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Review

Supercritical fluid extraction coupled directly with Fourier transform infrared spectrometry

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Abstract

The combination of sample preparation and chromatographic separation via a hyphenated technique is becoming somewhat routine. For example, numerous reports are available on supercritical fluid extraction (SFE) coupled with gas chromatography (GC) and supercritical fluid chromatography (SFC). The employment of SFE on line with spectrometric analysis is considerably more novel with only a couple of laboratories having reported on the technique. Fourier transform infrared (FT-IR) spectrometry currently serves as the only notable, quantifiable example to date. This manuscript reviews the state-of-the-art concerning SFE–FT-IR and its application to primarily textile fiber finishes. The adaptability of FT-IR detection for a variety of SFE protocols (e.g. static, dynamic, static–dynamic, direct analysis, intermediate trapping) and fiber (e.g. polyurethane, polyamide, polyester) finishes is described.

Contents

1. Introduction

The potential for on-line directly coupled supercritical fluid extraction (SFE) with flow cell Fourier transform infrared detection (FT-IR) has not been fully realized. Largely, this is because of the many variables for consideration in the method optimization of such a substantial on-line system. FT-IR has been routinely used for both supercritical fluid chromatography (SFC) [1] and

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SFE–SFC, but more recently it has been shown on a limited scale to be an excellent selective detector for the direct analysis of SFE products without prior chromatographic separation [2]. Such a closed SFE–FT-IR system would eliminate the loss of any extracted volatile analytes and not require the use of a flow restrictor. On the other hand a high-pressure, small-volume flow cell would be needed. The combination of SFE with flow cell FT-IR, however we feel offers excellent opportunities in a broad array of applications. The state-of-the-art of SFE–FT-IR (which is very limited) is reviewed here.

2. SFE–SFC as a model for SFE–FT-IR

In order to appreciate in part the experimental difficulties encountered in SFE–FT-IR, an understanding of the more proven technique of SFE–SFC is instructive. A typical system schematic for an on-line SFE–SFC marketed by Suprex [3] is given in Fig. 1. In the "load" position, the sample is dynamically extracted with supercritical fluid. The fluid decompresses into a tee and the analytes are flushed towards the cryotrap. Upon complete extraction, the valves move into the "inject" position and a fresh flow of supercritical fluid is backflushed through the trap. This flow directs analytes out of the trap and onto the head of the column for chromatography. Other SFE–SFC units using alternative plumbing and valve schemes exist, but all follow this same format, broken into three basic modes: extract, trap, and transfer to the column for chromatography.

Of these three modes, trapping and transfer of analytes from the trap are definitely the main points for improvement in on-line SFE–SFC. Polar compounds are usually recovered in higher yields from open tubular column traps than from sorbent-filled traps due to the better deactivation of the former [4]. The large surface areas of packed traps are more conducive to larger sample volumes, however. In either case, care must be taken to insure that breakthrough of the analytes from the trap does not occur. This is done by operating at a low enough trap pressure

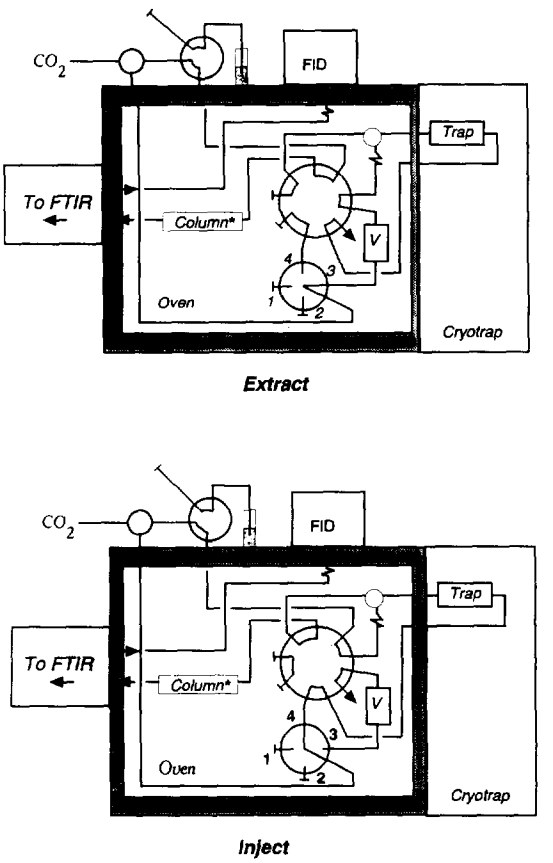

Fig. 1. On-line SFE–SFC system schematic. FID = Flame ionization detector.

and/or trap temperature to limit analyte mobility on the trapping materials [5]. Studies performed using a stainless-steel tube trap showed that there was an optimal temperature range over which to trap [6–8]. Operating a cryotrap at too high a temperature can lead to sample discrimination, peak broadening, or loss of volatile analytes. The preferred cryotrapping range is therefore estimated between −50 and 0°C, depending upon the analytes.

Once extraction and trapping are complete, the analytes are removed from the trap with the supercritical fluid (SF). In essence, this is a second extraction and may require some extra means of focusing the analytes to promote their introduction to the column or flow cell as a tight band. Solute focusing is achieved by two primary

means: phase ratio focusing and partition coefficient focusing. An excellent review of these techniques was recently published by Koski and Lee [4]. Phase ratio focusing is performed when an increase (either gradual or abrupt) in stationary phase promotes a decrease in the linear velocity of the front of a solute band relative to that of the back of the solute band. The result is a compression of the total analyte band. An example of phase ratio focusing in SFE–SFC occurs at the interface between transfer line tubing from the trap to the column heads. In contrast, partition coefficient focusing results from a reduction in the solvating power (density) of the supercritical fluid. This can be implemented by either decreasing the pressure or increasing the temperature. Transfer of the analytes from the trap to the column may be aided by elevating the trap temperature to quickly desorb analytes from the trap surface. Keeping the trap and transfer lines at temperatures below that of the oven, however, will result in a temperature rise as the analytes are transferred. This rise in temperature will result in a drop in density, and hence, aid in solute focusing as the analytes deposit onto the column head.

