Determination **of iodine value and glyceride evaluation in lipids** using an FTIR process analyser

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Abstract

A variety of triglycerides are analysed at 80°C using a static-optics FTIR spectrometer (the IRmadillo) to replicate industrial oil refining processes. A calibration curve using PLS has been built for these chemicals giving an iodine value (IV) prediction error of ± 7 for a range of 0 to 260. Additional analysis of the samples shows that PLS-DA enables classification of the chemicals with 100% effectiveness. The authors believe this will translate into effective and efficient monitoring of melting point and solids content at a variety of temperatures, improving efficiency and reducing costs for edible oil processing.

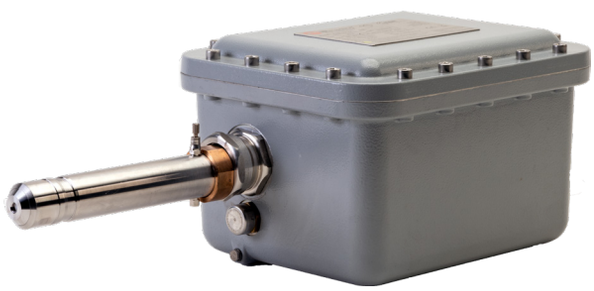
Introduction

The Iodine Value (IV) is a measure of the degree of unsaturation of oils and fats. It is defined as the amount of iodine (grams) absorbed by 100 g of oil or fat. IV can provide an estimation of melting point and oxidative stability which relate to the degree of unsaturation.

Mid-infrared FTIR spectroscopy is a very powerful technique for on-line analyses – such as determining iodine value – because it directly observes fundamental stretching and bending modes of molecules, giving intense signals that are easy to interpret (most notably in this case, the C-H stretches and bends of double bonds in unsaturated molecules).

The American Oil Chemists Society (AOCS) has a recognised technique for the determination of IV for triglyceride-based oils and fats based on near-infrared (NIR) spectroscopy.* While functional, NIR spectroscopy is inherently limited in its capability because of the quality of information available using NIR wavelengths.

Furthermore, conventional FTIR instruments are not suitable for industrial installations because they make use of moving optics and



IRmadillo™

Key Words

- Iodine value (IV)
- Lipids & fats
- Triglycerides
- Melting point
- Oil processing
- FTIR (mid-infrared) spectroscopy
- In-line process monitoring

Features & Benefits

- Vibration tolerant
- Long-term stability
- Low maintenance
- Compact design
- Real-time, multi-component analysis
- Easy to use

fragile fibre probes, which struggle to operate in environments with moving machinery and vibration.

However, the IRmadillo is based on static-optics FTIR spectroscopy, removing the fragility associated with fibre cables and moving optics in conventional FTIR instruments. This provides consistent performance and reliability. The rugged IRmadillo also has a rigid probe that allows for direct insertion into any process line for immediate analysis.

Here we present how the IRmadillo can be used to simultaneously measure the IV value of triglycerides and provide classification information, that the authors believe could be used for more informative real-time measurements such as melting point.

Experimental

The instrument was purged before and throughout the measurement with a supply of dry nitrogen and allowed to thermally stabilise prior to use. A background scan of 30 minutes was performed.

A range of triglycerides were purchased from Nu-Chek Prep and used without any further purification of modification. Samples were placed into the sample cell of an IRmadilloDiamond and heated to 80°C. These samples were scanned for 120 s with ten repeats.

The spectra were then analysed using Camo Analytics Unscrambler 10.5, with an extended multiplicative scattering correction (EMSC) applied to remove the temperature effects on the baseline, followed by partial least squares (PLS) modelling.

