Application Note No. 070

The Analysis of Mineral Oil in Sunflower Oil

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Introduction

The low-level detection and quantification of food grade mineral oil in sunflower oil is a difficult analytical problem. The sunflower oil matrix is viscous and contains a high proportion of high molecular weight compounds, which can quickly lead to a contaminated liner, injector, column and detector. A large mineral oil peak can be selected for the quantification, which is relatively volatile so that all of the sample is not necessarily analysed, and with the injection volume kept to a minimum to reach the required detection limits this helps to reduce the problem. However, there is still a build-up of involatile components.

Selective exclusion can be used to only transfer those peaks of interest from the injector onto the column, thereby keeping the majority of the involatile components in the liner and greatly reducing contamination of the column and detector. The remaining sample may be vented through the split line, by heating the injector to a very high final temperature, and then trapped. Or, when dealing with very small sample volumes it may be kept in the liner which is then changed at regular intervals. Finally, if the sample volume is larger and/or quite dirty, Difficult Matrix Introduction (DMI) can be used. The sample is injected into a DMI microvial held in the liner, this may be manually replaced at regular intervals, or with the Focus-DTD the liner exchange may be automated to replace the microvial for each sample. The sample matrix is kept within the microvial which may be disposed of allowing reuse of the liner.

In this instance, venting of the involatiles with a high final injector temperature was used, although automated DMI would be better when there is a high sample throughput and minimal operator interaction is required.

Principles

There were three stages to this work:

1) Inject the sample in splitless mode to obtain a reference chromatogram of both the sunflower and mineral oils, and optimise the majority of the injector conditions
2) Select the mineral oil peak for identification and quantification in sunflower oil
3) Optimise the Optic method in expert mode to selectively transfer the identified mineral oil peak onto the column, while minimising the transfer of the involatile components using Selective Exclusion

The principles of selective exclusion, when venting the involatile sample components, are to:

1) Inject the sample at a cool injector temperature
2) Heat the injector in splitless mode to a determined temperature (isothermal temperature) for a determined time (isothermal time) to transfer the peak of interest
3) Switch to split mode with a very high flow rate and heat the injector to its maximum temperature to clean-up the liner and trap the involatile components. Only 1-2% of these higher components are transferred to the column due to splitting.

When carrying out this analysis using automated DMI the principles are to:

1) Load the microvials into the SepLiners, cap and place in sample tray
2) The Focus-DTD then places the SepLiner into the injector head, injects the sample, seals the injector and starts the analysis
3) After injecting at a cool temperature the injector heats in splitless mode to a determined temperature (isothermal temperature) for a determined time (isothermal time) to transfer the peak of interest
4) The injector remains at this temperature but switches to split mode with a lower flow rate
5) At the end of the run the Focus-DTD removes the liner and microvial containing the involatiles, replaces it with a new SepLiner and microvial, then injects the next sample

The same principles of isothermal temperature and time are used, whether venting or using DMI, to transfer the peak of interest while excluding the involatile components.

Instrumentation & Conditions

- ATAS Optic 2-200 programmable injector
- HP5890 with FID

Optic Conditions

Liner: ATAS Fritted
Mode: Expert
Gas Flows: Split: 350
Vent: 50 ml/min
Initial temperature: 40 °C
Ramp rate 1: 4 °C/s
Isothermal temperature: 300 °C

Isothermal time: 5 mins
Ramp rate 2: 16 °C/s
Final temperature: 600 °C
Splitless time: 6 mins
Constant pressure: 14 psi

GC conditions:
Column: RH5-MS 30 m x 0.32 mm i.d. x 0.25 µm film
Initial Temperature:40 °C (2 mins)
Ramp Rate: 15 °C/min
Final Temperature: 350 °C (10 mins)
FID temperature: 350 °C

Reference Chromatogram

Firstly, the splitless conditions for both the injector and oven were optimised for a 1 µL injection of sunflower oil and a 1 µL injection of food grade mineral oil, to ensure total transfer of the sample to the column for analysis. This enabled us to obtain reference chromatograms of both oils for optimisation of the selective exclusion step and to enable a peak to be selected for the quantitation of mineral oil. The reference chromatograms are shown in Figure 1.

