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Separation and identification of sulfanilamides by capillary supercritical fluid chromatography–Fourier transform infrared spectroscopy

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Abstract

The separation of several sulfanilamides by capillary SFC using a capillary column coated with a biphenyldimethyl silicone column has been achieved. A very high starting pressure (~200 atm) and final pressure (~500 atm) was used to elute these very polar solutes. A universal SFC–FT-IR interface has been made by modification of a commercially available direct deposition GC–FT-IR interface. A new heating device allowed a partial solution to the problem of restrictor plugging by very polar compounds eluting from capillary columns. The low detection limit (about 1 ng for sulfamethazine) allows trace amounts of compounds in complex mixtures to be detected and identified provided that they are chromatographically separable. When methanol-modified CO_2 was used as the mobile phase to increase the separation efficiency of capillary SFC for polar analytes, results were not encouraging because of the poor stability of the stationary phase in the presence of methanol. © 1997 Elsevier Science B.V.

Keywords: Interfaces, SFC–FT-IR; Detection, SFC; Fourier transform-infrared spectroscopy; Sulfanilamides

1. Introduction

Sulfanilamides are drugs that are commonly used to combat a variety of bacteria [1]. Several techniques have been developed to analyze sulfanilamides, the most frequently used of which is high performance liquid chromatography (HPLC) [2–7]. The major disadvantage of HPLC for residue analysis of sulfanilamides in complex matrices is that an extensive clean-up step is needed prior to the analysis. Gas chromatographic methods have been shown to be sensitive and specific but the non-volatile nature of sulfanilamides means that conversion to the N_1-methyl or N_1-acyl derivative is required. Nose et al. [8] have successfully acetylated the amino group of sulfanilamides with dimethylformamide dimethylacetal to prepare volatile derivatives that could be separated by gas chromatography (GC). They reported that 14 sulfanilamides have been separated by GC and subsequently identified by mass spectrometry.

Supercritical fluid chromatography (SFC) has received attention in recent years because of its capability to separate more polar and less volatile compounds than GC, while potentially having better resolution than HPLC [9–12]. Packed column SFC has been applied to the separation of sulfanilamides by Perkins and Games [13] and Taylor et al. [14], but an unsuccessful attempt to separate this class of compounds using capillary columns was reported by the former authors [13].

In this contribution, we report the successful

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separation of sulfanilamides by capillary SFC without derivatization using unmodified CO_2 as the mobile phase. In light of the high polarity of sulfanilamides, a fairly polar stationary phase is needed for capillary SFC to achieve any retention, and hence separation. If, however, the stationary phase is too polar, all the analytes might be totally retained in view of the nonpolar nature of the mobile phase. Apparently a stationary phase of intermediate polarity, in conjunction with a mobile phase that has a high enough solvent strength to dissolve the analytes, is needed.

To obtain structural information on the eluites from a capillary SFC column, an on-line interface to a Fourier transform infrared (FT-IR) spectrometer was used. Because of the similarity of capillary GC and SFC, it is reasonable to base the design for the SFC–FT-IR interface on that of contemporary GC–FT-IR interfaces. Two approaches have been used for GC–FT-IR that can also be used for SFC–FT-IR, namely the flow-cell [15,16] and the solvent elimination [17,18] methods.

Interfaces based on flow-cells cannot be directly applied to SFC–FT-IR measurements at very high pressure because of absorption of much of the incident infrared radiation by the mobile phase and the possibility of fracture of the cell windows. The spectrum of supercritical CO_2 contains several strong absorption bands that limit the path-length of the flow-cell, resulting in reduced sensitivity [15,16]. The path-length of SFC–FT-IR flow cells, when neat CO_2 at relatively low pressure is used as the mobile phase, is generally not greater than 5 mm. The low polarity of CO_2 only allows non-polar or medium-polar compounds to be separated unless the pressure is raised well above 300 atm, but above 425 atm damage to the windows becomes likely [19]. To the best knowledge of these authors, no SFC–FT-IR measurements involving the use of flow-cells have been reported when the pressure at the outlet of the column is greater than 350 atm. If a small amount of a polar modifier is employed to improve the separation of polar compounds by SFC, severe spectral interferences can result, even if the concentration of modifier does not exceed 2%.

