

# Near infrared acousto-optic tunable filter spectrometer extractograms of carbon dioxide supercritical fluid extraction

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## Introduction

On-line monitoring with near infrared (NIR) spectroscopy allows quantitative analysis and possibly qualitative information as well. The rapid system employed allowed transient monitoring in cases where changes in composition would be abrupt in time or as a function of a moving fluid.

Supercritical fluid extraction (SFE) is a modern alternative way for preparative methods such as caffeine removal from green coffee beans prior to roasting or to recover flavors and spices from the crude plant sources. Analytical SFE is used as a separation technique prior to determination by another method such as HPLC or spectroscopy. In our laboratory, we have been concerned with selective SFE to eliminate open column silica gel fractionation of the petroleum ether extract or to reduce the sample work-up time. Detectors for supercritical fluid chromatography (SFC) include ultraviolet spectroscopic and hydrogen flame ionization types. The former being used with packed column SFC and the latter being used with capillary SFC.

In SFE detectors are seldom used but the ability to monitor a dense fluid under supercritical conditions is desirable. What near infrared has to offer is a window in the spectrum of CO<sub>2</sub> (a common extraction fluid that does not contain C–H bonds). By monitoring hydrocarbon absorbing species, a nearly universal detector for organic compounds would result. Rapid scanning ability would allow distinction between aliphatic and aromatic compounds. Also, alcohols and amines should be readily identified. What acousto-optic tunable filter spectrometers have to offer is a rapid random wavelength access and the potential of scanning on-the-fly.

The object in selective SFE in the particular separation problem that serves our analytical needs is to obtain polar lipid that is relatively free of non-polar lipid. It is desirable to streamline the usual solvent extraction followed by open column fractionation by combining these or eliminating fractionation. During selective SFE it is necessary to determine when most of the readily extractable lipid has been removed prior to extraction of the desired, more polar material. The selectivity may involve pure CO<sub>2</sub> followed by modified CO<sub>2</sub> or it could employ CO<sub>2</sub> of different densities to achieve selectivity.

## Experimental

The Kansas State University research model acousto-optic tunable filter spectrometer (TFS) was equipped with a high pressure flow through cell that had a 1 mm aperture, 10 mm pathlength and an 8  $\mu$ L volume. The monochromator of the TFS consists of a near infrared transmitting solid state device composed of tellurium dioxide with crossed Glan–Thompson polarizers designed for

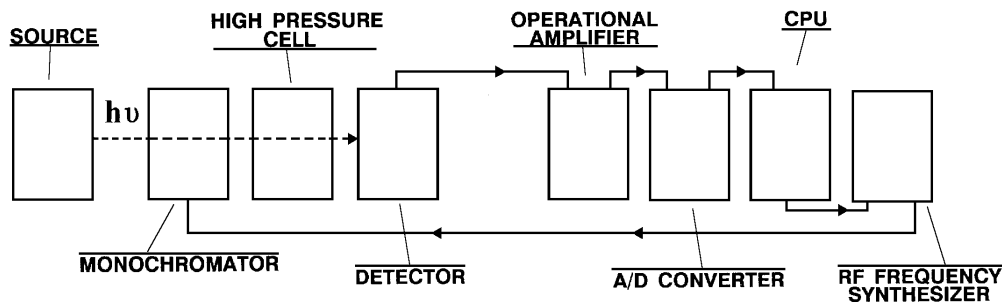


Figure 1. Overall arrangement of the KSU research model acousto-optic TFS.

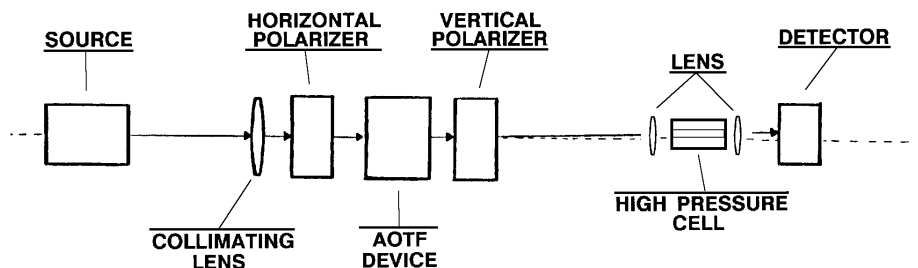


Figure 2. Optical layout of the AOTF spectrometer with a high pressure cell incorporated for SFE monitoring.