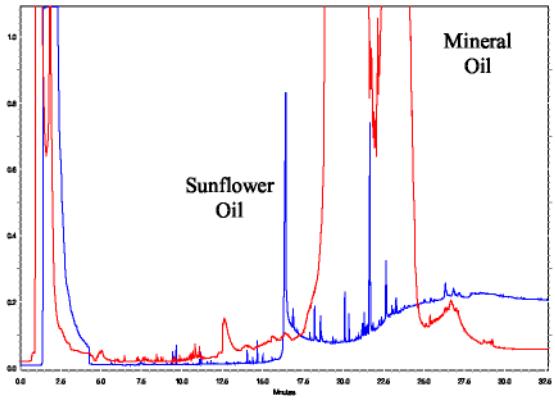

Figure 1: *Reference chromatograms of sunflower and mineral oils*

Selection of Mineral Oil ID Peak

Ideally, we wanted to select a large peak, to enable us to get a better detection limit, eluting at the front end of the chromatogram and therefore shortening the run time and decreasing the amount of heavy compounds analysed.

Unfortunately, the largest peak at the front end of the trace was a polar, tailing peak, which wasn't large enough to reach the required detection limits when injecting only 1 µL. Therefore, a later running large peak with a retention time of 19.6 minutes was selected. This could be detected down to 5 ppm with a 1 µL injection in both sunflower oil and DCM. Figure 2 shows this peak spiked in sunflower oil at a concentration of 5000 ppm compared to an injection of pure sunflower oil.

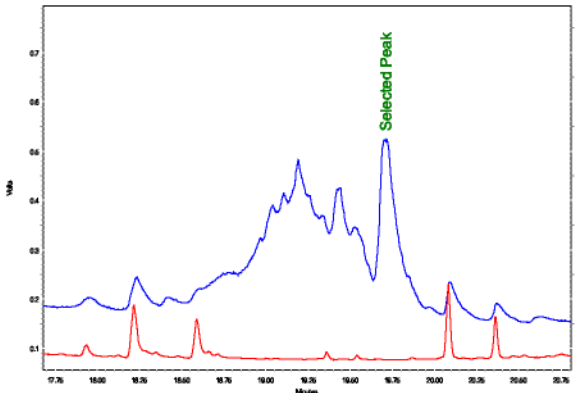

Figure 2: *Sunflower oil spiked with 5000 ppm mineral oil(upper trace) compared to sunflower oil (lower trace)*

Selective Exclusion

To prevent the transfer of the later running sample components from the injector onto the column and also to clean-up the liner after each injection, selective exclusion was used to remove the back end of the chromatogram by heating the injector to a high final temperature with a high split flow and trapping the components.

To determine the isothermal temperature necessary for transfer of the selected peak, a hydrocarbon mixture was injected using the same conditions. The retention time of the selected peak compared well to the retention time of C29, therefore the approximate boiling point would be 441 °C. Using the selective exclusion graphs, an ideal isothermal temperature for total transfer of the selected peak is 222 °C. However, due to the viscosity of the sample it takes a long time to transfer the selected peak and an isothermal temperature of 300 °C for 5 minutes was found to be optimal. The Optic conditions used are shown in Figure 3.

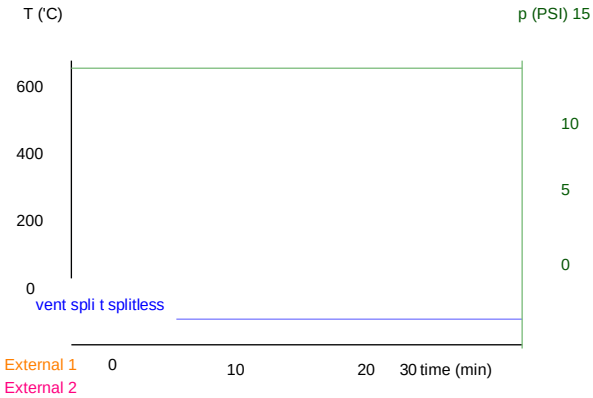

Figure 3: *Optic conditions used for transfer of the selected mineral oil peak in sunflower oil, while excluding the later running components*

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The comparison of an injection of 1 uL of sunflower oil spiked with 5000 ppm mineral oil with and without selective exclusion to pure sunflower oil is shown in Figure 4, and an enlargement is shown in Figure 5.

