APPLICATION NOTE

Differential Scanning Calorimetry

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# Detecting the Adulteration of Extra Virgin Olive Oil by Controlled Cooling DSC

## Introduction

Food adulteration normally makes the news with cases like melamine in milk[1]. However, high-value products are often subjected to adulteration by lower-value materials and this can be difficult to detect. As a high-priced produce, a pint of extra virgin olive oil (EVOO) is close in cost to that of a half gallon of food-grade olive pomace oil. University of California at Davis has reported that the majority of the extra virgin olive oils sold in California fail the tests for the same (EVOO), using a variety of techniques (ultraviolet and visible spectroscopy [UV/Vis], gas chromatography [GC], liquid chromatography [LC]), and wet methods[2]. However, considering the way EVOO is made, one would expect a relationship to its thermal properties.

Differential scanning calorimetry (DSC) is commonly used to analyze foods in both quality control and research labs[3, 4]. DSC is often used to compare materials on heating, but cooling studies often give more information as materials can respond more thermodynamically under controlled cooling[5].

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## Experimental

### Materials

Initial samples of four commercial olive oils were obtained locally and then samples of high-grade EVOO were obtained directly from small producers. In addition, samples of freshly pressed mono and multi-varietal EVOO, along with refined and salvage oil with known processing histories, were also obtained. All samples were stored in a cool, dark room, when not used, under $N_2$ purge.

### Instrumental

4-8 mg samples of the various oils were pipetted into pre-weighted and matched aluminum DSC sample pans (PerkinElmer Part No. 02190041). These were then run on a PerkinElmer DSC 8500 under $N_2$ purge at 20 cc/min and cooled from room temperature to -60 °C at a rate of 5 °C per minute. A two-stage refrigerated cooler was used. Once at -60 °C, they were held there for three minutes to ensure complete cooling. Then, the samples were heated back to room temperature at 10 °C per minute. All samples were run in triplicate and the results averaged.


*Figure 1.* The DSC 8500 is a dual furnace power compensated design differential scanning calorimeter capable of very precise control on heating and cooling.

## Results

The commercial samples of olive oil show distinct thermal differences. Below, extra virgin (solid), refined (dashed), and pomace (dotted) olive oils are shown during the cooling run.

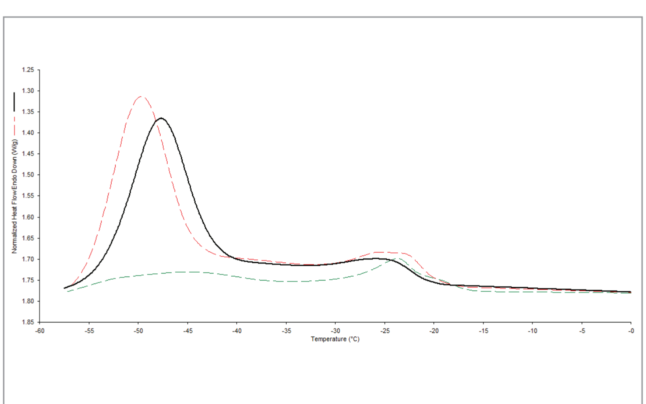


*Figure 2.* Grocery store grades of extra virgin, refined and pomace olive oils were run by controlled cooling in the DSC. Notice the distinctive fingerprints, particularly of the pomace oil, which lacks the low temperature peak.

As shown in Figure 3, we ran a series of EVOO samples that we were reasonably sure were truly extra virgin, as well as two received directly from a Texas-based producer who could assure this. While preliminary, the data shows some interesting features. First of all, the higher-temperature peak appears in the same temperature range as the pomace oil peak but is very small, even compared to the grocery store EVOO. This data suggests that the grocery store EVOO may be diluted with another oil.

Secondly, it appears that there are shifts in the peak shapes and temperatures with the varietal and origin of the oil. For example, note the difference in shape and peak position of the low temperature peak between the Spanish Arbeguina and the Spanish Arbosana. Origin appears to complicate, as seen in the Texas versus Spanish Arbeguina scans. Futher work would be needed to see if this holds, but based on previous work with nut oils[6], it seems likely.

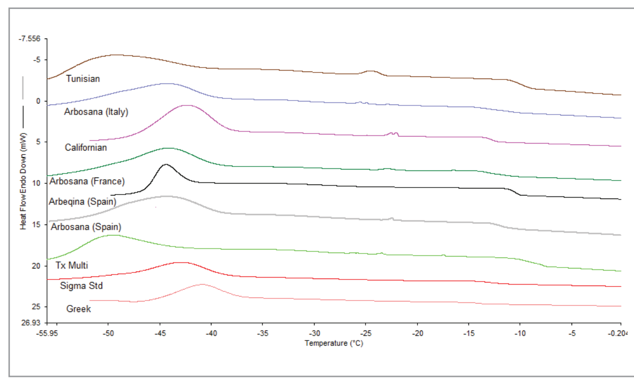


*Figure 3.* High-quality EVOO from small batch suppliers. The Texas EVOOs were of known origin. Note the lack of strong "pomace peak".

