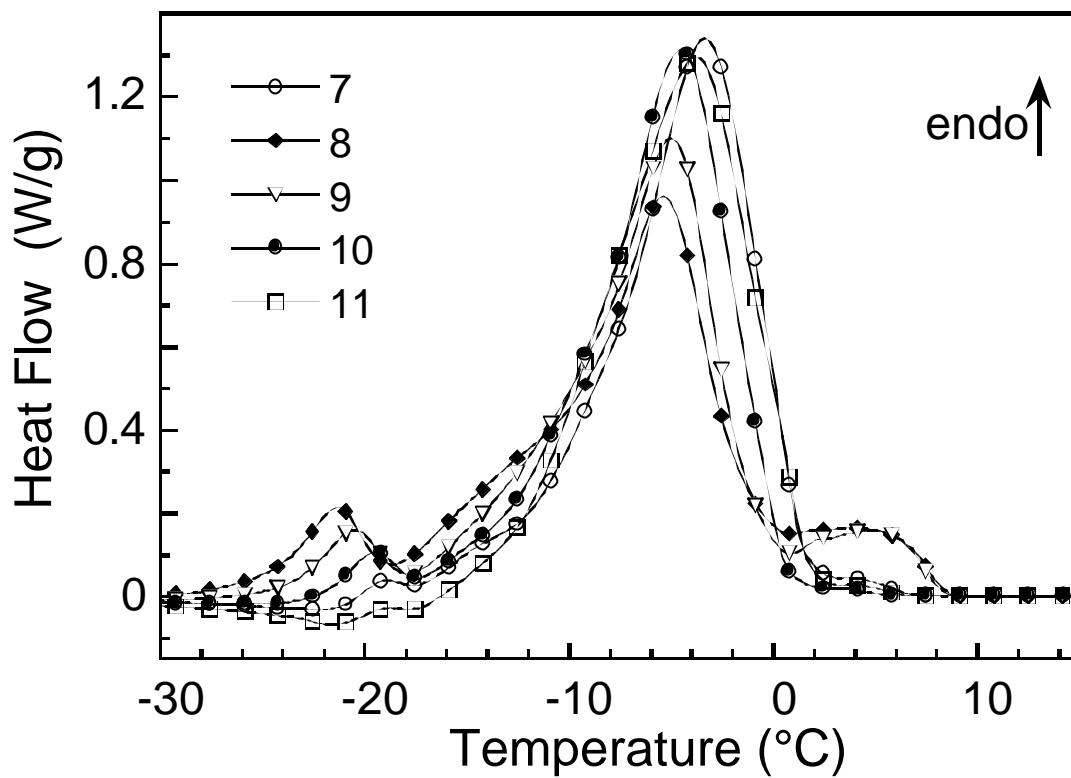


Figure 3. "Fast authentication of .....", G. Salvetti et al.