3. Justification for SFE–FT-IR

The coupling of SFE to FT-IR must take into account many of the considerations that were described for SFE–SFC. Intermediate trapping will be necessary if the kinetics of extraction are slow and if the level of extracted analyte is near the limit of detection of the infrared spectrometer. Obviously, the employment of an FT-IR as opposed to a grating and/or single frequency unit will enhance the detection capability. In many cases direct transfer into the IR flow cell may be feasible without the necessity of intermediate trapping. In either case the net result of this pairing is reduced analysis time as well as reduced analyte exposure to the environment and technician. Because SFE transfers all extractable sample into the FT-IR system, the detector sees the near-maximum sample concentration and with CO_2 as the fluid there is minimal background interference in the detector. CO_2 absorbs in the IR region at 3504–3822 cm^{-1}, 2137–2551 cm^{-1} and below 900 cm^{-1}, but these Fermi bands may be subtracted from the final spectrum to regain the fingerprint region [9].

Flow cell SFE–FT-IR has the benefit of being a non-destructive technique permitting placement of a second detector post flow cell for added data collection. The incorporation of a spectrometric detector also places less demand on the fractionation step in that the front-heart-back of an extraction plug can be examined for the presence of co-extracting analytes. Unless the co-extracting components are part of an homologous series, the selectivity of the infrared should afford adequate detectability of the analytes provided they are present in quantities that exceed their detection limit.

Situations currently exist in the "real world" where sample preparation and analysis are routinely conducted by mixing the matrix with an appropriate solvent, removing a portion of the solvent extract from the mixing flask, and determining the analyte quantity in this extract by, for example, FT-IR. The use of SFE in place of liquid extraction affords greater advantages in terms of direct coupling to the FT-IR (Fig. 2), automation of the complete process, and reduced organic solvent consumption. Furthermore, since selective extractions can be easily achieved in SFE by controlling the density and/or temperature of the supercritical fluid and selective detection is possible by varying the IR detection frequency, a formal chromatographic step during the analysis may not be necessary for many mixtures.

4. SFE strategies

SFE can be accomplished by using either a static, dynamic, or coupled static–dynamic mode. A static extraction refers to one where a fixed amount of fluid is used to interact with the analyte/matrix (e.g. tea bag + cup of water). Normally, the extraction vessel containing the

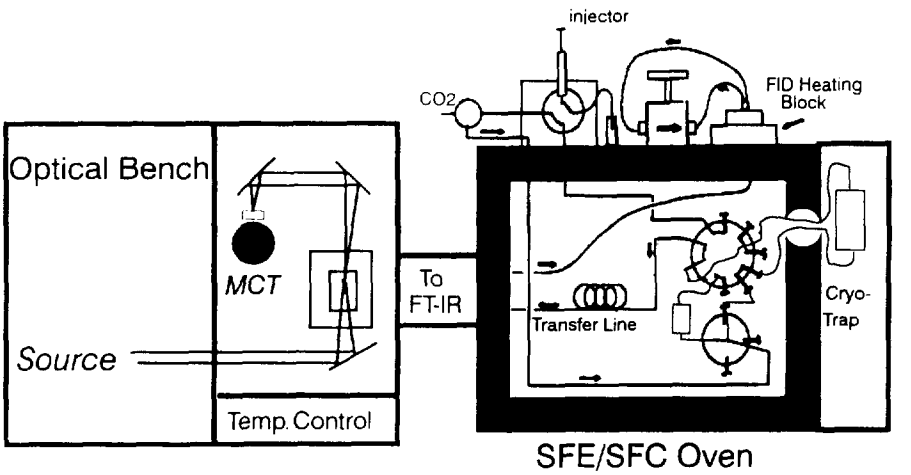

Fig. 2. SFE–FT-IR system schematic (Nicolet 710 SX FT-IR).

matrix is pressurized with the chosen fluid at a certain temperature. The high diffusivity of the SF is then utilized to access the analyte/matrix. Alternatively, a recirculation pump may be used to cycle the SF through the matrix. After the extraction is thought to be completed a valve is opened at the outlet of the cell to allow analyte to be swept from the cell via decompression. Without a recirculation pump homogeneity of the SF phase above the matrix may not be possible. A static extraction may not be exhaustive if insufficient fluid has been used.

A dynamic extraction, on the other hand, employs fresh SF which is continuously passed over and/or through the sample matrix (e.g. coffee maker). A dynamic extraction can be more exhaustive than a static one; however, impurities in the SF become a concern when using large amounts of fluid during an extraction. Another experimental problem with a dynamic extraction relative to a static extraction is an enhanced probability that the use of more SF would remove extractable matrix components. In spite of these problems, dynamic extraction is the favored strategy in at least 90% of the cases.

A combination of an initial static period followed by a dynamic one is gaining popularity especially for situations where analytes must diffuse to the matrix surface in order to be extracted such as the removal of additives from a polymer. The extraction starts in strictly a static mode. There is no net flow through the system. When the extraction has proceeded for a given amount of time, the system is put into a dynamic mode by the switching of valves. Fresh SF enters the vessel thereby replacing the original SF which has exited through the restrictor.

