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Oil Analysis by Fast DSC

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Abstract

Thermal analysis of Olive and Sunflower Oil is done by Fast DSC to evaluate its potential to replace DSC for adulteration detection. DSC measurements take hours, Fast DSC minutes. Peak temperatures of the crystallisation peak in cooling for different Olive and Sunflower Oils are both comparable to DSC, but not always distinguishable. The heating curves of Olive and Sunflower Oil show more differences. Compared to DSC, Fast DSC shows lower peak temperatures for heating curve peaks.

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1. Introduction

The last several years multiple food fraud cases have surfaced. Due to its premium price and a production volume of approximately 3 million tonnes per year olive oil is vulnerable for adulteration by the addition of cheaper vegetable oils [1].

Differential Scanning Calorimetry (DSC) has been suggested as a possible method for verifying quality [2], determining varietal and geographical origin [3, 4] and detecting adulteration of Extra virgin olive Oil [5, 6]. DSC is preferable to other methods because it is fast, no pre-treatment of the oil is necessary and the use of environmental damaging solvents is not required.

Although DSC is faster than other analytical techniques such as gas chromatography and high performance liquid chromatography, a single measurement still takes about three hours. Companies buying olive oil need fast

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authentication on delivery. Fast DSC with scanning rates of 100 to 300 °C/s results in measurements of a few seconds and may therefore be a preferable method. To investigate the applicability of Fast DSC to oil adulteration detection four different Extra virgin olive Oils (EVOO) and three different Sunflower Oils (SFO) have been analysed.

2. Experimental

2.1. Samples

Four EVOO and three SFO samples bought in local stores in the Netherlands were used in the analysis (Table 1).

Table 1. List of analysed oils.

| Oil type | ID | Store | Olive type | Pressing method | Origin |
|----------|-----------|---------------|------------|-----------------|------------------|
| EVOO | Arbequina | Oil&Vinegar | Arbequina | Cold pressing | Cataluña, Spain |
| | Sítia | Oil&Vinegar | Koroneiki | Cold pressing | Sítia, Greece |
| | Puglia | Oil&Vinegar | Coratina | Cold pressing | Puglia, Italy |
| | Melilla | 'Homemade' | - | - | Melilla, Morocco |
| SFO | Goldsun | Deen | - | - | - |
| | AH | Albert Heijn | - | - | - |
| | Dirk | Dirk vd Broek | - | - | - |

2.2. Fast DSC analysis method

Oil samples were analysed with a Flash DSC1 of Mettler-Toledo. A Fast Liquid DSC sensor was used [7]. As reference 2-butanol was used because of its low melting point of -115 °C and boiling point of 99.5 °C. The sample size is on the order of 10 nl (~9 µg).

The following temperature program was used: heating from -100 to 60 °C with a rate of 300 °C/s, isotherm at 60 °C for 10 ms, cooling back to -100 °C at a rate of -100 °C/s, isotherm at -100 °C for 5 s, repeated five times. First heating curves are not shown because these differ from all the following heating curves, possibly due to the very slow cooling from room to base temperature. The machine was purged with dry nitrogen to prevent icing.

Repeatability of measurements with the same chip shows a maximum standard deviation (SD) of typically 0.6 °C for the cooling peak temperature. Reproducibility of measurements with different chips shows an SD of typically 1 °C. STARE software was used to analyse the thermograms, which have peaks that are exothermic up.

3. Results and Discussion

3.1. Influence of the scanning rate

Increasing the cooling rate causes the crystallisation peak temperature to shift to lower temperatures, the peak height and area increase as expected, see Fig.1. The enthalpy of crystallisation (peak area divided by scan rate) slightly increases as well, which is unexpected. In the cooling curve there is an artefact (oscillation?) which moves to lower temperatures at lower cooling rates. At higher scanning rates the cooling curves stop at higher temperatures because the cooling rate can no longer be sustained when approaching the base temperature.

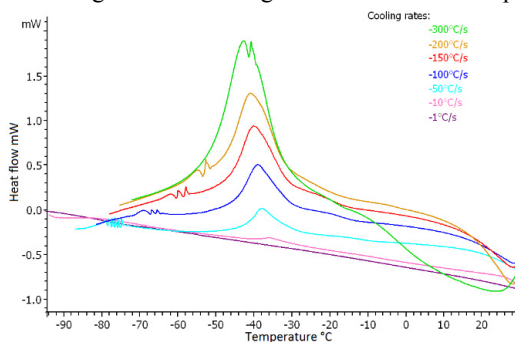


Fig. 1. Cooling curves of olive oil vs IPA with different cooling rates -1 to -300 °C/s.