use in the near infrared on either side of the AOTF crystal. The tuning is driven with RF (ultrasonic) input via a piezoelectric transducer from a frequency synthesizer controlled by a microprocessor (PC). The source is a reflectively enhanced quartz tungsten halogen lamp. Quartz lens are used after the source and before the detector. The detector is a small area TE cooled extended range InGaAs(P) photovoltaic device. An operational amplifier and A/D converter were used between the detector and the CPU used for signal processing. Figure 1 shows the arrangement of the modules in a block diagram. Figure 2 shows the optical path involved. Quantitative data from liquid monitoring with the 1986 forerunner of the current KSU instrument was presented at the 1987 Denver ACS meeting.<sup>1</sup> Development of later generation versions were reported at a dozen presentations at Pittcon and FACSS meetings from 1990 to the present time.<sup>2,3</sup> The final version has been in use since 1993 and has been described in detail by Eilert.<sup>4</sup>

The pumps used for the supercritical fluid system were a Haskell (Burbank, CA) 122 : 1 pneumatic amplifier pump driven by compressed air, and for later experiments a Varian single stroke piston pump mechanically driven by a motorized screw. The former operated at constant pressure and the latter was controlled by the motor speed and actuation resulting from a set point compared to an in-line pressure transducer. Figure 3 shows the supercritical extraction system used.

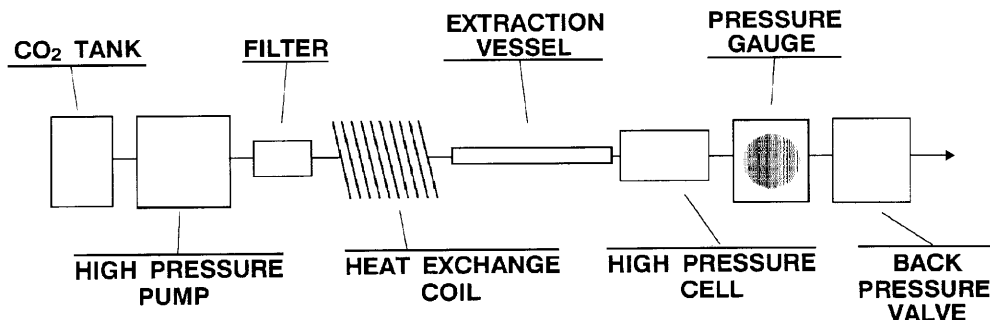


Figure 3. Components of the SFE monitoring system.

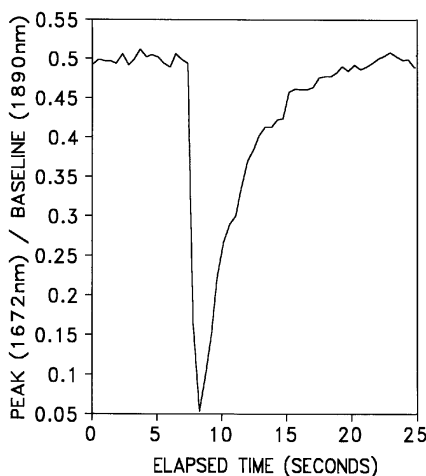


Figure 4. Ratio of absorption and baseline wavelengths for benzene obtained from spectra collected when benzene was injected into supercritical CO<sub>2</sub>. (Adapted from data of Wetzel and Eilert.<sup>5</sup>)