A viable SFE–FT-IR interface should obviously allow for each of these protocols. Furthermore, the option of analyzing the extract directly in real time or after focusing on a cryotrap and re-mobilization is attractive. This latter option may afford one the opportunity of using a modified fluid for the extraction step to disrupt matrix–analyte interactions and pure CO_2 to mobilize extracted analyte from the ballistically heated cryotrap to the FT-IR flow cell.

5. Typical experimental conditions

A Suprex MPS/225 SFE–SFC has been shown to be ideal for this application. A 1 m × 0.010 in. I.D. (1 in. = 2.54 cm) transfer line of high-quality stainless steel (Upchurch Scientific, Oak Harbor, WA, USA) was installed in place of a column between the extraction vessel and the IR flow cell. This line was joined by a zero dead volume union to the 50-μm fused-silica transfer line leading to the high-pressure IR flow cell

(Nicolet, Madison, WI, USA). Adequate backpressure was maintained by a 60 μm I.D. deactivated fused-silica tapered restrictor attached to the flow cell exit transfer line. The restrictor tip was housed within a flame ionization detector heating block to reduce plugging of the exit orifice. Stainless-steel extraction vessels (0.167 ml) were purchased from Keystone Scientific (Bellefonte, PA, USA). A Nicolet 710 SX FT-IR (Madison, WI, USA) spectrometer and computer data system were used to collect and interpret the IR data. The system thermostatically maintained the flow cell at 35°C and the flow cell transfer lines at the corresponding oven temperature (75–120°C). FT-IR data were collected at 3 scans/s and 8 cm^{-1} resolution. The FT-IR flow cell had a volume of 1.4 μl and a 5 mm path length. SFE-grade carbon dioxide was provided by Air Products and Chemicals (Allentown, PA, USA).

Analyte was passed through the IR flow cell as a single plug. Once the analyte had totally eluted and the baseline had been reestablished, data collection was stopped and a Gram–Schmidt plus reconstruction of the IR data was plotted. Analyte quantity was derived from the total area of the peak given on the Gram–Schmidt reconstruction. So long as the analyte absorbance is of relatively low intensity, quantitation by this method should be linear and valid [10]. In the event of co-extractants, an IR window of 20–40 cm^{-1} at which the analyte uniquely absorbs can be chosen, and a plot of the detector signal versus time for the run data can be made over this region. The integrated area of the peak produced by this plot can be interpreted as analyte quantity by correlating the value to a calibration curve. Alternatively, quantitation may be conducted from the IR spectrum by determining the integrated absorbance or absorbance intensity for a given analyte. Quantitation performed from the IR spectrum (i.e., integrated absorbance of a specific IR region) proved to be equally reproducible, although slightly more time consuming as an IR spectrum must first be generated from the collected data files.

It should also be mentioned that reproducibility and noise are quite dependent upon the chosen flow-rate for the transfer of analyte into the IR flow cell. Faster flows (i.e. ≥ 0.5 ml/min CO_2 liquid flow) will promote the elution of the analyte as a sharp, single plug and reduce the tailing effects seen with lower flow-rates (0.1 ml/min CO_2 liquid flow). Such rapid flows, however, produce inherently noisy IR backgrounds as the flow cell content is changing with every scan. Thus, a compromise should be sought in the choice of flow-rate, and it may prove highly beneficial to employ a variable restrictor rather than a fixed restrictor to more readily maintain this optimal flow-rate.

6. SFE–FT-IR scenarios

For analytes which are readily solubilized in CO_2, the direct dynamic and direct static–dynamic SFE–FT-IR methods are quite successful. The elimination of the trapping process should reduce both analysis time as well as potential analyte loss due to incomplete trapping and/or recovery. Analytes which are not as readily solubilized by supercritical CO_2, however, pose more of a problem. Fig. 3 shows the anticipated differences in extraction profile between a highly soluble analyte (A) and an analyte which is solubility limited (B) in supercritical CO_2 [2] Note that for the solubility limited analyte, dynamic extraction will yield a lengthy, low-volume plug in the FT-IR that may prove difficult to quantify. It may, in fact, produce a flat plateau peak profile rather than a curve, evidence of an analyte having reached its maximum solubility within the fluid. Static–dynamic extraction may yield plug shape improvement for both solubility cases since it permits concentration of the analyte in a small volume of CO_2 prior to a dynamic flushing of the vessel. The third segment of Fig. 3 represents potential plug shape for both solubility cases in which cryotrapping has been employed. For any analyte bound within a difficult matrix, cryotrapping can yield excellent results and be a definite improvement over trapless methods. The results from cryotrapping SFE–FT-IR can vary depending upon

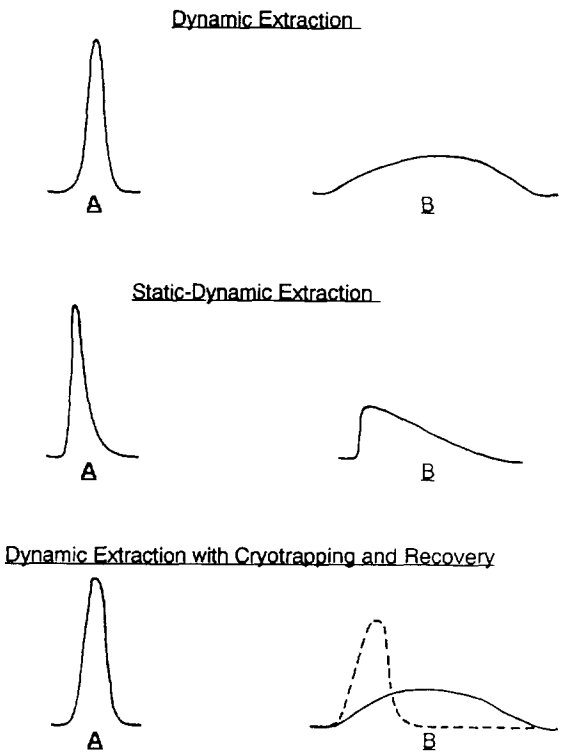

Fig. 3. Extraction Profiles for SF-soluble (A) versus SF-solubility limited (B) analytes.