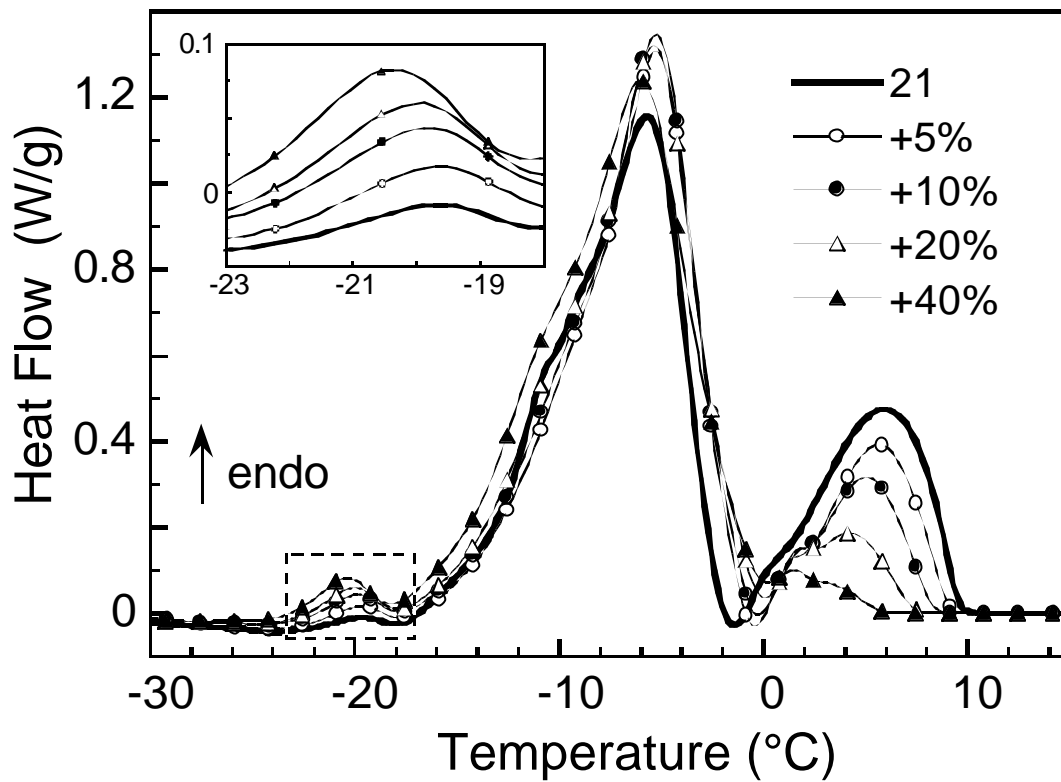


Figure 4. "Fast authentication of .....", G. Salvetti et al.

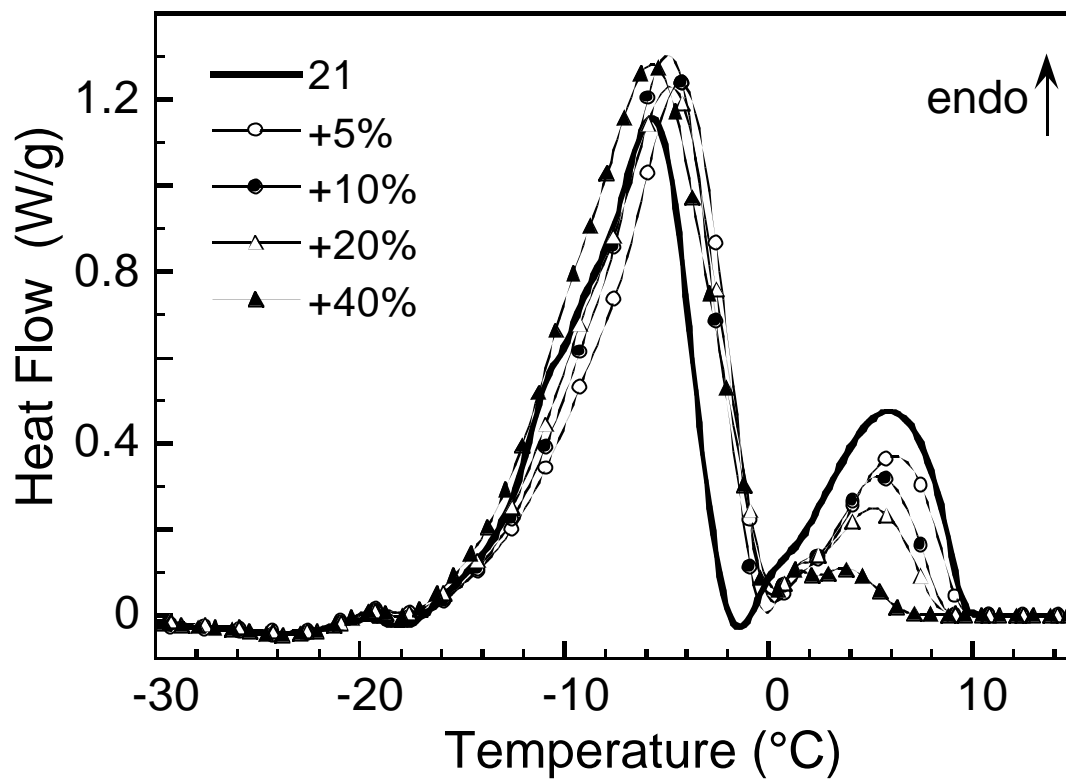


Figure 5. "Fast authentication of .....", G. Salvetti et al.