To circumvent these difficulties, an SFC–FT-IR interface was used in which the mobile phase is eliminated prior to the measurement of the infrared spectrum of each eluite. A GC–FT-IR interface based on this principle is commercially available from the Digilab Division of Bio-Rad Laboratories (Cambridge, MA) under the name Tracer [20]. An analogous SFC–FT-IR interface has been built by Griffiths et al. [17,18] by modifying the Tracer for SFC. With this interface, identifiable infrared spectra were obtained from injected quantities as low as 1 ng of polar analytes (e.g., caffeine or acenaphthenequinone) eluted with CO_2 at relatively low pressure [18]. In this paper we report the application of this interface at pressures up to 500 atm.

2. Experimental

2.1. Materials

The following sulfanilamides were used as probe molecules in this study: sulfapyrazine, sulfamethazine, sulfanilamidoquinoxaline, sulfamethoxazole, sulfamoxole and N-(*p*-methoxy benzoyl)sulfamethazine, the structures of which are shown in Fig. 1. These compounds were used as received and showed no evidence of impurities when injected into capillary supercritical fluid chromatography with a biphenyl column.

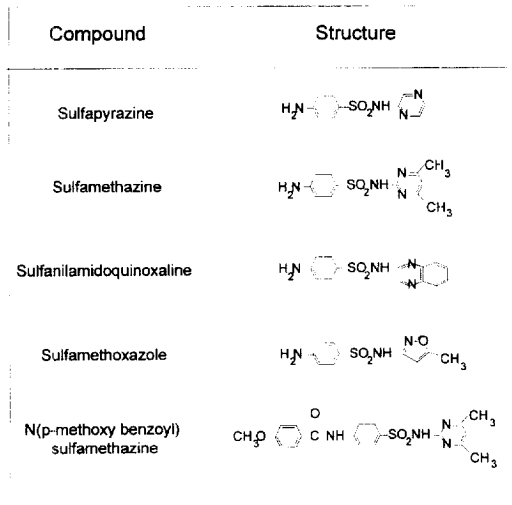

Fig. 1. Structures of sulfanilamides used in this work.

2.2. Instrumentation

A Computer Chemical Systems (CCS) a Model 5000 SFC–GC, with the pump replaced by Model 7000 fluid delivery system when high pressures were required, was used for all SFC separations. The maximum pressure attainable with the CCS Model 5000 is 5000 p.s.i. (~340 atm). When pressures above 350 atm are used, many commercially available restrictors provide a flow-rate that is high enough so that the plate height is significantly increased. To obtain an acceptable efficiency for capillary SFC under very high pressure, a home-made integral restrictor was used that yielded a flow-rate of 4.5 ml/min (gas) at a pressure of 500 atm.

Three capillary columns were tested: a 10 m long, 100 μm I.D. capillary column with a 0.50 μm thick film of a cross-linked polydimethylsiloxane stationary phase in which 30% of the methyl groups have been replaced by biphenyl groups (SB-Biphenyl-30, Dionex, Lee Scientific Division, Salt Lake City), a 10 m long, 100 μm I.D., with a 0.50 μm thick film of a cross-linked polydimethylsiloxane stationary phase in which 50% of the methyl groups have been replaced by cyanopropyl groups (SB-Cyanopropyl-50, Dionex) and a 10 m long, 100 μm I.D., DB-5 capillary column with a 0.40 μm thick film of a cross-linked polydimethylsiloxane stationary phase in which 5% of the methyl groups have been replaced by phenyl groups (DB-5, J&W Scientific, Folsom, CA).