the trap temperature and CO_2 density, as well as analyte solubility. Cryotrapping may result in peak broadening for even highly soluble analytes, depending upon how effectively the extract is removed from the trap and focused onto the head of the column. For a solubility limited analyte, the result can also vary. The dashed line in the figure represents an analyte which has been effectively removed from the trapping surface, as opposed to the solid line which depicts a far more gradual elution of the analyte from the trap. It would be assumed, however, that if a solubility limited analyte with no matrix interactions extracts gradually for the direct SFE methods, it will likewise require a similar amount of time/fluid to be removed from the trap. In these cases, changes in conditions (i.e. increased fluid density or use of modified fluid) may prove more beneficial than changes in plumbing.

The hypothetical plug shapes represent the elution of single components with different solubilities. Multicomponent extractants make such problems even more complex, as the components may have vastly different degrees of solubility. The resulting profile may be broad and more indicative of total solubility limitation, when in fact several components may be highly to moderately soluble in CO_2. The gradual extraction of the less soluble components can sufficiently broaden the extraction plug to make quantitation difficult. For such cases as these where solubility limitations pose a problem, dynamic extraction with cryotrapping may be necessary so that the analyte(s) may be exhaustively extracted first and then transferred into the FT-IR as a whole. But, as was shown in Fig. 3, this can prove to be an imperfect solution, since an analyte which is solubility limited in CO_2 can sometimes have as much difficulty removing itself from a trapping surface as it did from the original analyte matrix. Alternatively, direct static–dynamic extraction may help concentrate the more soluble elements of a mixture and hence create a more quantitable extraction plug while the less-soluble elements continue to gradually extract. The principal advantage of not trapping the analytes prior to FT-IR detection is that contamination of the system due to incomplete analyte recovery from the trap may be avoided. Thus, the ability of the SFE–FT-IR system to perform a variety of extraction methods is a definite advantage, especially for the study of complex mixtures containing analytes of varying solubility.

7. SFE–FT-IR applied to fiber finishes

Finishes of three fiber types (polyurethane, polyamide and aramid) have been studied and quantitative recovery was achieved in each case using direct, dynamic SFE. Off-line SFE of each finish showed it to be above 89% extractable in supercritical CO_2 [11]. Table 1 shows the basic ingredients of the finishes used for each fiber. The polyurethane fiber was primarily coated with a poly(dimethylsiloxane) oil finish, present on

Table 1
Fiber finish components (generic)

Polyurethane, 98.3% extractable
(1) Poly(dimethylsiloxane) oil
Polyamide, 91.9% extractable
(1) Glycerol triesters
(2) Alcohol ethoxylates
(3) Alcohol polyethylene oxide–ethylene oxide blocked surfactants
(4) Phosphites
(5) Poly(ethylene glycol) derivatives
(6) Fatty acid soaps
Aramid, 89.0% extractable
(1) Substituted phenol
(2) C_8–C_{18} Triglycerides
(3) Sorbitol derivatives (2)

the fiber at about 3% (w/w). The remaining two fibers were treated with much less finish than the polyurethane (i.e., 0.5–1%). As shown in Table 1, the nylon polyamide fiber required more complex finishing agents. Kevlar aramid was treated with a multicomponent finish that consisted predominantly of triglycerides very similar to those found in natural oil.

The polyurethane finish exclusive of the fiber proved to be the easiest finish for extraction (i.e., most CO_2-soluble). The recoveries of the polyamide and aramid finishes were determined to be lower due to the low solubility of certain finish components in CO_2. Off-line dynamic SFE (350 atm CO_2, 75°C, 1.2 ml/min liquid flow-rate, 20 min) of the individual sorbitol-based components, for example, resulted in recoveries of only 27–30%. This type of finish component is present in the aramid finish and in fact comprises 20–30% of finish. Other components (i.e., fatty acid soap, certain copolymers) were difficult to extract, but these are present at very low percentages in the finishes.

Initially fortified fiber matrices were examined via on line SFE–FT-IR. A series of polyurethane finish standards in methylene chloride were made, and 0.17-ml extraction vessels were filled with unfinished polyurethane fiber matrix (about 2–3 mg). A known standard was then injected (80 μl) onto the fiber matrix bed, and the solvent was allowed to evaporate (about 2–4 h, ambient conditions). The vessel was then sealed and inserted into the system, and its content were extracted using the static–dynamic configuration.

Usually, quantification would be done directly from the Gram–Schmidt reconstruction. This was not possible for the polyurethane analysis, however, due to the presence of several coextractives. The presence of these coextractives is a problem since the quantities of these coextractives will vary greatly with the quantity of fiber used as a matrix. Thus, instead of using the Gram–Schmidt reconstruction (which denotes the total IR signal produced over the course of the run), a plot of the IR signal for a finish-selective region over the course of the run was made. For the polyurethane finish, the ν(Si–CH_3) absorbance between 820–790 cm^{-1} was chosen, since the other dominant regions of the polydimethylsiloxane spectrum are shared by the absorbances of the co-extractants. Examples of a Gram–Schmidt plot and the subsequent integrated transmittance plot for a 2-μg sample of finish spiked onto pre-extracted fiber are given in Figs. 4 and 5. The peak area was determined from the integrated transmittance plot using a γ-threshold of 20 V/scan. From these data, a calibration curve was successfully established for polyurethane finish. Using the propagation of errors technique [12], the limit of detection (LOD) was calculated to be 3.7 μg for polyurethane finish, and the limit of quantitation