## Results

This constitutes the first report of progress in monitoring an actual extraction. Wetzel and Eilert previously demonstrated by valve injection simulation that NIR rapid monitoring by acousto-optic TFS was possible.<sup>4,5</sup> In that case, analyte peaks of a transient that appeared in the energy spectrum on-the-fly were tracked with scans at 0.45 second intervals from their appearance until their disappearance 9.2 seconds later (Figure 4). In that experiment, single scans were run without coadding to achieve the short time constant required when changes were of a short duration. Figure 5 shows the spectrum of pure CO<sub>2</sub> without lipid and another spectrum with lipid obtained during the extraction. Figure 6 shows an analyte dependent band at different stages of extraction. An extractogram is shown in Figure 7 where a pneumatic pump was used. The extraction time was long in this case and the pump cycle (note periodic episodes) is observed, however, the profile of

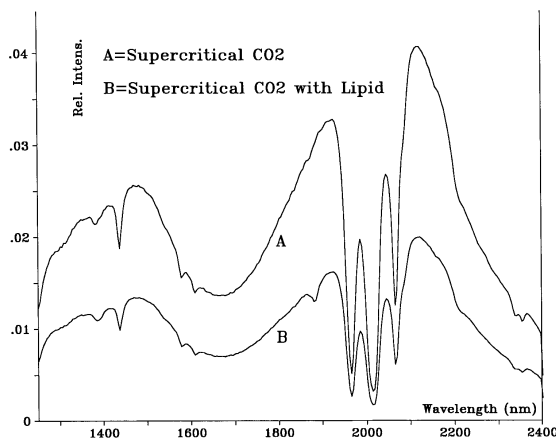


Figure 5. Energy spectra of supercritical CO<sub>2</sub> and CO<sub>2</sub> with lipid.

the analyte concentration in the effluent is tracked effectively. Figure 8 shows the extractogram resulting with a motor driven piston pump. An induction period prior to pressure build-up and subsequent flow is observed.

These extractions were done without a prior static extraction period. Also, they were done at moderate CO<sub>2</sub> density to test under slow extraction conditions to simulate a preparative situation. The profiles shown (extractograms) are the result of a running mean of three points. Of concern prior to the experiment was the issue of sensitivity to small amounts of analyte present in a part of the extract of a minor component from a limited sample. In preparative work, this would not be expected to be an issue. With only CO<sub>2</sub> present we expected to be able to monitor organic analyte. Using a polar modifier (methanol) with the CO<sub>2</sub> presents a new challenge. Surprising results from the first attempt are encouraging for monitoring effluent in the presence of a constant

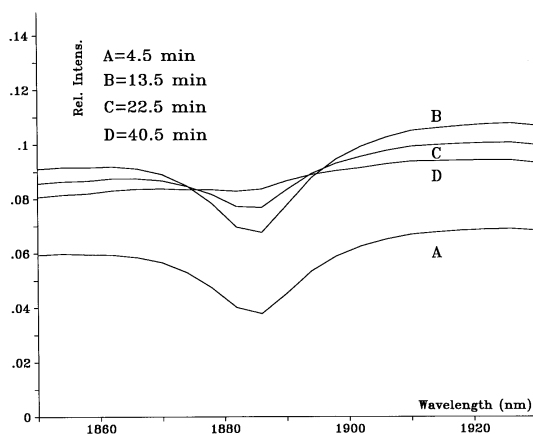


Figure 6. Analyte peak at various times of extraction.

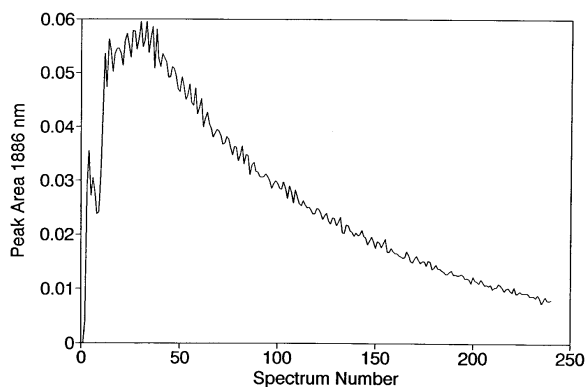


Figure 7. Extractogram (analyte peak area vs spectrum number) of an extraction made using a pneumatic pump where each spectrum required a 27 second collection time.