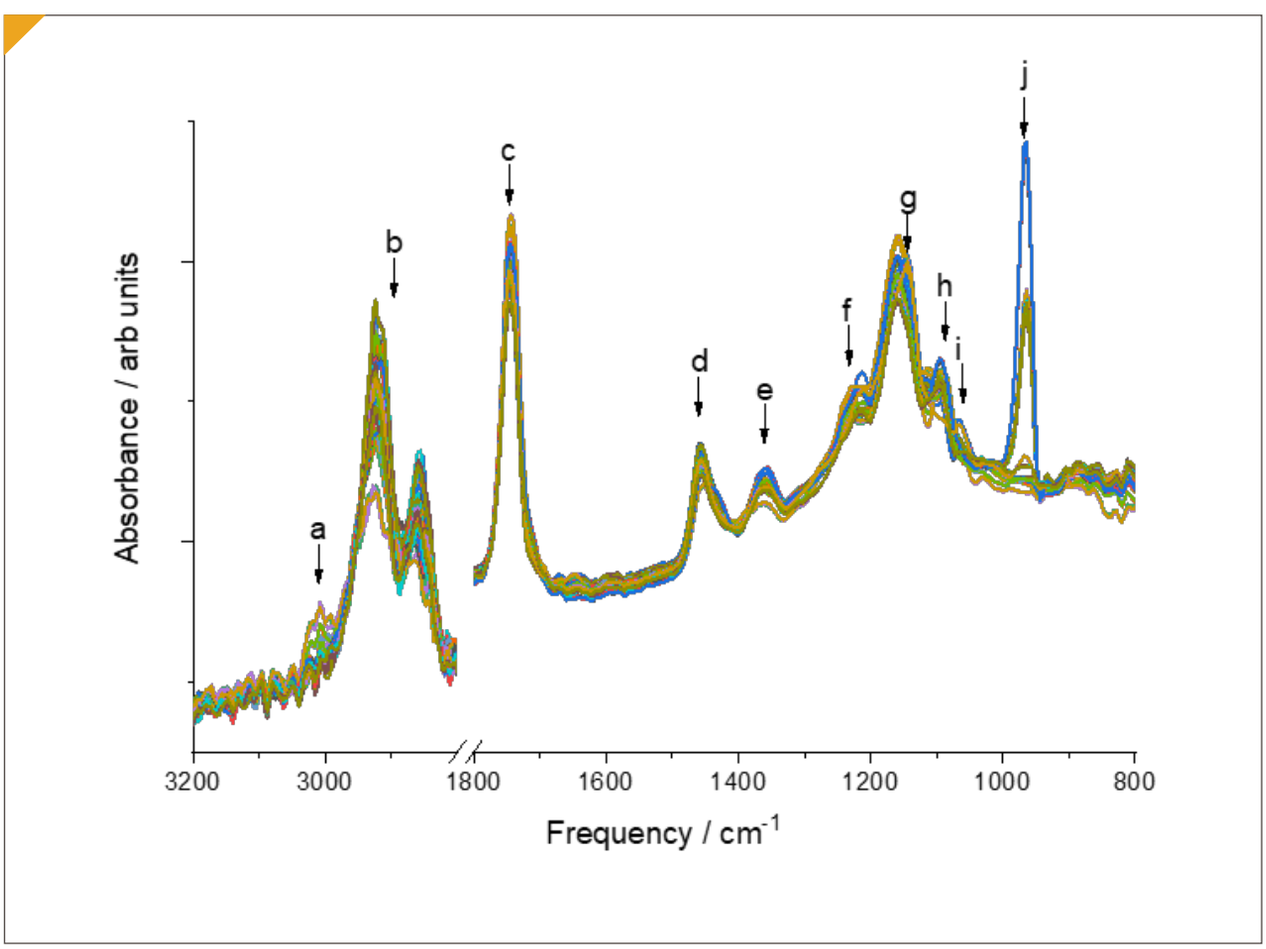


Figure 1: Spectra generated by the IRmadilloDiamond from anayses of multiple tricglycerides generated to produce a calibration model for iodine value and overlain to clearly show consistency and the key peaks of interest.

