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DESIGN AND INDUSTRIAL APPLICATIONS OF A REMOVABLE PROBE INTERFACE FOR DIRECT CAPILLARY SUPERCRITICAL-FLUID CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

An interface coupling capillary supercritical-fluid chromatography (SFC) with a commercial quadrupole mass spectrometer has been assembled and utilized to investigate problems involving separation and identification in the consumer products industry. The design of the interface allowed positive and negative ion chemical ionization mass spectra to be obtained on a Hewlett-Packard 5985 gas chromatograph–mass spectrometer without instrumental modification. Changeover from gas chromatography–mass spectrometry (GC–MS) to SFC–MS was accomplished in minutes without the need to remove chromatographic columns or vent the vacuum system. The interface included provisions for maintaining SFC oven temperature to the ion source region and for independent heating of the flow restrictor terminus. The system allowed for choices of restrictor design, column flow-rate and chemical ionization reagent gas. Chromatographic conditions developed using SFC with flame ionization detection were readily transferred to the SFC–MS system with only a small change in chromatographic efficiency. No compromises to MS operating parameters were required. Examples of the evaluation and use of the SFC–MS system on samples and problems of concern in the consumer products industry are described.

INTRODUCTION

Supercritical-fluid chromatography (SFC) has developed as an important separation technique for problems not amenable to gas chromatography (GC) and liquid chromatography (LC). As with these other chromatographic techniques, the use of mass spectrometry (MS) is recognized as one of the most versatile detection methods available for SFC[1,2]. The interface of SFC with MS has now left the research phase of development and is being applied to a wide range of analytical problems[1–12]. These applications have been facilitated by the numerous interfaces developed for coupling SFC to a wide variety of commercial GC–MS and LC–MS systems[1,3–12]. Many of these instruments require the mass spectrometer to be dedicated for an extended period of time to SFC–MS operation. For many laboratories, such dedication of the mass spectrometer to one operating mode is not always practical and it is preferable to have a system which can convert from one operational mode to another with a

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minimum of down-time. It is also advantageous to have a means to test the performance of an SFC–MS interface with relation to other modes of introduction or detection.

An interface has been developed, based on the capillary–direct injection method pioneered by Smith and co-workers[1,2], for coupling a commercial capillary SFC system with a Hewlett-Packard 5985 GC–MS system. The design permits positive ion (PICI) and negative ion chemical ionization (NICI) mass spectra to be obtained on a range of analytes, using a wide variety of CI reagent gases. No modification of the mass spectrometer or chromatograph was required. The interface incorporates an independently heatable region for the SFC flow restrictor and allows coaxial introduction of CI reagent gas. A number of the current SFC flow restrictor designs can be accommodated. Conversion from GC–MS or direct insertion probe (DIP)–MS operational modes to SFC–MS or from SFC with flame ionization detection (FID) to SFC–MS can be accomplished in a matter of minutes. This flexibility permits a wide range of independent or interrelated experiments to be run on the two instruments, permitting evaluation of the performance of SFC–MS with respect to GC–MS, DIP–MS or SFC–FID.

Efforts to couple SFC to the HP5985 mass spectrometer first required considering designs previously developed in other laboratories. Henion *et al.*[3] interfaced an HP5985 with packed column SFC using a momentum separator. The underlying reason for this approach was the desire to produce electron impact (EI) ionization mass spectra. Refinements of this and of the MAGIC LC–MS interface of Willoughby and Browner[13] have led to commercial momentum–separator interfaces for LC–MS and SFC–MS. This design was not pursued because there was no specific need for EI spectra, and this approach required additional pumping and dedication of the instrument to SFC–MS. The use of open-tubular column SFC minimizes the gas load on the vacuum system, so additional pumping to reduce the load is not warranted.