"SFE" grade CO_2 (Scott Specialty Gases) was used for all separations, as it was found to have a significantly lower concentration of nonvolatile impurities than any grade of CO_2 from any other manufacturer. "Optima" grade methanol (Fisher Scientific) was used to modify the supercritical carbon dioxide.

To enable compounds of low-volatility or high polarity to be separated by SFC, a few further modifications to the Tracer (Digilab Division of Bio-Rad, Cambridge, MA) besides those recently described by Norton and Griffiths were employed. The outlet of the capillary SFC column was connected to a 50 μm I.D. fused silica transfer line that is heated to the same temperature as the SFC oven. An integral restrictor was connected to the end of this tubing and heated resistively to 150°C. The ZnSe window on which the eluites are deposited was cooled to −10°C to ensure that the solutes are trapped on the ZnSe surface efficiently. The window and motor are mounted in a vacuum chamber that allows a pressure of about 0.1 mTorr to be attained. Under these conditions, carbon dioxide is effectively eliminated from the path of the infrared beam. A 100 μm wide track was obtained by this device under typical operating conditions.

3. Results and discussion

3.1. Separation of sulfanilamides using capillary SFC

For the separation of polar compounds, conventional chromatographic practice would lead one to predict that both a polar stationary phase and a mobile phase of high solvent strength would be needed. When neat carbon dioxide was used for the separation of the sulfanilamide test compounds using stationary phases of various polarities, the width and shape of the peaks varied dramatically. The result of eluting sulfamethazine from the relatively nonpolar DB-5 column using neat carbon dioxide at a pressure of 300 atm led to a broad peak with capacity factor k'~0, indicating that the interaction between the stationary phase and the analyte was too weak to permit retention and, therefore, good chromatography using neat CO_2, even by varying the temperature to optimize the peak shape. Excessive peak broadening and lack of retention were observed when lower pressures were employed. On the other hand, the peaks were excessively retained on the polar Cyanopropyl-50 column even at pressures greater than 300 atm, implying an excessively strong interaction between the analyte and the stationary phase. Presumably, sulfanilamides would not be able to be eluted from this column by SFC unless a more polar mobile phase were to be used.

Unlike the nonpolar and very polar stationary phases, the biphenyl-substituted column gave acceptable retention of sulfamethazine, with only slight peak tailing being observed. This result indicated that under optimized conditions, the sulfanilamides might be separable using neat CO_2. The other

sulfanilamides shown in Fig. 1 are much more polar than sulfamethazine and were more strongly retained on the biphenyl column. Although all the sulfanilamides studied were able to be eluted from the Biphenyl-30 column using neat CO_2 as the mobile phase, it was necessary to use a very high pressure to increase the strength of the mobile phase in order to effect a good separation in a reasonable time. Under these conditions, however, the diffusivity of the solutes in the CO_2 mobile phase is decreased so that a very low flow-rate is required. To this end, a home-made integral restrictor was mounted in the FID that gave a flow-rate of 4.5 ml/min (gas) at a pressure of 500 atm.

To study the SFC retention behavior of the sulfanilamides, the capacity factors of the six compounds shown in Fig. 1 were first measured at four different temperatures with the same restrictor; the results are summarized in Fig. 2. It can be seen that the retention times for sulfanilamides are excessively long if the density is kept at 0.4 g/ml (~200 atm at 40°C). This result indicates that when pressure-programming is used to separate a mixture of sulfanilamides, a high starting pressure can be used.