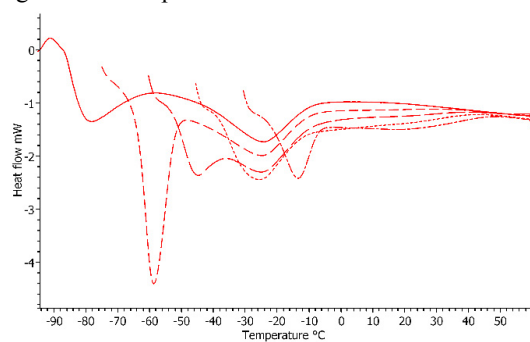


Fig. 2. Heating curves of Puglia EVOO vs 2-butanol measured from different starting temperatures, heating 300 °C/s.

3.2. Influence of the base temperature

The heating curves show three peaks, one exothermic, and two endothermic, see Fig. 2. The exothermic peak is present when the measurement is started at -100 °C, but it disappears when the measurement is started at higher

temperatures. The coldest endothermic peak shifts to higher temperatures and increases in peak height when started at higher temperatures. The second endothermic peak is at first not influenced by the base temperature. However, when the coldest endothermic peak comes closer to the second one these two peaks seem to merge together.

The crystallisation peak in the cooling curve is not affected by the base temperatures until this becomes too high.

3.3. Thermograms of different EVOO and SFO

Cooling curves of EVOO and SFO vs 2-butanol show one major exothermic peak around $-40\text{ }^{\circ}\text{C}$, peak A, with a tiny shoulder (Fig. 3) about $20\text{ }^{\circ}\text{C}$ higher. The peak temperature, peak height and enthalpy of the various oils tested have been listed in Table 2.

Table 2. Peak temperature, peak height and enthalpy of different peaks of different EVOO and SFO.

| Oil type | ID | Peak A | | | Peak B | | Peak C | | Enthalpy B+C (mJ) |
|----------|-----------|------------------------------|------------------|-----------------|------------------------------|------------------|------------------------------|------------------|-------------------|
| | | PeakT ($^{\circ}\text{C}$) | Peak Height (mW) | Enthalpy A (mJ) | PeakT ($^{\circ}\text{C}$) | Peak height (mW) | PeakT ($^{\circ}\text{C}$) | Peak height (mW) | |
| EVOO | Arbequina | -34.2 | 0.91 | 0.16 | -19.2 | 1.4 | -79.4 | 1.0 | 0.21 |
| | Sitía | -35.7 | 0.99 | 0.18 | -18.9 | 1.8 | -73.1 | 2.2 | 0.49 |
| | Puglia | -38.6 | 0.79 | 0.13 | -22.4 | 1.1 | -78.1 | 1.3 | 0.21 |
| | Melilla | -39.5 | 0.80 | 0.12 | -21.8 | 1.8 | -73.9 | 2.4 | 0.48 |
| SFO | Goldsun | -40.1 | 0.64 | 0.11 | -21.6 | 1.1 | -79.4 | 1.5 | 0.29 |
| | AH | -40.5 | 0.60 | 0.10 | -21.9 | 1.1 | -82.1 | 1.2 | 0.23 |
| | Dirk | -43.9 | 0.47 | 0.07 | -25.0 | 0.8 | -82.4 | 1.0 | 0.15 |

Previous studies applying DSC also reported this major exothermic peak around $-40\text{ }^{\circ}\text{C}$, as well as a minor exothermic peak at $-13\text{ }^{\circ}\text{C}$, with an enthalpy of around 65 J/g [5, 8]. The major exothermic peak in cooling curves is associated with the solidification of major triacylglycerols (TAG) in olive oil [5]. Maggio et al. analysed 69 different EVOO samples and reported peak temperatures for the major exothermic peak ranging from $-46\text{ }^{\circ}\text{C}$ to $-32\text{ }^{\circ}\text{C}$ [8].

The enthalpy of this crystallisation peak measured in the present study is about five times smaller than reported in other studies, this is not yet understood. Measurements on lysozyme show an excellent agreement between Fast DSC and DSC regarding the enthalpy of phase transition [7]. And the scanning rate of cooling does not seem to have a considerable influence on the enthalpy (Fig.1).