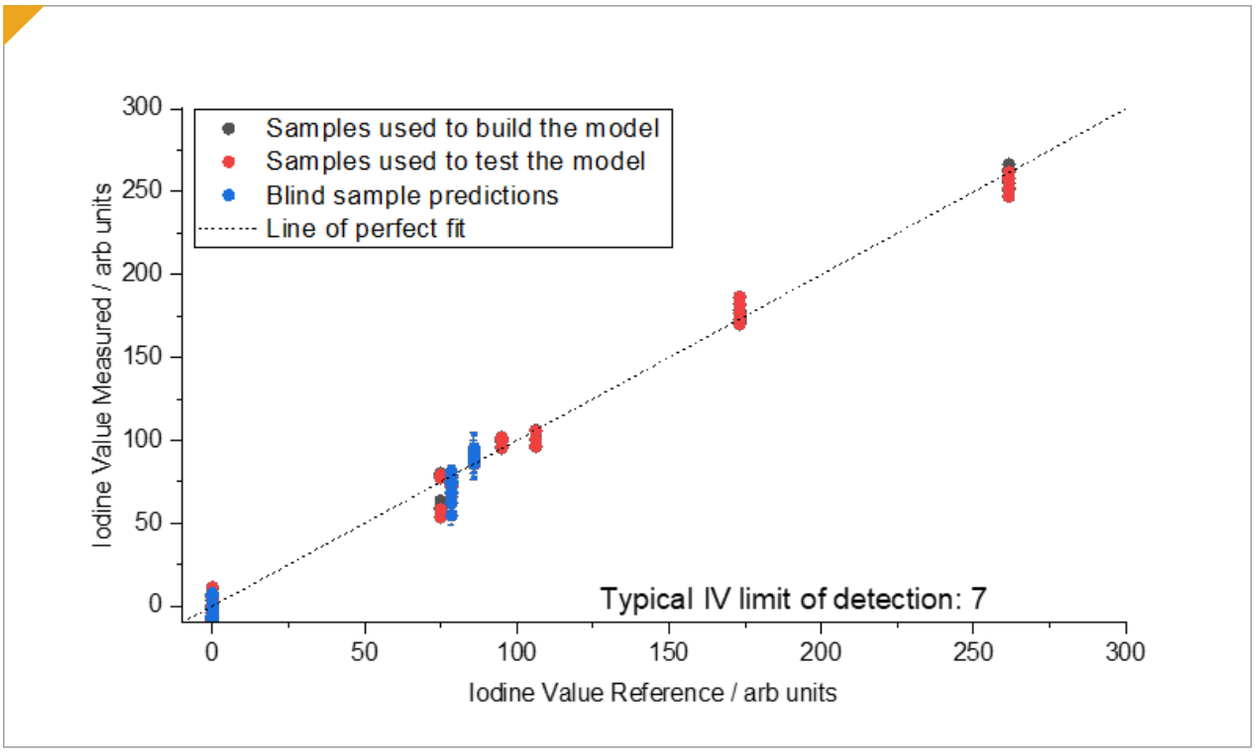


Figure 2: Plot of reference vs measured iodine values for Nu-Chek Prep saturated and unsaturated triglycerides.

Results and Discussion

The spectra are shown in Figure 1, which highlights the key absorbance peaks of interest. Using the frequency regions of 648–1800 cm^{-1} and 2900–3050 cm^{-1} uses the full range of information available in FTIR spectra, while ignoring the low signal region inherent in diamond-tipped ATR probes.

One of the benefits of FTIR over NIR is that a full spectral assignment is possible. The bands highlighted in Figure 1 are assigned here:

a) C=C-H stretch
b) C-H stretches
c) C=O stretch
d) CH2 “scissors” vibration
e) CH3 bending
f–i) C-O-C and C-C stretches
j) C=C-H bend in trans bonds

A PLS model for IV of triglycerides is shown in Figure 2. This model was built using an EMSC transform – used to remove any baseline artefact caused by subtle changes in probe coverage due to temperature gradients and air bubbles.

The average error across this concentration range (which is used as a limit of detection – LoD) is 7. The error of prediction for blind samples is 8.

An additional benefit of FTIR spectroscopy is that it gives high specificity of individual chemicals. The clear differences between the spectra shown in Figure 1 means that qualitative analysis can be performed such as principal component analysis (PCA).

Figure 3 shows the scores plots PCA analysis for the first 4 principal components, with the samples coloured by species. PC 1 vs PC 2 shows that there is a clear difference between the saturated and unsaturated chemicals, with a line of saturated species (A), unsaturated (B) and trilinoelaidin - a doubly unsaturated species - sitting clear of the other chemicals (C).

When other elements are considered (the additional plots) then further distinctions are seen. By performing a partial least squares discriminant analysis (PLS-DA) on this data it is possible to identify the triglyceride of interest with 100% accuracy.

The authors believe that this will translate into more meaningful and useful data for on-line processing such as melting point and solids content at various temperatures.