Chromatograms showing the pressure-programmed separation of six sulfanilamides on a Biphenyl-30 column at temperatures of 110, 130 and 150°C are shown in Fig. 3. For each chromatogram, the pressure was held at 3000 p.s.i. (~200 atm) for 10 min, and then ramped at 200 p.s.i./min to a final pressure of 7500 p.s.i. (~510 atm), where it was held for 20 min. It may be noted that most compounds had not eluted before the pressure had reached its final value. Several sulfanilamides were also found to be thermolabile. For the separations performed at oven temperatures of 110 and 130°C shown in Fig. 3A and B, respectively, the peak heights and widths for all analytes did not vary significantly. When the oven temperature was increased to 150°C, however, the sulfamoxole peak vanished and a small peak (marked with an arrow in Fig. 3) appeared at a retention time of about 29 min. Apparently, sulfamoxole decomposed between 130 and 150°C.

3.2. Investigation of the performance of the SFC–FT-IR interface

As noted above, a modified Tracer direct deposition GC–FT-IR interface was used to obtain the infrared spectra of the eluites separated from SFC in real time. Interferograms were block-averaged at intervals of 4 seconds, and chromatograms could be constructed from the spectral data either using the Gram–Schmidt (GS) vector orthogonalization algorithm [21] or by integrating the absorbance between specified wavenumber limits [22]. The latter technique yields a chromatogram that is characteristic of only those functional groups (FGs) that give rise to a band in the specified spectral region. Hence FG chromatograms are more selective than GS chromatograms.

A major problem was observed when compounds of low solubility were analyzed by this device. In the Tracer GC–FT-IR interface, a heating cartridge was used to maintain the temperature at the end of the

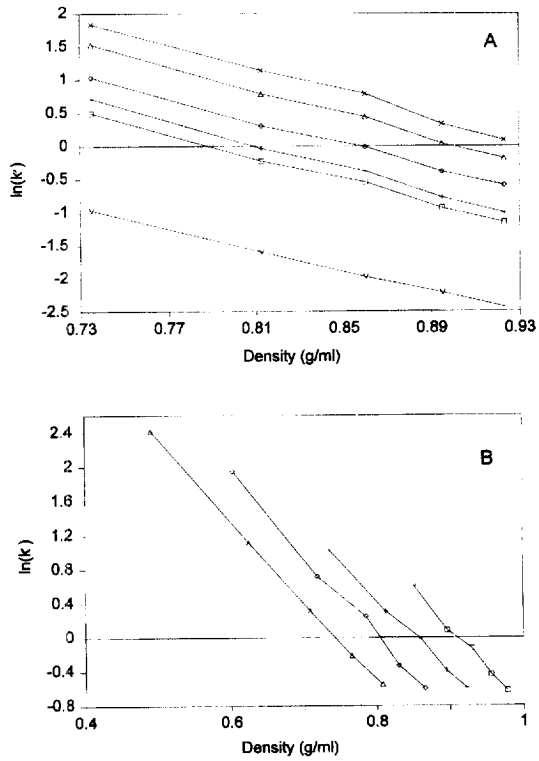

Fig. 2. (A) Capacity factor vs. density for six sulfanilamides at 60°C; sulfamethoxazole (□), sulfapyrazine (+), sulfamethazine (◇), sulfamoxole (△), sulfanilamidoquinoxaline (×), and sulfisoxazole (▽). (B) Capacity factor vs. density for sulfamethazine at 40 (□), 60 (+), 80 (◇) and 100°C (△) using a biphenyl capillary column.