Attempts to replicate the efforts of Hawthorne and Miller[4–6] by simply guiding the SFC flow restrictor through a capillary direct interface (used for GC) into the ion source were unsuccessful. With the HP5985 such an approach requires the vacuum system of the mass spectrometer to be vented to replace a capillary GC column with the SFC restrictor. The later works by this group[5,6] did use the newer HP5988 instrument which eliminated the need to vent the vacuum chamber. This method, wherein the GC/SFC–MS interface region is maintained about 100°C above column temperature to help heat the restrictor tip[4], was found workable at high SFC column velocities (4–10 times higher than used for other interface designs) and with the more volatile and lower-molecular-weight materials. This was the case with both polished and frit-type restrictors. High volumetric flow-rates led to excessive gas loads in the ion source chamber and the inability to operate the SFC through the practical density range of carbon dioxide. The use of higher temperatures in the interface block did not improve the performance of this approach. The inability to transport higher-molecular-weight and lower volatility analytes was reason to abandon this approach.

The use of Smith's capillary–direct approach with an HP5985 was recently reported by Owens *et al.*[7]. In that effort the interface used a 6.4 mm O.D. × 4.8 mm I.D. stainless-steel probe and a custom machined vacuum seal. The design incorporated a 20-mm heated region for the restrictor and experiments utilized tapered restrictors. The vacuum system of the mass spectrometer was equipped with a cryogenic

pumping system but still operated with a partial pressure of $1.0 \cdot 10^{-4}$–$1.5 \cdot 10^{-4}$ Torr carbon dioxide in the ion source chamber. This was due to use of restrictor aperatures much larger than were used for SFC–FID[7]. Finally, the system was run at low MS resolution and high detector voltages to increase system sensitivity[7].

Details of the SFC separation process, the direct injection process for SFC–MS and the advantages of SFC–MS have been fully described elsewhere[1]. This report focuses on the design, construction and evaluation of the probe-mounted interface. Application of the system to selected analytical problems from the consumer products industry are also addressed. A brief comparison of the parameters required for operation in SFC–FID *versus* SFC–MS, and the relative efficiency of SFC–MS separations will be made and the effects of using the mass spectrometer in a direct injection mode for SFC–MS will be described.

EXPERIMENTAL

Chromatography

All work was conducted on the Model 602 SFC–GC system (Lee Scientific, Salt Lake City, UT, U.S.A.) which consisted of a computer-controlled syringe pump for delivery of supercritical carbon dioxide (AGL, Clifton, NJ, U.S.A.), a Model 7526 helium-actuated HPLC-type injector (Rheodyne, Cotati, CA, U.S.A.) with a 0.5-μl internal volume, a gas chromatograph oven capable of isothermal or temperature-programmed operation and a GC-type flame ionization detector. The Lee Scientific computer and software (Ver. 2.0) enabled either pressure or density programming of the mobile phase. All injections were made at ambient temperature and split using the "T" supplied by the manufacturer[14]. The split ratio, usually about 50:1, was controlled by the flow through a length (50–60 mm) of 10 μm I.D. fused-silica capillary tubing. Chromatography was conducted at 100°C, isothermal, using a fluid density ramp on a 10 m × 50 μm I.D. fused-silica open-tubular column coated with a 30% biphenyl–70% methyl polysiloxane (SB-Biphenyl-30) stationary phase from Lee Scientific. Three types of SFC flow (pressure) restrictor were used, the "frit" restrictor from Lee Scientific[1], both a shorter length supplied for FID use and the longer "MS-frit", where the frit material is at the end of a 1-m length of deactivated 50-μm fused-silica tubing, the polished "Guthrie" type[1,15] and the tapered[1,16], both fabricated from deactivated 50-μm fused-silica tubing. A detailed comparison of the various restrictor designs was beyond the scope of the current work. In all cases the restrictor was attached to the column terminus using a zero-dead-volume union (MVSU/003; SGE, Austin, TX, U.S.A.). The restrictor terminus was kept flush with the interface probe exit. Efforts were made to keep the mobile phase linear velocity between 2 and 2.5 cm/s, or a volumetric flow-rate of about 4 μl/s, measured at a density of 0.2 g/ml.