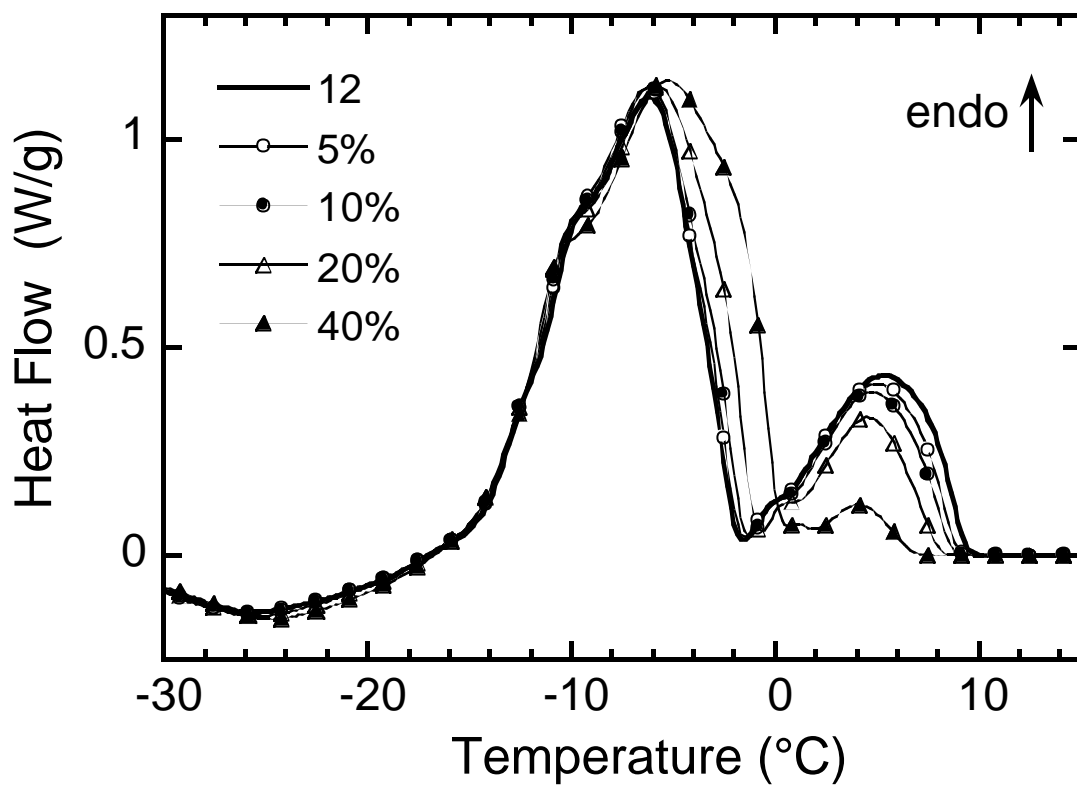


Figure 6. "Fast authentication of .....", G. Salvetti et al.