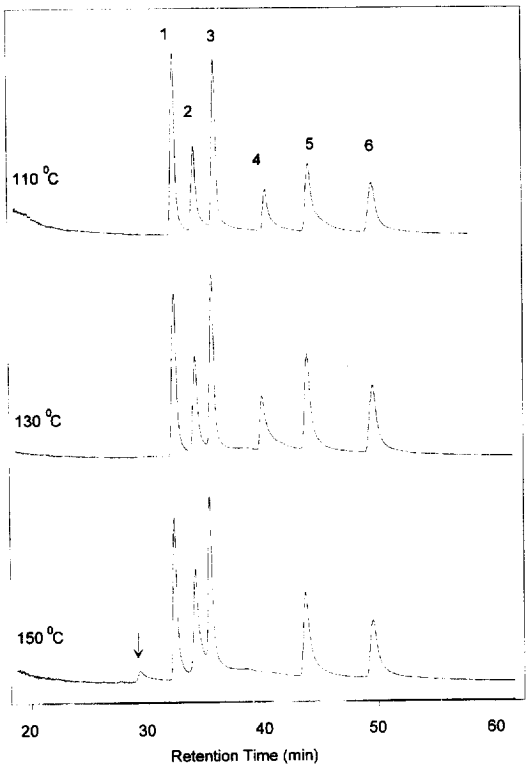

Fig. 3. Separation of sulfanilamides using a biphenyl-30 column: (1) sulfamethoxazole, (2) sulfapyrazine, (3) sulfamethazine, (4) sulfamoxole, (5) sulfanilamidoquinoxaline and (6) N-(*p*-methoxy benzoyl)sulfamethazine.

transfer line. The same device was used for the SFC–FT-IR interface to heat the restrictor. The volume of the heating cartridge must be as small as possible to reduce the obscuration of the infrared beam. Additionally, it should be located as close to the tip of the restrictor as possible for efficient heating of the restriction zone in order to prevent the restrictor from being plugged by eluites precipitated because of the change in density. In practice, however, the heating device occupies some space so there is a short distance over which the restrictor is not heated, leading to the restrictor occasionally being plugged by compounds of low volatility.

To overcome this situation, the configuration of the heater was modified. The restrictor was mounted in a heated stainless steel tube through which helium gas was passed, so that the hot helium raises the temperature of the transfer line. The heated helium gas heats the tip of the restrictor more efficiently than the cartridge heater, and less plugging by compounds of low volatility was observed. Volatile compounds were sometimes lost by evaporation into the flow of warm helium, however. Since fewer plugging problems were observed for analytes that have higher solubility in CO_2, the original heater configuration was usually employed for more volatile compounds.

An ideal interface between any chromatograph and an FT-IR spectrometer should operate without a significant loss of the chromatographic resolution. In the direct deposition SFC–FT-IR interface, the ZnSe window is controlled by a stepping motor, the speed of the translation of which can be controlled to obtain the best compromise between resolution and sensitivity of the detection of the eluites. Typically, the higher the translation speed of the window, the higher is the resolution but the lower is the sensitivity. The optimum speed to translate the IR window is such that it moves a distance that is equal to the width of the track in a time that is equal to the full-width at half-height (FWHH) of the narrowest peak in the chromatogram. The translation speed of the IR window is much higher for GC–FT-IR than for SFC–FT-IR because the peak width in SFC is much broader than in GC. Thus the components of many samples separated by capillary SFC can be stored on a single 50×25 mm ZnSe window before it needs to be removed and cleaned.

3.3. Investigation of the SFC–FT-IR detection limit for sulfanilamides

Sulfamethazine was used as a test compound to optimize the conditions for the identification of sulfanilamides eluting under high pressure from a capillary SFC column by on-line FT-IR spectrometry. The relationship between injected quantity and the peak area of the functional group (FG) reconstructed chromatogram is shown in Fig. 4. The linear range was determined to be about two orders of magnitude. Typical spectra of an analyte injected at high and low concentration are shown in Fig. 5. From these data it can be inferred that the minimum identifiable quantity for the SFC–FT-IR analysis of sulfanilamides is of the order of 1 ng, and the detection limit is a little less.

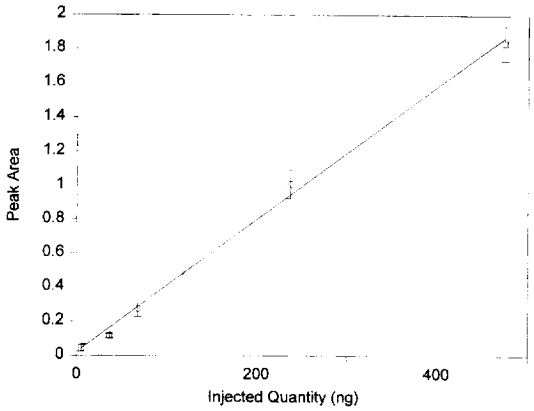

Fig. 4. The injected quantity vs. peak height for the chromatogram reconstructed by integrating the absorbance in the N–H stretching region.