Samples were obtained from numerous sources and used in solution in dichloromethane or chloroform (certified ACS grade, Fisher Scientific, Fair Lawn, NJ, U.S.A.). Sample preparation involved dissolving a weighed amount of sample in appropriate solvent and diluting to the working concentration. Concentrations used for more complex mixtures, such as nonionic surfactants, were 1–10% by weight and 1 to 5 mg/ml for single compounds or simple mixtures.

Mass spectrometry

MS was conducted on a Hewlett-Packard (Palo Alto, CA, U.S.A.) Model 5985B GC–MS system operated in both positive and negative chemical ionization modes. The MS system was comprised of a convertible EI/CI ion source and a single quadrupole mass analyzer. Ion source chamber pumping was accomplished using a 680 l/s (air) diffusion pump, which cannot be valved off from the vacuum chamber. Any interface design that would require venting the vacuum system to atmosphere would need 4–8 h to cycle from shut-down to start-up. The ion source chamber was equipped with a vacuum interlock for insertion of the tuning probe or the direct insertion probe. The tuning probe or DIP mates with a tapered port on the source, so the source volume is relatively well confined, with respect to the GC–EI-MS configuration, when solid samples are introduced or for operation in CI mode. The system was controlled by an HP-1000 E series computer system. Ion source temperature, for both PICI and NICI was 200°C with a starting ion source pressure, measured on the ion source chamber vacuum gauge, of $1.2 \cdot 10^{-4}$ Torr. The ion gauge, calibrated for nitrogen, was not corrected for the various gases present. This pressure value is what is routinely used for GC–CI-MS and DIP–CI-MS. Depending on the flow restrictor used for SFC, the ion source chamber pressure would range from $2.0 \cdot 10^{-4}$ to $4.5 \cdot 10^{-4}$ Torr at the end of the density programmed SFC–MS separation (410 bar, 0.765 g/ml). No effort was made to maintain a constant carbon dioxide/reagent gas ratio. Methane, isobutane, ammonia, 1% ammonia in methane, argon and Freon-12 were used as reagent gases for CI. All gases were of the highest available purity and obtained from AGL. Electron multiplier voltages used for PICI and NICI were similar to those used for GC–MS and DIP–MS. The mass range scanned depended on the sample being analyzed. The mass spectrometer was tuned using the Hewlett-Packard computer-controller tuning procedures. The system was always operated at unit mass resolution to m/z 614 (from perfluorotributylamine).

Interface probe design

The SFC–MS interface probe was assembled using a 1.27 cm O.D. × 0.85 cm I.D. leak probe (HP part No. 05985-20585), the same type of probe used for the tuning probe. This permitted use of the vacuum interlock and proper mating with the ion source without modification. A 35 cm length of 0.16 cm O.D. stainless-steel

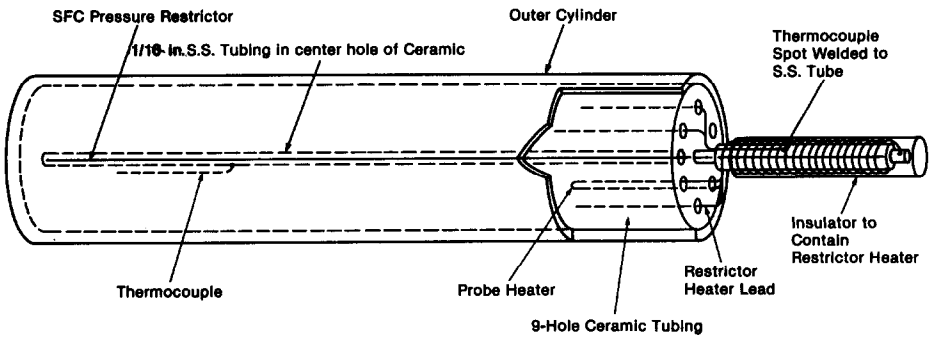

Fig. 1. Schematic diagram of the mass spectrometer end of the probe-mounted SFC–MS interface detailing the ceramic tube support and restrictor heater. S.S. = stainless steel.