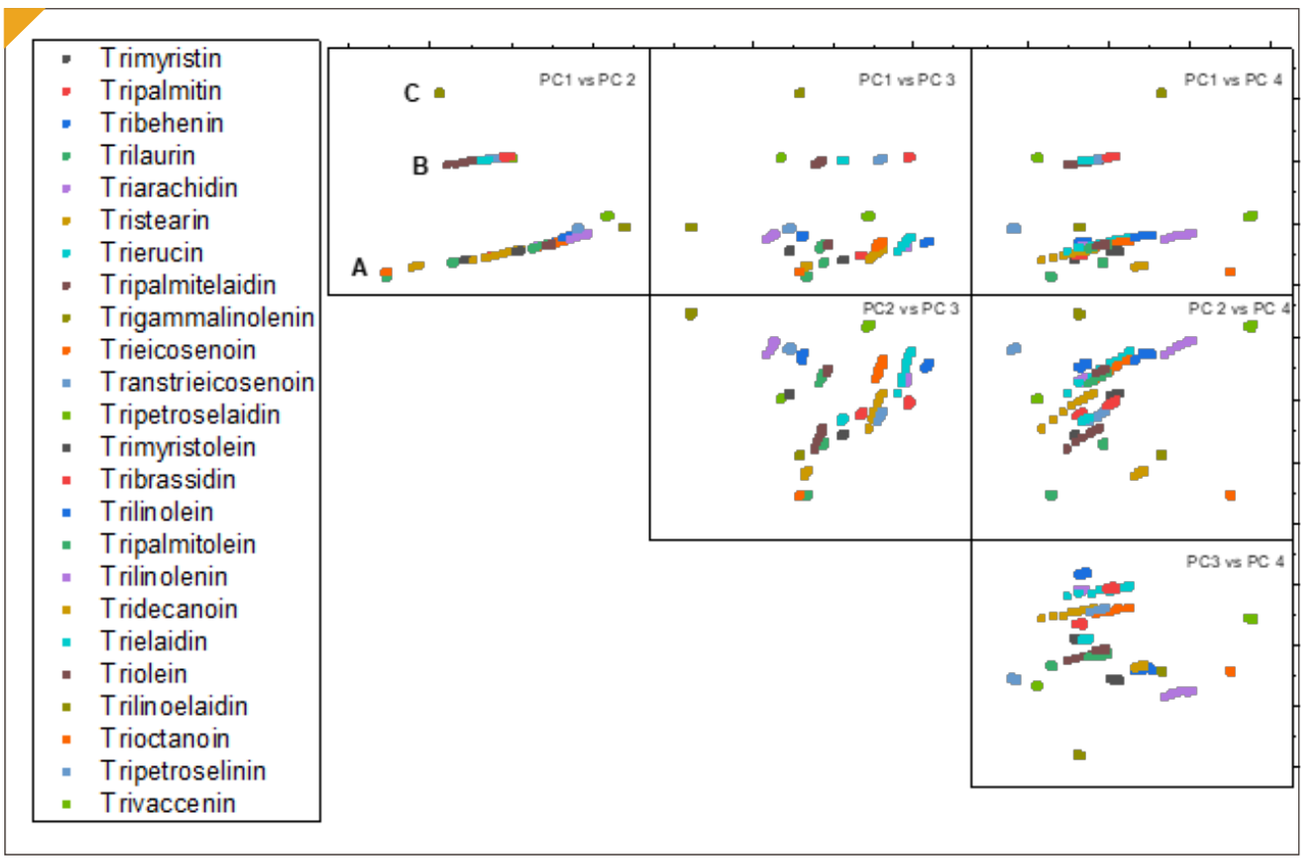


Figure 3: Cluster of scores plots for PCA analysis of triglyceride spectra – showing clear clusters of individual chemicals enabling identification. Axes have been removed for clarity.

Conclusions

These results show that it is possible to build meaningful IV calibrations with a static optics FTIR spectrometer. Calibrating these instruments requires substantially fewer samples than an equivalent NIR instrument, the instrument itself is inherently more robust and reliable than many NIR and standard FTIR instruments, and can be installed directly onto the process line of interest without the need for laying fragile fibre cables.

Keep in mind

The IRmadillo can run multiple different calibrations at once.

What does this mean for you?

This means that IV measurements can be performed as well as qualitative measurements such as classification without the need for additional instruments.

References

AOCS Standard Procedure Cd 1e-01, Revised 2017, Iodine Value by Pre-calibrated FT-NIR

Interested in finding out more?

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Contact us and let us know about your process monitoring and what you'd like to measure in real time.

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