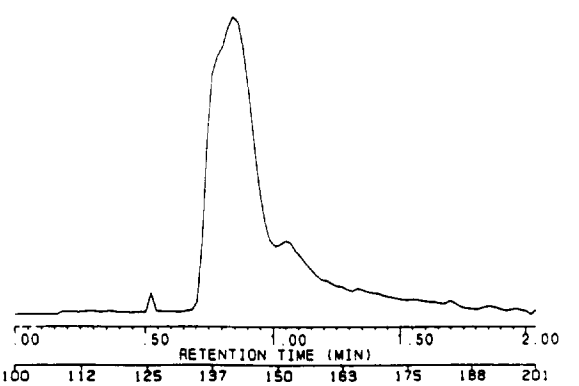

Fig. 4. Gram–Schmidt reconstruction of SFE–FT-IR analysis of polyurethane fiber finish: 2nd x-axis is data files.

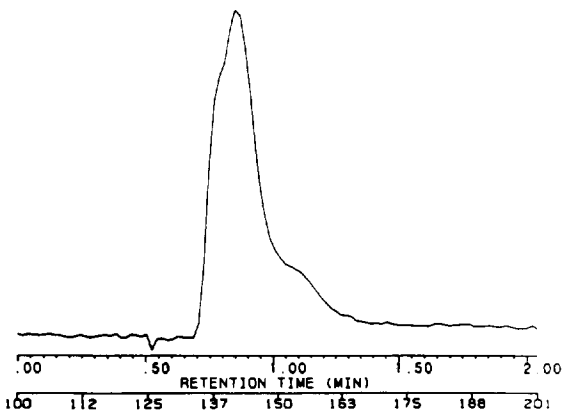

Fig. 5. Integrated transmittance plot (820–790 cm^{-1}) from SFE–FT-IR analysis of polyurethane fiber finish: 2nd x-axis is data files.

(LOQ) was 12 μg. The R.S.D.s for each of the four points were reasonable (5–9%), with the highest error obtained at the extreme ends of the calibration curve.

For the other two fibers, solutions of the polyamide and aramid finishes (0.05–5.0 mg/ml) were made in methylene chloride, and 10 μl of a given standard was injected onto the appropriate preextracted fiber matrix. Four runs per calibration data point were made, with four points per calibration plot. For the polyamide finish, quantitation was performed with the ν(C–O) stretch between 1120 and 1100 cm^{-1}. The resulting plot was very linear ($r = 0.99993$), with a calculated detection limit of 0.25 μg and a limit of quantitation of 0.84 μg. R.S.D.s for each of the four points ranged from 6.5 to 21%, with the lowest error near the center of the testing range (i.e., 5–15 μg). The aramid finish did not produce as linear a calibration plot, however. The point placement resembled a curve more than a line, and the correlation coefficient ($r = 0.992$) further indicated this. R.S.D.s for the aramid calibration points ranged from 5.7 to 14%. For aramid fiber finish, integrated transmittance was performed with the ν(C–H) stretch at 2940–2920 cm^{-1}. Using the observed calibration curve data, the LOD for the aramid finish was calculated to be 4.6 μg with a LOQ of 15 μg.

Actual polyurethane, polyamide and aramid finished fiber samples were analyzed via SFE–FT-IR using the same conditions noted for generating each calibration curve. These results were then compared to the results obtained for the same batch of fiber analyzed by current DuPont laboratory methods. The results of this comparison are given in Table 2. The resulting means and standard deviations were then compared. In all cases, a lower percent finish on yarn (FOY) is observed for the SFE data as compared to solvent techniques. This is not too surprising as organic solvents many times tend to extract components from a matrix more vigorously than supercritical CO_2 and thus remove more of the oligomer and organic components present in the fiber. Analysis by DuPont of the polyurethane, polyamid and aramid fibers extracted in our laboratory revealed little or no remaining finish on the fiber during subsequent liquid extractions.

The static–dynamic direct method proved to be very useful for three fiber finishes; however, the method was challenged when a more complex finishing system was used (i.e., a finish with a larger number of components several of which that exhibit limited solubility in 100% supercritical CO_2). The finish currently applied to Dacron polyester fibers (i.e. polyethylene terepthalate, PET) is an example of such a system. The finish is comprised of seven components. Off-line extractions of these components with 100% CO_2 found them to range in extractability from 25–100% [13]. The previously described fiber finish study had shown that the static period provided

Table 2
Comparison of SFE–FT-IR results with solvent extraction–IR results for three fiber finishes using the static–dynamic method

Fiber	Average FOY ± S.D. (%)	
	SFE–FT-IR[a]	Solvent extraction–IR[b]
Polyurethane	1.46 ± 0.102	2.09 ± 0.19
Polyamide	0.243 ± 0.022	0.422 ± 0.014
Aramid	0.770 ± 0.080	0.888 ± 0.083

FOY = Percent finish on yarn.
[a] $n = 5$.
[b] $n = 10$.

ample time and sufficient CO_2 to extract the majority of the finish; whereas, the dynamic period was able to both complete the extraction and transfer the extract from the vessel to the FT-IR flow cell. This could not be achieved with the Dacron polyester finish. The amount of CO_2 used during the static period was not sufficient for exhaustive extraction of the analytes. The slow flows used during the dynamic extraction, although necessary to maintain low FT-IR noise levels, were not fast enough to quickly extract the remaining analyte; resulting in the tailing of peaks for several minutes well above the practical IR threshold (Fig. 6). The negative peak at data point 162 is likely due to a density shift encountered when the valve is switched from the load to inject position. The positive peak prior to data point 162 is the on-set of finish extract.