tubing was used to contain the fused-silica flow restrictors and to supply CI reagent gas. This tube was supported in the probe inside a 22 cm length of nine hole ceramic tubing. A schematic diagram of the MS end of the interface probe is given in Fig. 1, illustrating the stainless-steel and ceramic tubes. The ceramic tube also provided a means of heating the interface probe, as a nichrome wire was passed through two of the holes and used as a heater. A thermocouple, silver-soldered to the tube containing the restrictor, was used to monitor temperature in the probe. The steel tube exited the leak probe to the SFC oven via a reducing tube fitting. This allowed a tube fitting "T" to be used to supply the CI reagent gas. CI reagent gases were metered through a fine metering valve. The flow restrictor was held in the "T" using a graphite-filled vespel ferrule (GVF/003, SGE) which provided a vacuum seal. The region external to the SFC oven and MS interlock was wrapped with heating tape and insulator to maintain oven temperature. The Model 602 SFC system was supplied with holes pre-cut in the oven wall and access panels in the cabinet to facilitate interface of the oven with an MS system. This feature allowed the SFC column to remain in the oven and reduced the need for externally heated zones in the interface. The mass spectrometer end of the interface probe (Fig. 1) was fitted with a nichrome wire wrapped around an insulator, sheathing the end of the stainless-steel tube. A second insulator covered the nichrome wire. A thermocouple, silver-soldered to the steel tube inside the insulator, enabled the temperature on the steel tube to be monitored. This heater was capable of temperatures of about 500°C, and heated on a 30–35 mm length of the end of the flow restrictor. This is approximately equal to the length in the heated zone in the Lee Scientific flame ionization detector. The electrical and thermocouple leads were admitted through holes in the ceramic tube. There was no vacuum seal on the MS end of the probe; all seals were made with tube fittings external to the vacuum system. The restrictor heater fits the ion source mating fitting in a manner analogous to the tip of the direct insertion probe, placing the restrictor terminus within 5 mm of the CI source volume entrance. An early version of the interface did not include the extra restrictor heater and relied on the ion source block to heat the restrictor. As the interface utilized the probe obtained from the instrument manufacturer, a tight fit to the CI source was assured. The interface probe was operated at SFC oven temperature and the restrictor heater temperature was varied between 100°C and 400°C.

RESULTS AND DISCUSSION

Supercritical-fluid chromatography

The first effort at a probe-mounted interface did not incorporate a restrictor heater, which permitted evaluation of the need for a restrictor heater in addition to heat from the ion source block. The ability of the vacuum system of the mass spectrometer to operate under SFC–MS conditions was also evaluated with the early interface version. Fig. 2A shows the carbon dioxide SFC–MS total ion chromatogram, positive ion CI-MS, for the separation of a poly(ethylene glycol) methyl ether [$HO(CH_2CH_2O)_nCH_3$] sample, average molecular weight ($\overline{MW}$) 550 daltons. The mass spectrometer was scanned from 130 to 750 daltons at 6 s/scan. The chromatogram shown was not background subtracted. Without an external heater, the restrictor sheath was between column temperature (100°C) and ion source temperature (200°C). Reasonably good separation, defined as narrow peak widths (approx. 30 s