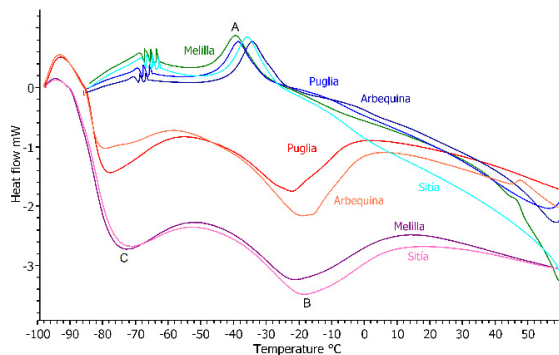


Fig. 3a. Heating curves (below) and cooling curves (above) of four different EVOO vs 2-butanol. Cooling $-100\text{ }^{\circ}\text{C/s}$, heating $300\text{ }^{\circ}\text{C/s}$.

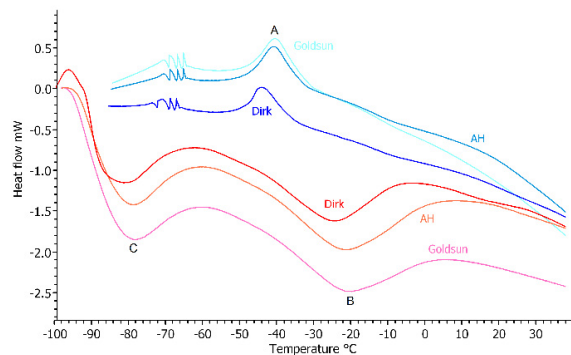


Fig. 3b. Heating curves (below) and cooling curves (above) of three different SFO vs 2-butanol. Cooling $-100\text{ }^{\circ}\text{C/s}$, heating $300\text{ }^{\circ}\text{C/s}$.

The heating curves of the four EVOO and three SFO all show an exothermic peak at about $-95\text{ }^{\circ}\text{C}$ and two endothermic peaks, indicated with B and C in Fig. 3.

Peak B is associated with the melting of the oil. However, with the Fast DSC this peak is detected at lower temperature ($-20\text{ }^{\circ}\text{C}$) than with DSC, with which the peak is detected at $-3.5\text{ }^{\circ}\text{C}$ [5]. The heating curve peaks show a rather small enthalpy just like the crystallisation peak (see Table 2). The exact value is difficult to determine because of the uncertainty about the base line, giving more variations in the enthalpy for peaks B+C than for peak A. An enthalpy of 75 J/g is reported for the melting peak in DSC measurements [9].

3.4. Distinguishing olive oil and sunflower oil

Measurements with oil as reference instead of 2-butanol demonstrate distinct differences between the two oils.

Cooling curves of oil against oil show a small differential peak (Fig. 4) for all three comparisons: SFO vs SFO, EVOO vs EVOO, and SFO vs EVOO, the last one giving the largest differential peak.

The heating curves show more interesting differences, with large peaks for the EVOO vs SFO samples, while Dirk vs Goldsun SFO gives no significant peaks. Furthermore, Puglia EVOO vs itself remarkably shows larger peaks than Dirk vs Goldsun, but still not as much as EVOO vs SFO.

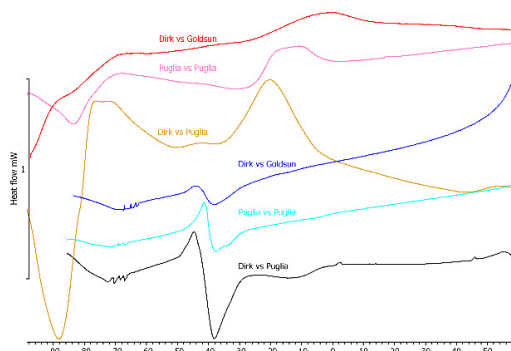


Fig. 4. Heating curves (above) and cooling curves (below) of oil vs oil. Cooling -100 °C/s, heating 300 °C/s.

4. Conclusions and outlook

It is shown that oil analysis can be performed with Fast DSC.

The crystallisation peaks of both olive oils and sunflower oils in cooling appear at the same temperatures as in DSC, and cannot easily be distinguished. They show a much lower (5x) enthalpy (ca 12 J/g) in our Fast DSC set up than found with DSC, presently unexplained. The heating curves show at least two major endothermic peaks, where the one associated with melting occurs at a lower temperature than in DSC. The enthalpy of the melting peak is comparable to that of the crystallisation peak.

When measuring olive oil vs sunflower oil, no significant crystallisation peak is present anymore, but large peaks remain in the heating curve. Future investigations will focus on the missing enthalpies, and on the reliability of the heating curve as an indicator of adulteration.

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