Since the flow-rate could not be increased for the dynamic extraction period, (when FT-IR data are being collected) the extraction process was enhanced during the static period by having a larger dead volume which gave rise to a larger amount of fluid–analyte interaction during the static extraction. Neither the static period with a greater amount of CO_2 nor the slow flow dynamic period were sufficiently exhaustive to quantitatively extract the finish from the commercial PET fiber sample. The processed finish was more difficult to extract than finish that was simply spiked onto a matrix indicating that there was either excessive diffusion of finish into the PET matrix or there was additional bonding of the finish to the matrix as a result of processing or aging.

Due to these extraction difficulties, the SFE–FT-IR method was then adapted to include intermediate trapping (Fig. 7). Given this scheme, the extraction procedure would become more flexible and could now be governed by a restrictor, separate from the outlet, which would allow faster CO_2 flows to dynamically extract the contents of the vessel and thereby eliminate the need for a static extraction period. The flow-rate

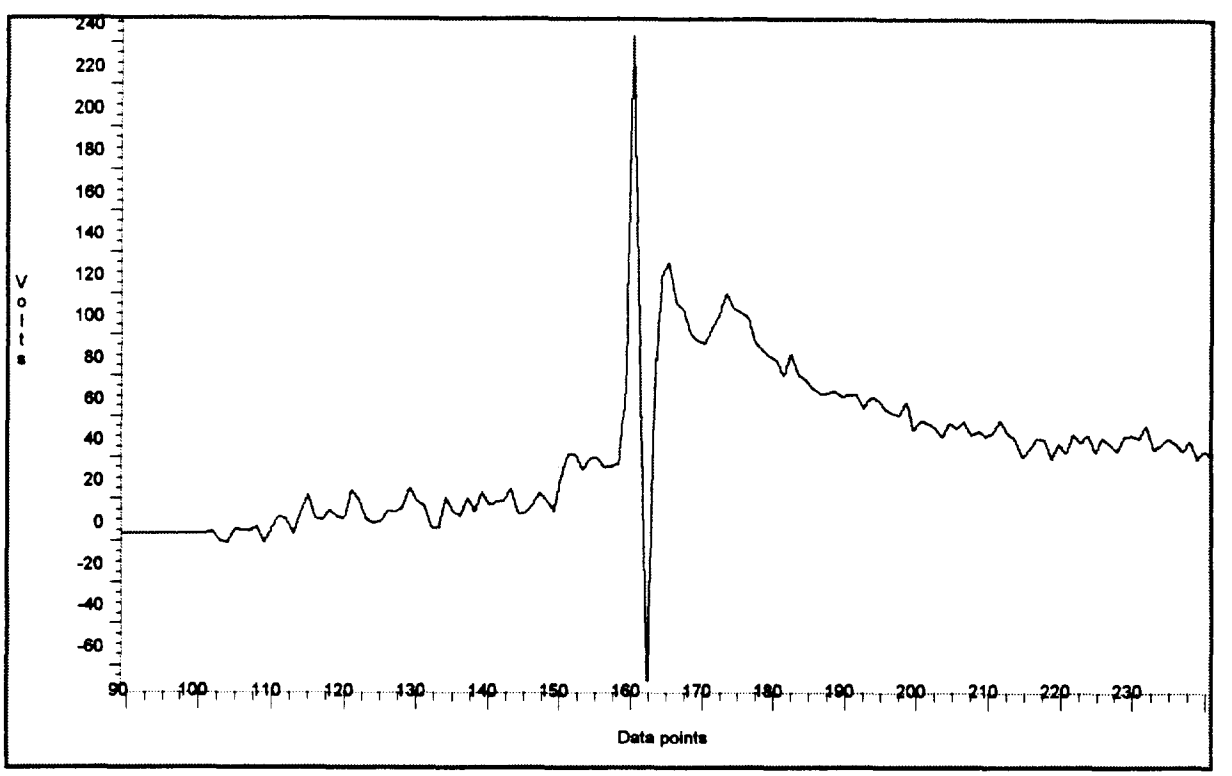

Fig. 6. Integrated transmittance plot for the 1120–1100 cm^{-1} region using the direct static–dynamic extraction scheme.