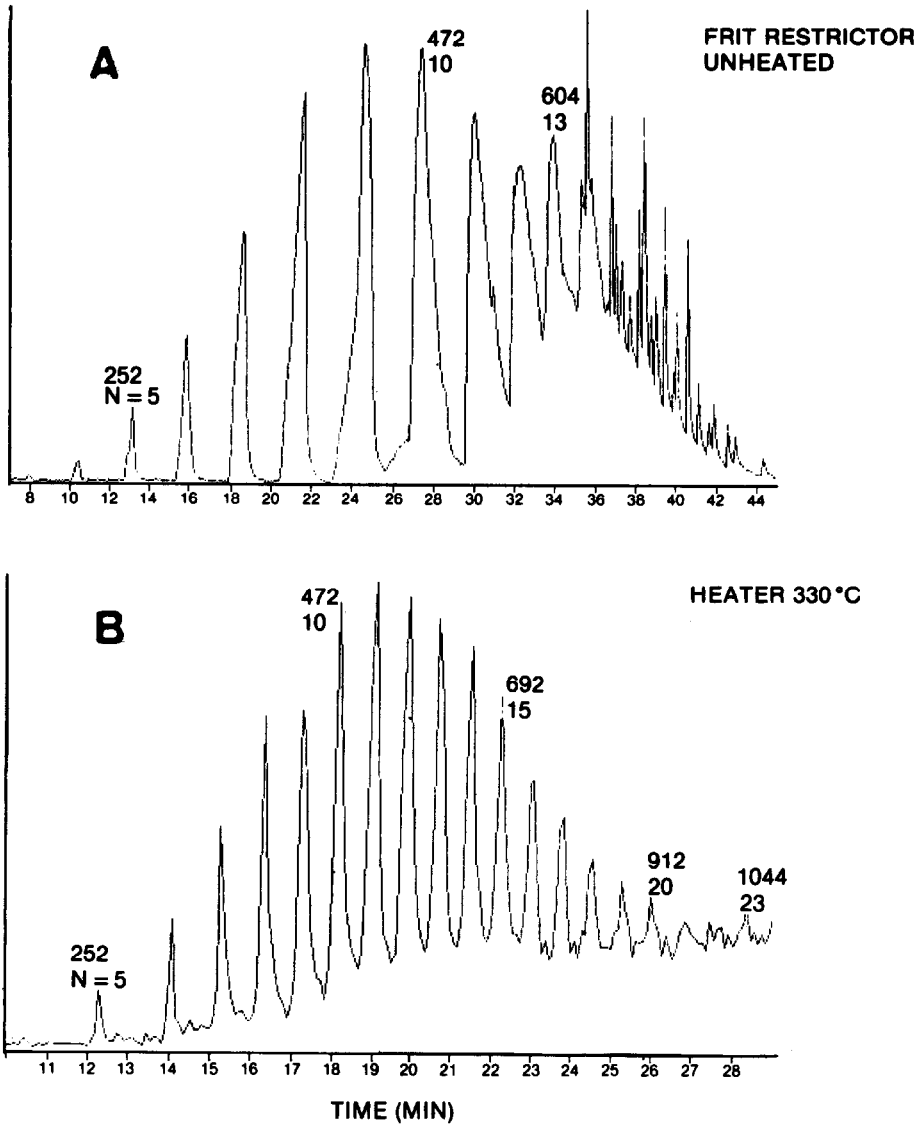

Fig. 2. Total ion chromatograms from the carbon dioxide capillary SFC–MS separations of poly(ethylene glycol) methyl ether (average mol.wt. 550) samples. Methane positive ion chemical ionization was employed for both samples, one obtained without additional flow restrictor heating (A) and one with a restrictor heater operated at 330°C (B).

full width at half hight) and baseline resolution, was achieved for early eluting components (up to $n = 8$) but higher-molecular-weight components could not be successfully transported and ionized. Mass spectra of components up to $n = 13$, 604 daltons, contained protonated molecules $(M + H)^+$ and structurally significant fragment ions. SFC with FID of this sample, as well as $\overline{MW}$ 750, under similar chromatograph-

ic conditions gave baseline separation of telomers up to $n = 20$ for MW 550 and $n = 26$ for $\overline{MW}$ 750 with no detector spiking or apparent discrimination against higher-molecular-weight components. For FID experiments the detector was operated at 395°C with the frit restrictor.