A mixture of five sulfanilamides was then separated under the same pressure program described in the Section 3.2 (Fig. 3), but with a different restrictor and the column temperature reduced to avoid thermal decomposition. The functional group chromatograms reconstructed by integrating the absorbance in the spectral region of 1640 to 1800 cm^{-1} are shown in Fig. 6. The spectra of two representative peaks obtained by averaging the data between the FWHH points of peaks 1 to 5 are shown in Fig. 7A and Fig. 8A. The sulfanilamide spectra obtained by this measurement were searched against the Georgia State Crime Laboratory (GSCL) Library of commonly abused substances, which is a database containing reference spectra of compounds prepared as KBr

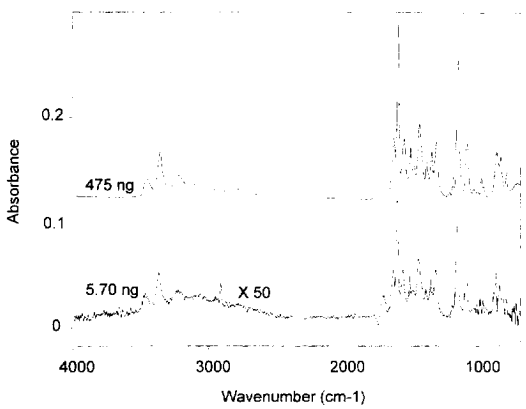

Fig. 5. On-line SFC–FT-IR spectra for injected quantities of 475 and 5.75 ng of sulfamethazine.

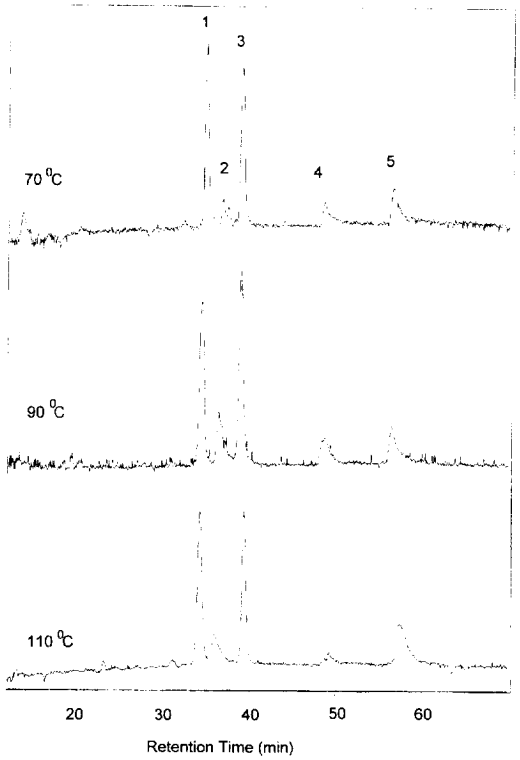

Fig. 6. Reconstructed chromatograms for SFC–FT-IR identification of the sulfanilamides by integrating the absorbance between 1640 and 1800 cm^{-1}. The separated components are: (1) sulfamethoxazole, (2) sulfapyrazine, (3) sulfamethazine, (4) sulfanilamidoquinoxaline and (5) N-(*p*-methoxy benzoyl)sulfamethazine.