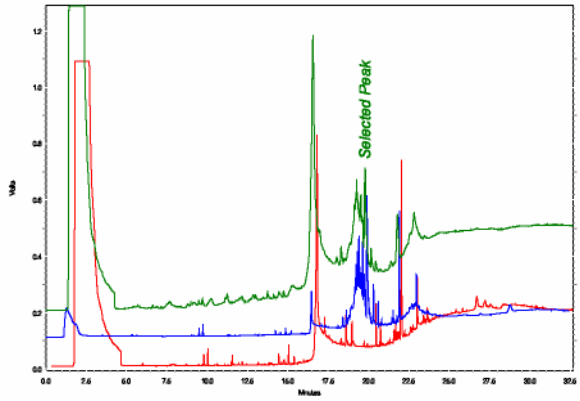

Figure 4: *Comparison of the analysis of 5000 ppm mineral oil in sunflower oil with (middle) and without (top) selective exclusion and pure sunflower oil (bottom)*

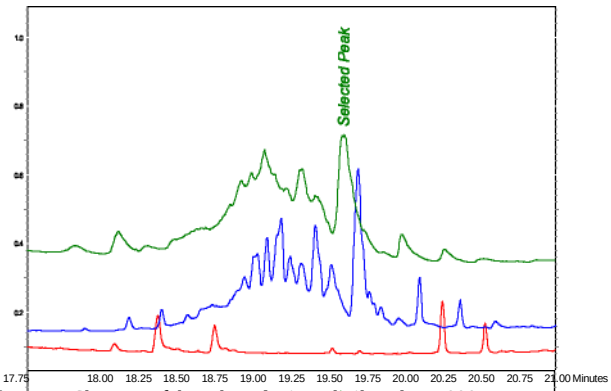

Figure 5: *Close-up of the selected mineral oil peak at 5000 ppm*

Figures 4 and 5 show that not only does selective exclusion reduce the amount of heavy sample components transferring from the injector to the column, but it also sharpens the peaks in the chromatogram and reduces the baseline.

Detection Limits

Figure 10 shows the analysis of 5 ppm mineral oil in sunflower oil with and without selective exclusion, compared to pure sunflower oil.

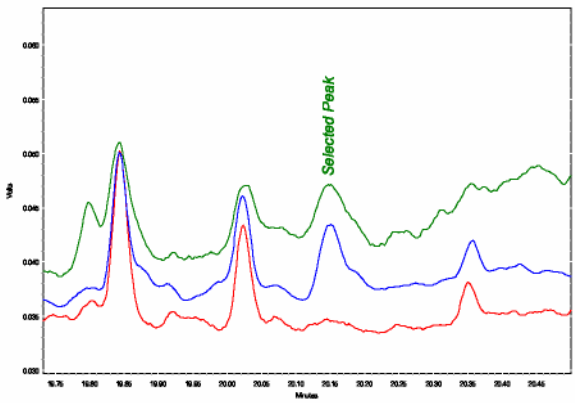

Figure 6: *5 ppm mineral oil in sunflower oil with (middle) and without (top) selective exclusion compared to pure sunflower oil (bottom)*

Conclusions

The use of selective exclusion in the analysis of mineral oil in sunflower oil and DCM enables the reduction of a build-up of involatile components in the injector on the column and detector. There are several different ways to remove these involatile components, depending on the environment in which analysis takes place.

Using selective exclusion also sharpens the peaks in the chromatogram improving resolution and therefore lowering detection limits when using an FID.

For further information about selective exclusion please see Technical Note No 18, or for a procedure of how to perform selective exclusion please see Technical Note No 18A.

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