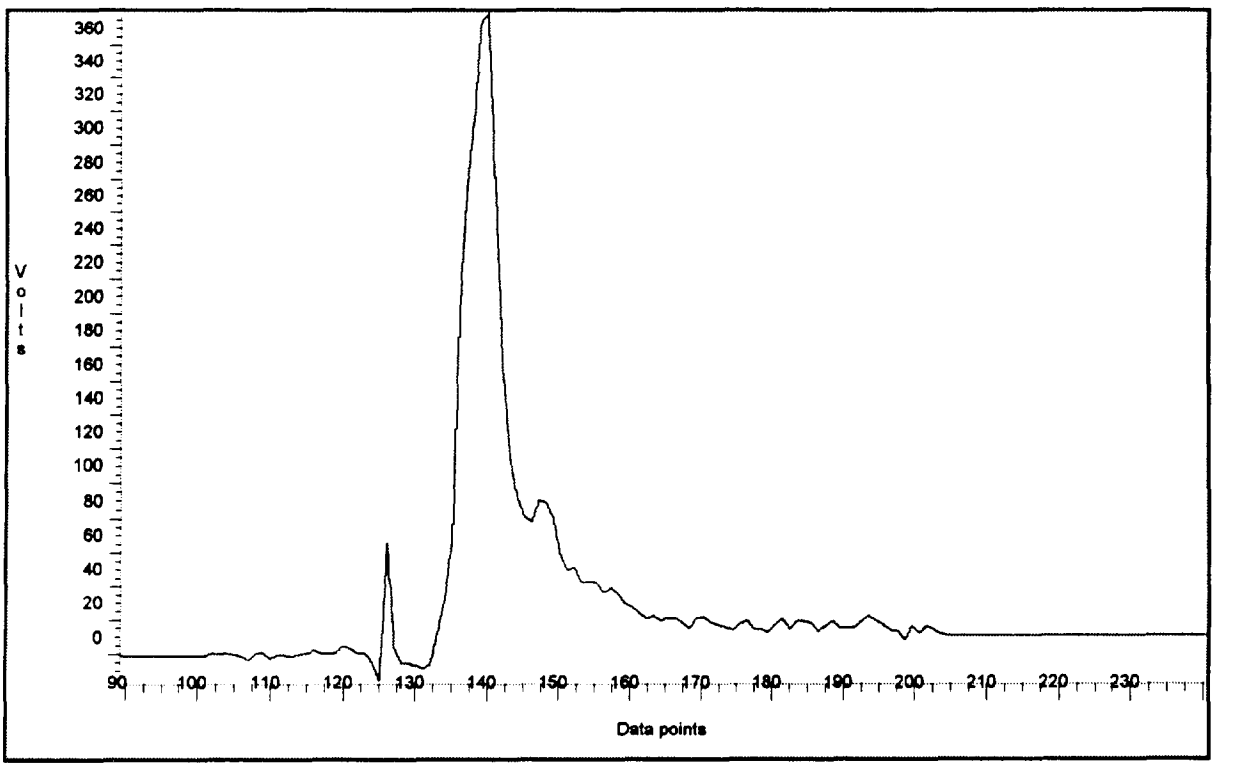

Fig. 7. Integrated transmittance plot for the 1120–1100 cm^{-1} region using the direct dynamic extraction scheme with trapping.

for dynamic extraction and trapping was held at approximately 0.6 to 0.8 ml/min as given by a 5 cm piece of 50 μm I.D. slightly tapered fused silica. The flow-rate for sample transfer from the trap to the flow cell was maintained at approximately 0.15 ml/min. The samples were extracted at 350 atm 100% CO_2 and 75°C (1 atm = 101 325 Pa). The extraction times for spiked samples ranged from 5 min for lower finish concentrations to 10 min for the higher finish concentrations. Exhaustive extraction was initially ensured by conducting a secondary extraction to confirm that no analyte could be seen above the chosen FT-IR threshold. The analytes were backflushed and eluted from the trap at 60°C and 350 atm. Sample transfer and IR collection took approximately 2–3 min. A spectrum of the extracted PET fiber finish in supercritical CO_2 is shown in Fig. 8.

A calibration curve was developed using the 1120–1100 cm^{-1} region of the spectrum. The correlation coefficient for this curve was 0.9997. The limit of detection (3σ) calculated using the propagation of errors technique [12] was found to be 0.65 mg and the limit of quantification (10σ) was 2.17 μg. A percent finish on yarn (% FOY) was calculated to be 0.27% ± 0.031. These data should be compared to the fiber finish solvent extraction values of 0.31% ± 0.035. Without the use of intermediate trapping, modifiers would most likely have had to been used in the extraction of this polyester finishing system if practical time and pressure considerations were to be met.

8. Additional SFE–FT-IR studies

Ikushima et al. [14] have cited the development of an on-line SFE–FT-IR system. They employed a JASCO Model 880-PU syringe pump in connection to a JASCO Model FT-IR 7300

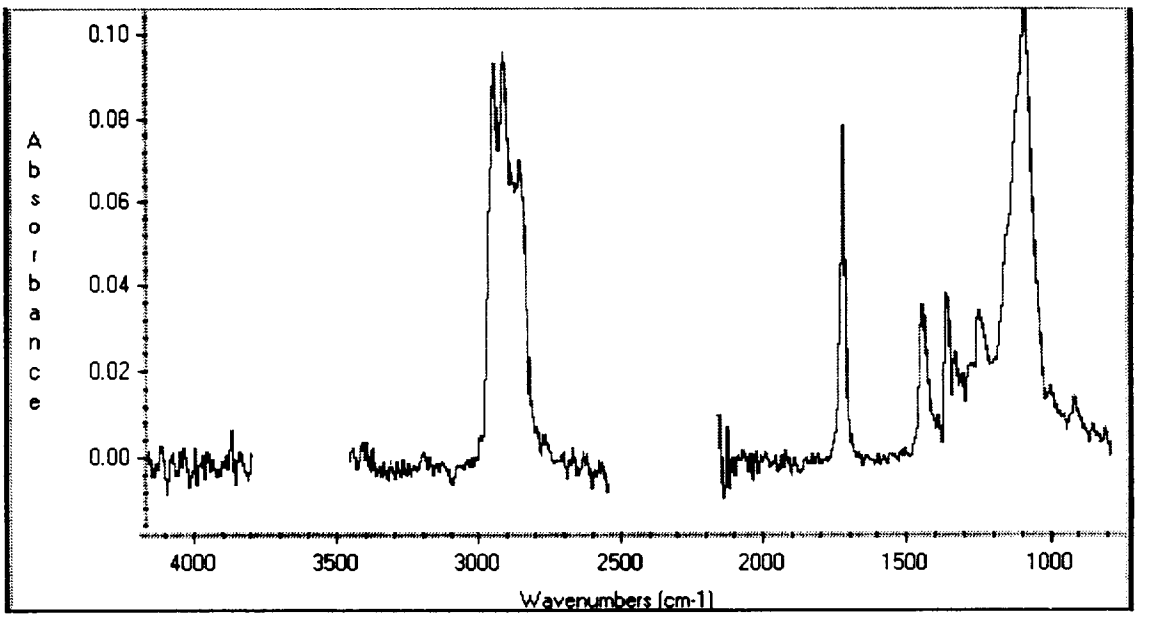

Fig. 8. Spectrum of extracted Dacron polyester finish dissolved in SF CO_2.