Characterizing these differences is often done by taking partial areas under the curve, as shown in Figure 4. This is shown for EVOO and a large high-temperature peak similar to that of the pomace oil was seen in all the grocery store samples in contrast to the truly EVOO samples in Figure 3.

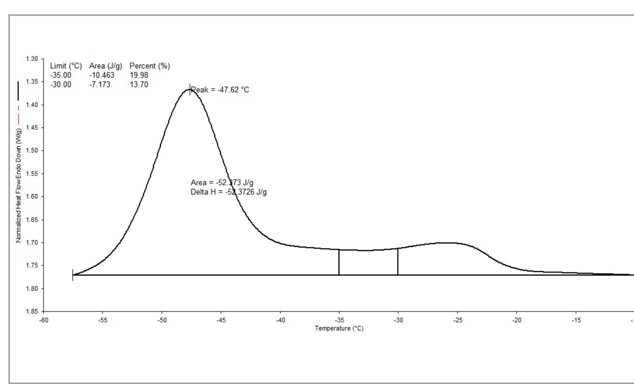


*Figure 4.* Multiple peak areas in a DSC scan analyzed by the partial areas technique. Only three partial areas are shown above for clarity.

With the "pomace peak" occurring in the -20 °C to -10 °C range and the major "EVOO peak", it appears likely that one could sort materials based on this approach. To test this, we created blends of EVOO and pomace oil in three amounts. The thermograms are overlayed in Figure 5. This data was used to construct a simple model from the partial area data shown above. Linear regression suggests we can estimate the addition of more than 7% olive oil-based adulterant to the olive oil. Based on this approach, we suspect the grocery store EVOO to have 12-15% adulterant or to be pressed at higher temperatures (see Figure 6). More exacting model techniques, such as those used in TIBCO Spotfire® software, are expected to give better results.

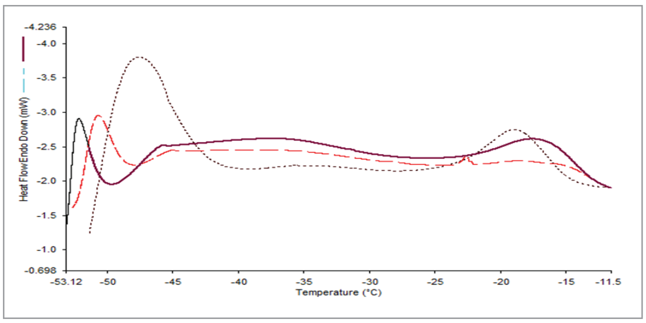


*Figure 5.* 25% EV (dashed), 50% EV (solid), and 75% EV (dotted) oils during the cooling run.

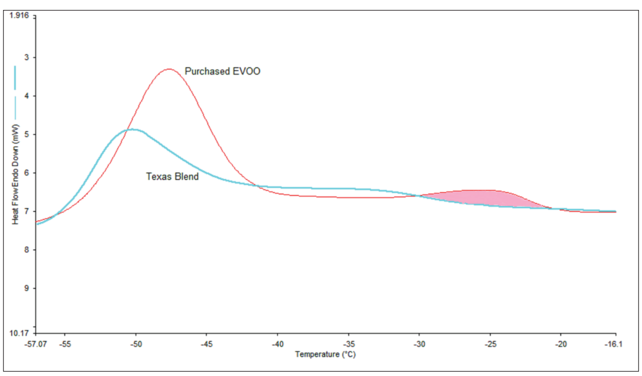


*Figure 6.* Overlay of the purchased EVOO and the Texas blend of known EVOO. The area of increased "pomace oil" is highlighted.

## Conclusion

Controlled cooling in the DSC represents a way to extract information from food products not normally accessible by other methods. Extra virgin olive oils have a distinct cooling profile that is different from lesser grades and apparently this profile is quite responsive to changes in composition. This gives a method for addressing adulterants as well as possibly identifying the varietal used to produce the oil. Futher work is planned on the effect of temperature and UV radiation.


## Acknowledgements

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## References


1. H. Hong. "China seizes 26 tons of melamine-tainted milk" CNN. http://www.cnn.com/2011/WORLD/asiapcf/04/27/china.tainted.milk/index.html
2. E. Frankel, R. Mailer, S. Wang, C. Shoemaker, J-X. Guinard, J. Flynn, and N. Sturzenberger, *Evaluation of Extra-Virgin Olive Oil Sold in California,* University of California at Davis: Davis, CA, 2011.
3. V.R. Harwalkar and C. Ma. *Thermal Analysis of Foods.* Elsevier: Amstedam, 1990.
4. D. Burlett, "Quality Control" in *Handbook of Thermal Analysis* V5, M Brown and P. Gallagher. Editors, Elsevier: Amsterdam, 715, 2008.
5. J. Menczel. *Thermal Analysis of Polymers.* Wiley: Hoboken. 2009.
6. S. Dyszel and B. Pettit, "*Determination of the country of origin of pistachio nuts by DSC and HPLC*" *Journal of the American Oil Chemists' Society,* 67, 947, 1990.



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