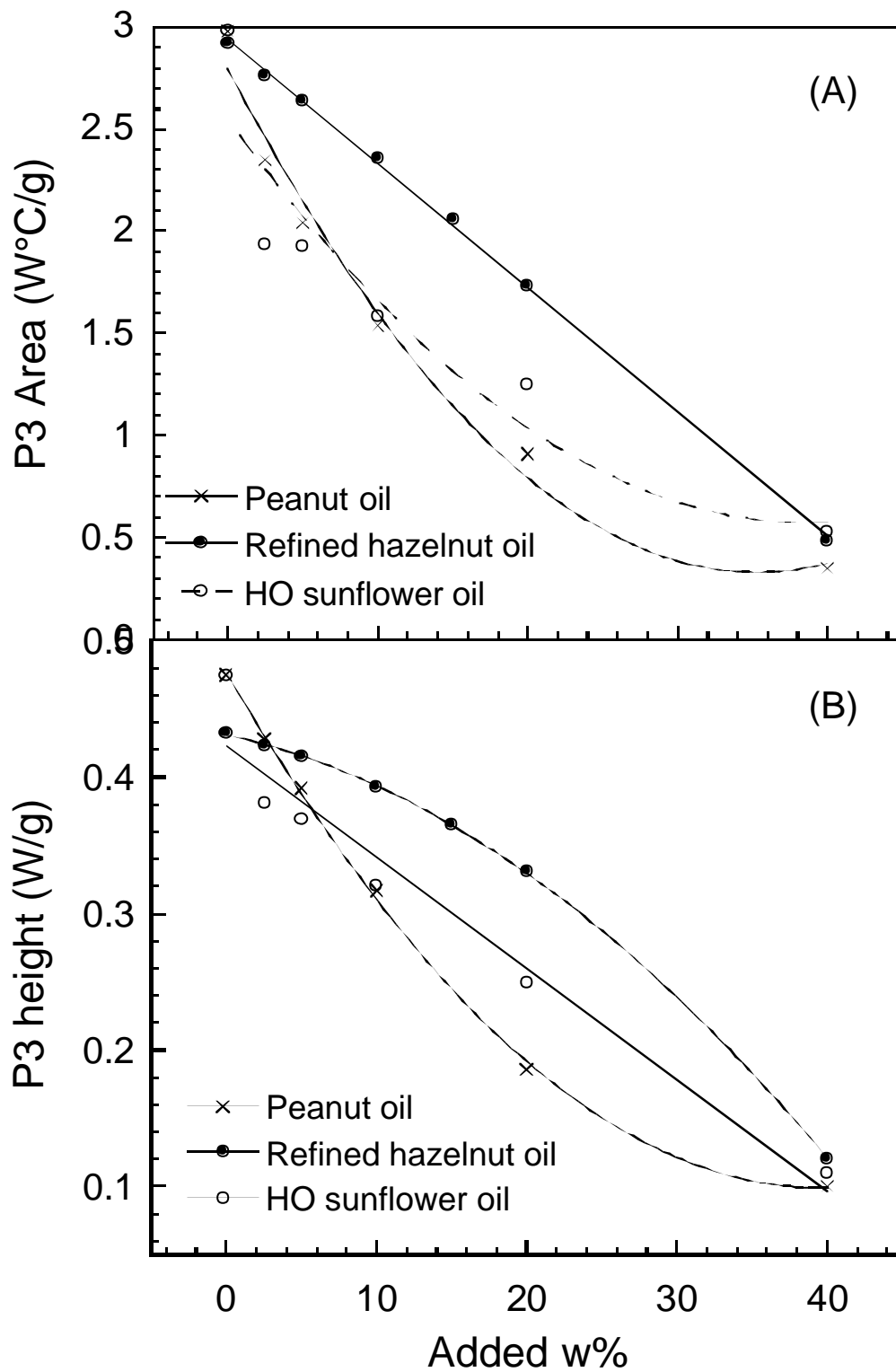


Figure 7. "Fast autentication of .....", G. Salvetti et al.

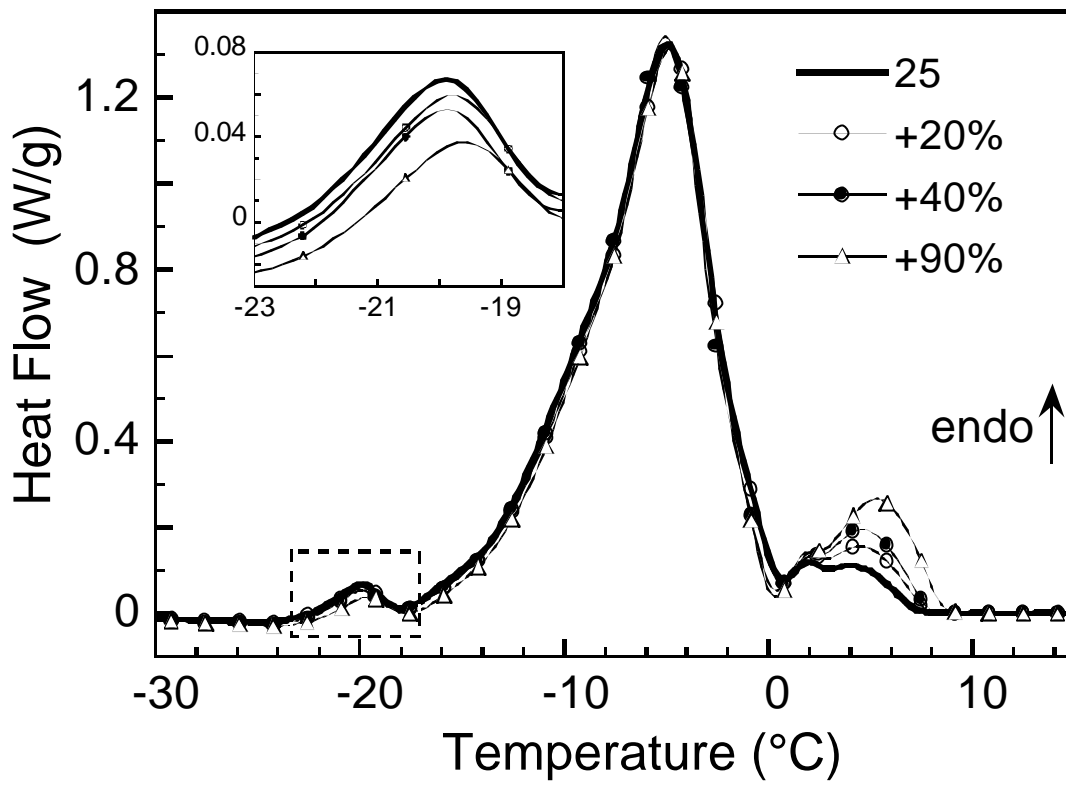


Figure 8. "Fast authentication of .....", G. Salvetti et al.