Fig. 2B shows the same poly(ethylene glycol) methyl ether sample separated using carbon dioxide SFC–MS and the interface incorporating the restrictor heater. In this example a frit restrictor was used and the restrictor heater operated at 330°C. All of the telomers found with SFC–FID were eluted and ionized, with peak shape and peak widths directly comparable to SFC–FID. The example illustrates the value of the added heated region in aiding transport of higher-molecular-weight analytes

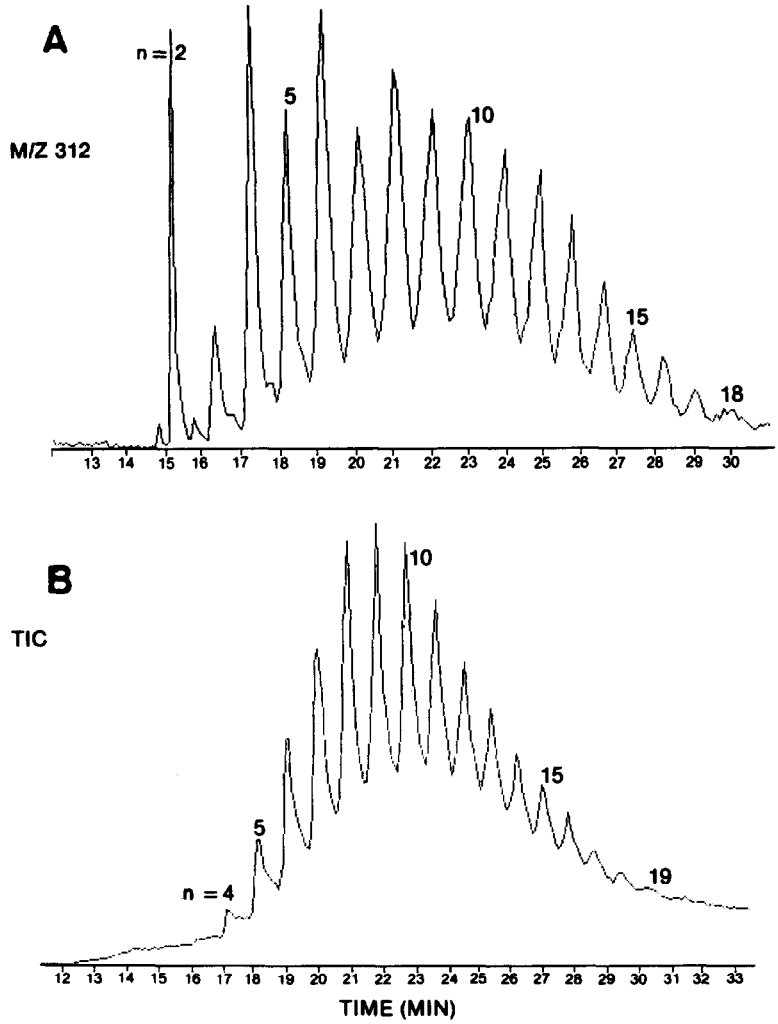

Fig. 3. Chromatograms from the capillary carbon dioxide SFC–MS separations of the ethoxylated surfactant Triton X-100. (A) *m/z* 312 selected ion chromatogram obtained in positive ion ammonia chemical ionization; (B) total chromatogram (TIC) obtained in methane negative ion chemical ionization.

for SFC–MS and the ability of the mass spectrometer to operate across the practical density range of carbon dioxide.