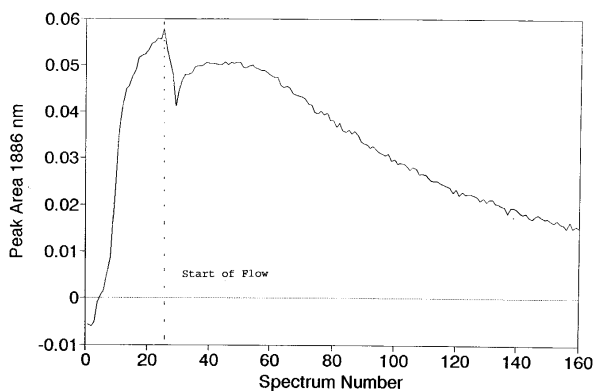


Figure 8. Extractogram obtained from a motor driven piston pump.

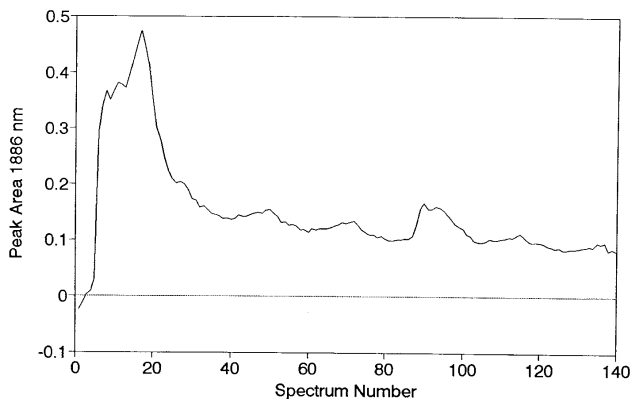


Figure 9. Extractogram of polar wheat flour lipid using 5% methanol in CO<sub>2</sub>.

methanol background. Figure 9 shows an extractogram of polar lipid from a flour sample when the extract fluid contained 5% methanol in CO<sub>2</sub>.

All spectra and extractograms are energy curves relative to scans against air. An absorbance profile obtained relative to pure supercritical CO<sub>2</sub> was shown to be similar to the energy curves. The extraction profile shows completeness of extraction. This tool should be helpful in conducting extractions for preparative and analytical purposes. Non-linearity of the energy curve is not a problem. Semi-quantitation may be inferred providing ratios are used and densities are maintained.

## Summary

Near infrared monitoring of supercritical fluid extraction is possible with a flow cell under supercritical conditions. The optical window in the CO<sub>2</sub> near infrared spectrum allows effective monitoring readily and discrimination between analyte and constant modifier background may also be possible. Rapid scanning on-the-fly with the acousto-optic tunable filter near infrared monitor allows quantitative monitoring to detect completeness of extraction and qualitative monitoring showing the difference between aromatic and aliphatic C–H, alcohols and amines. Excellent wavelength reproduction allows spectral subtraction.

## Acknowledgements

Without the monumental effort of Arnold Eilert as a full time research associate at KSU in development of NIR acousto-optic TFS into instruments worthy of quantitative work, this progress toward SFE IR monitoring would probably not have been taken place. Also, commercialized TFS versions may not yet have progressed to their present state of rapid competitive quantitative capability without the local long term commitment to instrument building.

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## References

1. D.L. Wetzel, G.J. Kemeny and A.J. Eilert, *Using an Acousto-Optic Tunable Filter in Near Infrared Spectroscopy*, American Chemical Society Meeting, Denver, CO, April (1987).
2. D.L. Wetzel and A.J. Eilert, *Quantitative Analysis with a High Duty Cycle Solid State Random Wavelength Access Near Infrared System*, 41st Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New York, NY, March, paper #1195 (1990).
3. D.L. Wetzel, *Fastest Gun in the West!*, 43rd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March, paper #1135 (1992).
4. A.J. Eilert, *Acousto-Optic Tunable Filter Spectroscopic Instrumentation for Quantitative NIR Analysis of Organic Materials*, Ph.D. Dissertation, Kansas State University (1995).
5. D.L. Wetzel and A.J. Eilert, *Rapid Scan NIR Acousto-Optic TFS of SFE Effluent*, 44th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, March, paper #122 (1993).