spectrometer to obtain the extraction dynamics of stearic acid methyl ester, linolenic acid methyl ester and DL-α-tocopherol. The extraction yield was correlated with a parameter derived from the solubility parameter concept. An on-line SFC system was also developed by introducing a separation column packed with silica gel or silver nitrate coated silica gel in line between the extractor and the FT-IR [15]. In their system only dynamic extraction could be performed.

More recently a simple and inexpensive fiber-optic interface for coupling SFE to FT-IR has been described [16]. The interface employed chalcogenide optics and a stainless-steel union cross. It could withstand pressures up to 400 atm and had a spectral window from 5000 to 800 cm^{-1}. The SFE–FT-IR interface was demonstrated by isolating caffeine from coffee and total petroleum hydrocarbons (TPHs) from soil. The determination of TPHs in soil by static (340 atm/77–80°C) on-line SFE–FT-IR yielded values in good agreement with both off-line SFE and Soxhlet extraction. (See Table 3). Transfer of the extracted organics into the IR cell was facilitated by holding the cell at atmospheric pressure until the extraction was complete. Fol-

Table 3
Comparison of on-Line SFE–FT-IR with off-line SFE–IR and Soxhlet extraction determinations of total petroleum hydrocarbons for selected soil samples

Sample	TPH, ppm (R.S.D., $n = 3$)		
	Off-line SFE–IR[a]	On-line SFE–FT-IR	Soxhlet[b]
Farm diesel	31 000 (3)	38 041 (24)	38 500 (11)
Farm gasoline	6 240 (5)	6 538 (17)	5 840 (3)

[a] Off-line SFE was performed for 30 min with collection in 5 ml of Freon-113.
[b] 4 h using 150 ml of Freon-113.

lowing extraction, the value separating the SFE cell from the IR cell was opened, and the extracted components were transferred as the CO_2 depressurized to about 250 atm. The detection limit (2932 cm^{-1} C–H stretching absorption) for TPHs, using a 48-s scan time, was found to be 1.6 ppm (mass TPHs/mass sample). The linear dynamic range of calibration for the TPH determinations was greater than three orders of magnitude.

9. Conclusions

The direct interface of SFE to FT-IR provides an alternative to liquid extraction–IR methods that require environmentally hazardous solvents, and exclusion of the column provides an additional time savings. Both recoveries and standard deviations have been shown to be compatible with solvent extraction data. Both the extraction flow-rate and trapping material can be optimized for any particular application thus allowing this method to be extended well beyond textile finishing systems. The method further proves itself in terms of reproducible quantitation, especially when one considers that the error values stated are for the inclusive method (sample preparation and analysis combined). The method can also be used to study extraction dynamics, as the solubility of analytes in CO_2 can be directly monitored by the FT-IR for varying extraction conditions. We have no doubt that there are other similar applications to be made with this system, and with equivalent degrees of success.

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References

[1] S. Shah and L.T. Taylor, *J. High Resolut. Chromatogr.*, 12 (1989) 599.
[2] C.H. Kirschner and L.T. Taylor, *Anal. Chem.*, 65 (1993) 78.
[3] *MPS 225 System Manual*, Suprex Corp., SFC Research Center, Pittsburgh, PA, 1991.
[4] I.J. Koski and M.L. Lee, *J. Microcol. Sep.*, 3 (1991) 481.
[5] J.W. King, in T.G. Squires and M.E. Paulaitis (Editors), *Supercritical Fluids —Chemical and Engineering Principles and Applications* (*ACS Symposium Series*, No. 329), American Chemical Society, Washington, DC, 1987.
[6] M.R. Anderson, J.T. Swanson, N.L. Porter and B.E. Richter, *J. Chromatogr. Sci.*, 27 (1989) 371.
[7] M. Ashraf-Khorassani, L.T. Taylor and P. Zimmerman, *Anal. Chem.*, 62 (1988) 472.
[8] Q.L. Xie, K.E. Markides and M.L. Lee, *J. Chromatogr. Sci.* 27 (1989) 365.
[9] M.W. Raynor, I.L. Davies, K.D. Bartle, A. Williams, J.M. Chalmers and B.W. Cook, *Eur. Chromatogr. News*, 1 (1987) 4.
[10] D.T. Sparks, R.B. Lam and T.L. Isenhour, *Anal. Chem.*, 54 (1982) 1922.
[11] C.H. Kirschner, S.L. Jordan, L.T. Taylor and P.D. Seemuth, *Anal. Chem.*, 66 (1994) 882.
[12] G.L. Long and J.D. Winefordner, *Anal. Chem.*, 55 (1983) 712A.
[13] S.L. Jordan, P.D. Seemuth and L.T. Taylor, *J. Textile Res.*, in press.
[14] Y. Ikushima, N. Saito, K. Hatakeda, S. Ito, M. Arai and K. Arai, *Ind. Eng. Chem. Res.*, 31 (1992) 574.
[15] Y. Ihushima, N. Saito, K. Hatakeda, S. Ito and T. Goto, *Chem. Lett.*, (1989) 1707.
[16] D.L. Heglund, D.C. Tilotta, S.B. Hawthorne and D.J. Miller, *Anal. Chem.*, 66 (1944) 3543.