disks. It has been noted previously that both direct deposition GC–FT-IR [23] and SFC–FT-IR [24] spectra show their greatest differences from KBr disk reference spectra in the spectral region above 2000 cm^{-1}, largely because the hydrogen-bonded O–H and N–H stretching modes are very susceptible to the crystallinity of the material, and the same result was found in this study. Spectral searching results using a spectral range of 2000 to 750 cm^{-1} are shown in Table 1. The value of Hit Quality Index (HQI) displayed in the right column of this table is a measure of the Euclidean distance between the unknown spectrum and each library entry: thus the smaller value of the HQI, the more closely the reference spectrum matches the unknown spectrum. In every case studied, the SFC–FT-IR spectrum of the sulfanilamide was matched more accurately by

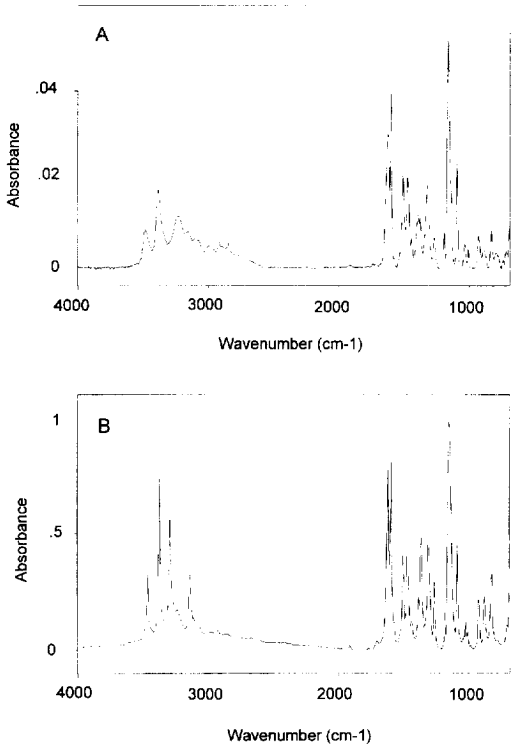

Fig. 7. (A) Spectrum of 60 ng of sulfamethoxazole (injected), average between the FWHH points of peak 1 of the chromatogram shown in Fig. 6; (B) KBr disk reference spectrum of sulfamethoxazole.

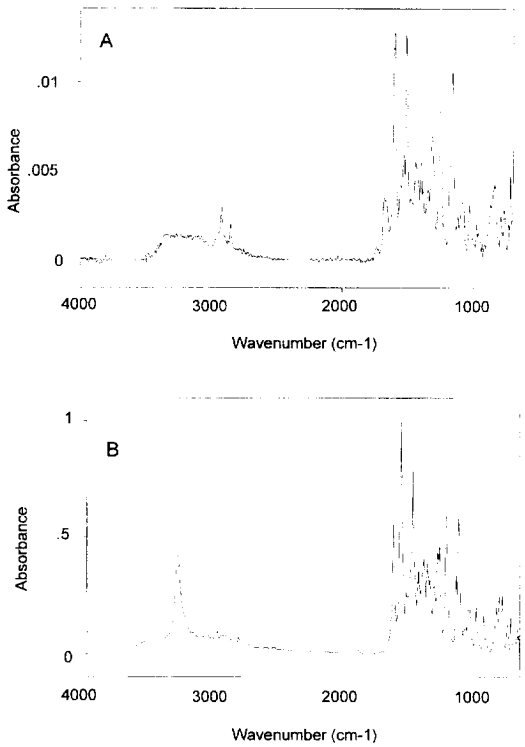

Fig. 8. (A) Spectrum of 60 ng of N-(*p*-methoxy benzoyl)sulfamethazine (injected), average between the FWHH points of peak 5 of the chromatogram shown in Fig. 6; (B) KBr disk reference spectrum of N-(*p*-methoxy benzoyl)sulfamethazine.

its own KBr-disk reference than by any other entry in the GSCL library. Two reference spectra of sulfanilamides prepared as KBr disks are shown in Fig. 7B and Fig. 8B. The similarity of the SFC–FT-IR and reference spectra below 2000 cm^{-1}, and the dissimilarity above 2000 cm^{-1}, is quite apparent from these figures.