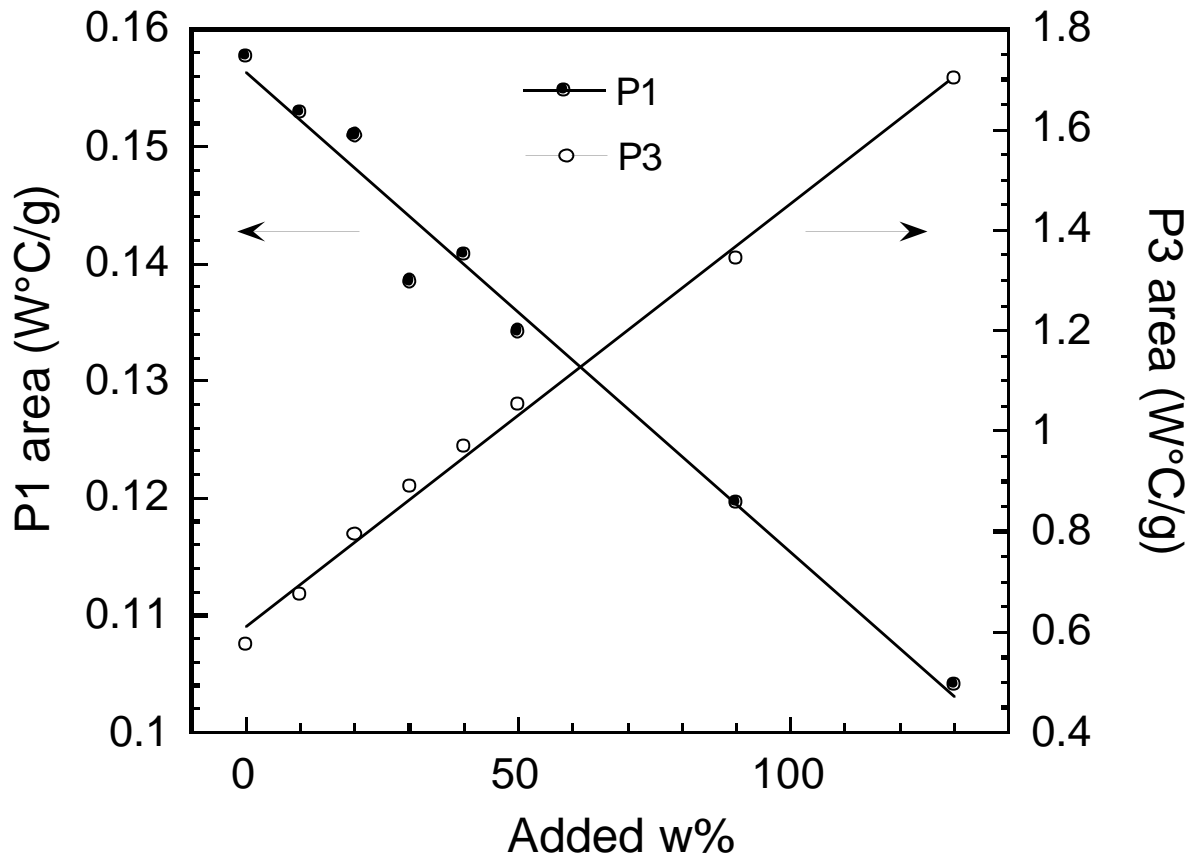


Figure 9. "Fast autentication of .....", G. Salvetti et al.