3.4. Investigation of the effect of modifiers on the separation of sulfanilamides

An important limitation to the use of an FID for SFC is that only a few polar modifiers such as H_2O and formic acid can be used. Common organic modifiers such as methanol, cannot be used as they generate a large, noisy background on the signal from the FID. The incompatibility with methanol-modified CO_2 is also one of the weaknesses of the flow-cell based SFC–FT-IR interface, because the mobile phase is completely eliminated in the direct-deposition SFC–FT-IR interfaces, it should be able to be used without modification when methanol-modified CO_2 is used as the mobile phase for capillary SFC. In this section, the result of separating sulfanilamides using methanol as a modifier with SFC–FT-IR detection will be briefly discussed.

As indicated by Wright et al. [25], when modifiers are added to CO_2 at a concentration of less than 2%, the effect on the capacity factor and peak shapes of capillary SFC is small because of the relatively inert surface of the fused silica and the polymeric stationary phases used in capillary columns. In addition, the density of supercritical fluid CO_2 with 5% modifier is not significantly greater than that of neat CO_2 at the same pressure [26]. Thus any change in retention time is probably caused by specific interactions between the modifier and stationary phase (e.g., blocking the active sites of the stationary phase for packed column SFC) or between the modifier and

Table 1
Result of searching SFC–FT-IR spectra (2000 to 750 cm^{-1}) of reprentative sulfanilamides against the Georgia State Crime Laboratory library of infrared spectra of commonly abused substances

Compounds	Hit	Name	HQI
Sulfamethoxazole	1	Sulfamethoxazole	0.371
	2	Sulfamerazine	0.521
	3	Sulfisoxazole	0.549
	4	Sulfacetamide	0.571
	5	2,4,6-Trimethoxyamphetamine	0.593
Sulfapyrazine	1	Sulfapyrazine	0.432
	2	Sulfanilamidoquinoxaline	0.432
	3	Sulfamethoxazole	0.454
	4	Sulfamerazine	0.460
	5	Sulfacetamide	0.488
Sulfamethazine	1	Sulfamethazine	0.388
	2	Sulfamerazine	0.415
	3	Sulfadimethoxine	0.521
	4	Sulfanilamidoquinoxaline	0.554
	5	Sulfacetamide	0.554
Sulfanilamidoquinoxaline	1	Sulfanilamidoquinoxaline	0.504
	2	Sulfamethoxazole	0.521
	3	Sulfacetamide	0.521
	4	Olivetol	0.526
	5	Sulfamethoxypyridazine	0.554
N-(*p*-Methoxy benzoyl)-sulfamethazine	1	N-(*p*-Methoxy benzoyl)sulfamethazine	0.282
	2	Pyrilamine	0.476
	3	Cisapride	0.526
	4	Metoclopramide	0.532
	5	Tripelennamine	0.549

the analytes rather than by a change in the thermodynamic properties of the mobile phase. In light of the possibility of specific interactions (such as hydrogen-bonding) between sulfanilamides and methanol, the same mixture injected for the chromatogram shown in Fig. 3 was separated using CO_2 with 5% methanol. The same conditions used to obtain the chromatogram shown in Fig. 6 were used for this separation to assist a comparison. The results indicate that the sulfanilamides were far less retained on the Biphenyl column after incorporating 5% methanol in the mobile phase. For example, the capacity factor of N-(*p*-methoxy benzoyl)sulfamethazine was changed from 3.10 to 1.65. This less retained behavior of sulfanilamides indicated that the polarity of the stationary phase should be increased. When the Biphenyl-30 column was replaced by the more polar Cyanopropyl-50 column, however, the stability of the stationary phase to modified CO_2 became a problem and the spectra of products formed by column bleed were recorded.

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