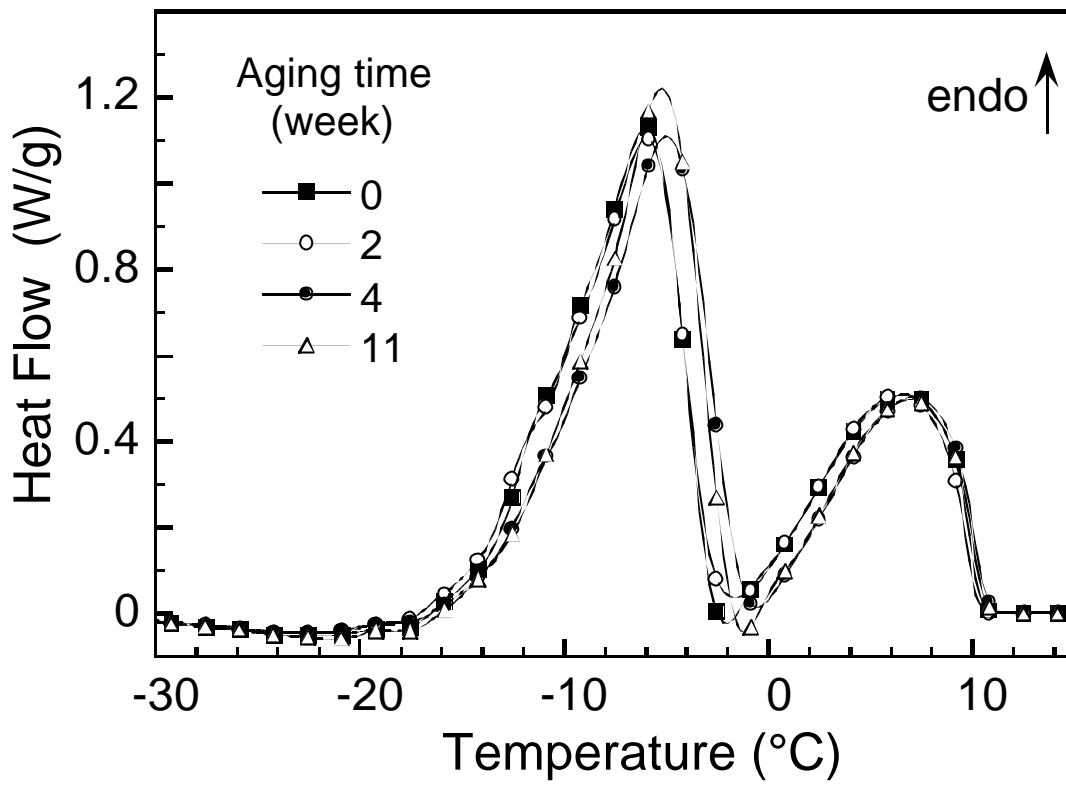


Figure 10. "Fast authentication of .....", G. Salvetti et al.

Extra virgin olive oils (EV00)													
Sample Number	Polyphenols	Acidity	N° perox	Origin	Cultivar					Fruity	Taste		
					Frantoio	Leccino	Moraiolo	Pendolino	Maurino		Bitter	Pungent	Median
1	96.00	0.15	9.65	Pistoia	50%	50%	0%	0%	0%	4.55	2.90	4.40	
2	111.00	0.20	9.20	Firenze	50%	10%	30%	10%	0%	3.00	3.80	3.90	
3	154.00	0.20	10.85	Firenze	20%	20%	60%	0%	0%	3.50	3.55	3.95	
4				Firenze	34%	30%	30%	3%	3%	5.50	6.45	5.30	
5	105.00	0.15	10.15	Grosseto	90%	0%	0%	10%	0%	4.55	4.05	5.35	
6	119.00	0.15	8.55	Siena	62%	20%	15%	3%	0%	4.75	4.05	5.35	
<b>Refined olive oils (R00)</b>													
No.	Acidity	N° perox	Origin	K232	K270	DeltaK							
7	0.06	0.80	ITALY	2.135	0.649	0.081							
8	0.10	2.80	TUNISIA	2.870	0.578	0.032							
9	0.09	0.60	ITALY	2.681	0.662	0.067							
10	0.06	0.90	ITALY	2.966	0.705	0.071							
11	0.12	0.70	SPAIN	2.025	0.576	0.066							

Table 1

<b>Commercial oils (quality declared in the label)</b>		
<b>No.</b>	<b>Sample</b>	<b>Origin/cultivar</b>
12	EVOO (IGP)	Tuscany/blend
13	Sunflower oil	
14	Grape-seed oil	
15	Soybean oil	
16	Corn-seed oil	
17	Olive oil	
18	Peanut oil	
19	EVOO	Tuscany/blend
20	EVOO	Liguria/taggiasca
<b>Oils from different suppliers</b>		
<b>No.</b>	<b>Sample</b>	<b>Origin / Supplier</b>
21	EVOO	Apulia / CNR-Bari
22	Refined hazelnut oil	Turkey / Carapelli-Florence
23	Crude hazelnut oil	Turkey / Carapelli-Florence
24	High oleic sunflower oil	Carapelli-Florence
25	Refined olive oil	ARPAT-Lucca
26	EVOO (crop seas. 2005-6)	Tuscany/ private prod.

Table 2