Although the ability to controllably heat the SFC flow restrictor aids the analysis of less volatile analytes, the current design does not display the marked effects of restrictor heater temperature found with the previously described interface[7]. Fig. 3 shows the SFC–MS chromatograms of Triton X-100, octylphenol ethoxylate with an average of about 10 moles ethylene oxide. This sample was analyzed as it is often used as a test mixture for SFC and to compare SFC with other techniques, many previous separations had been performed on this particular batch using SFC–FID and previous efforts[7] demonstrated restrictor heater temperature effects using this surfactant. Carbon dioxide SFC–FID with a frit restrictor had shown all telomers to $n = 19$ reproducibly eluted at restrictor heater temperatures from 300°C to 400°C, with expected small shifts in retention times due to variations in mobile phase viscosity and flow-rate at the restrictor. The same chromatographic conditions, including restrictor heater temperature, developed for SFC–FID were used for SFC–MS to produce the separations shown in Fig. 3. Variations in restrictor heater temperature of 50–75°C, shown in other interfaces to drastically alter the appearance of the SFC–MS reconstructed total ion chromatogram[7], did not show such profound effects here. This probe-mounted SFC–MS interface succeeds in duplicating nearly all the conditions found in the SFC–FID system, such that parameters developed for SFC–FID can be directly transferred to SFC–MS. Although not demonstrated here, SFC–MS extends the utility of SFC through the use of mobile phases not amenable to SFC–FID[1].

Mass spectra

Information on analyte identification, in the form of mass spectra, is the most tangible benefit of SFC–MS. Capillary-direct SFC–MS allows for use of any CI reagent gas in both positive and negative ion modes. Figs. 4 and 5 show the PICI mass

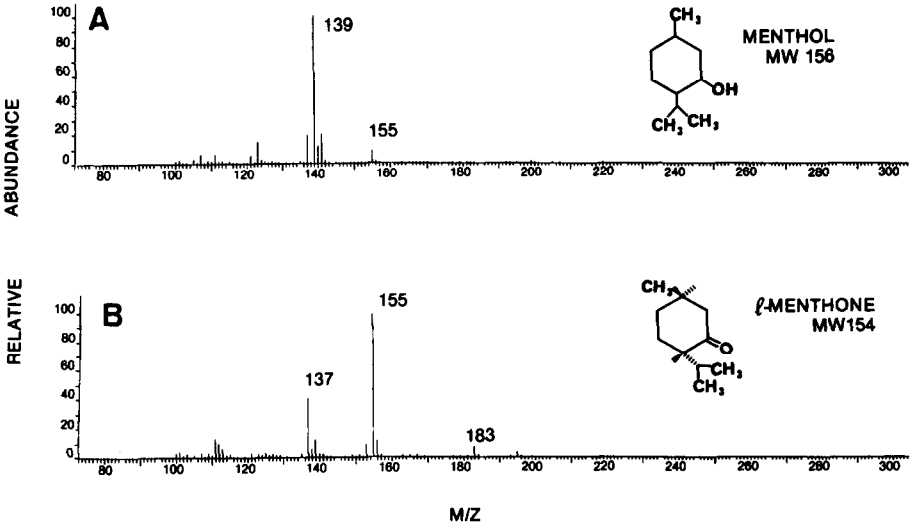

Fig. 4. Methane positive ion chemical ionization mass spectra of (A) menthol and (B) *l*-menthone, obtained following carbon dioxide SFC.

spectra of two flavor/fragrance compounds, menthol (Figs. 4A and 5B, MW = 156) and *l*-menthone (Figs. 4B, 5A and 5C, MW = 154), obtained following carbon dioxide SFC, using a variety of CI reagent gases. Irrespective of the fact that these particular compounds are amenable to GC–MS, many flavor and fragrance components do exhibit thermal lability and low temperature separations are obviously preferable for such samples. These two compounds highlight a common problem in flavor/fragrance analysis, very similar mass spectra from closely related structures. With the more energetic methane CI-MS both compounds show an ion at *m/z* 155. This is the protonated molecule $(M + H)^+$ for menthone (Fig. 4B) but corresponds to the loss of molecular hydrogen from the protonated molecule of menthol $(M + H - H_2)^+$. This type of loss is common in CI mass spectra of alkanes and alkanols. Common fragment ions are found at *m/z* 137 and *m/z* 139. The use of a mild CI

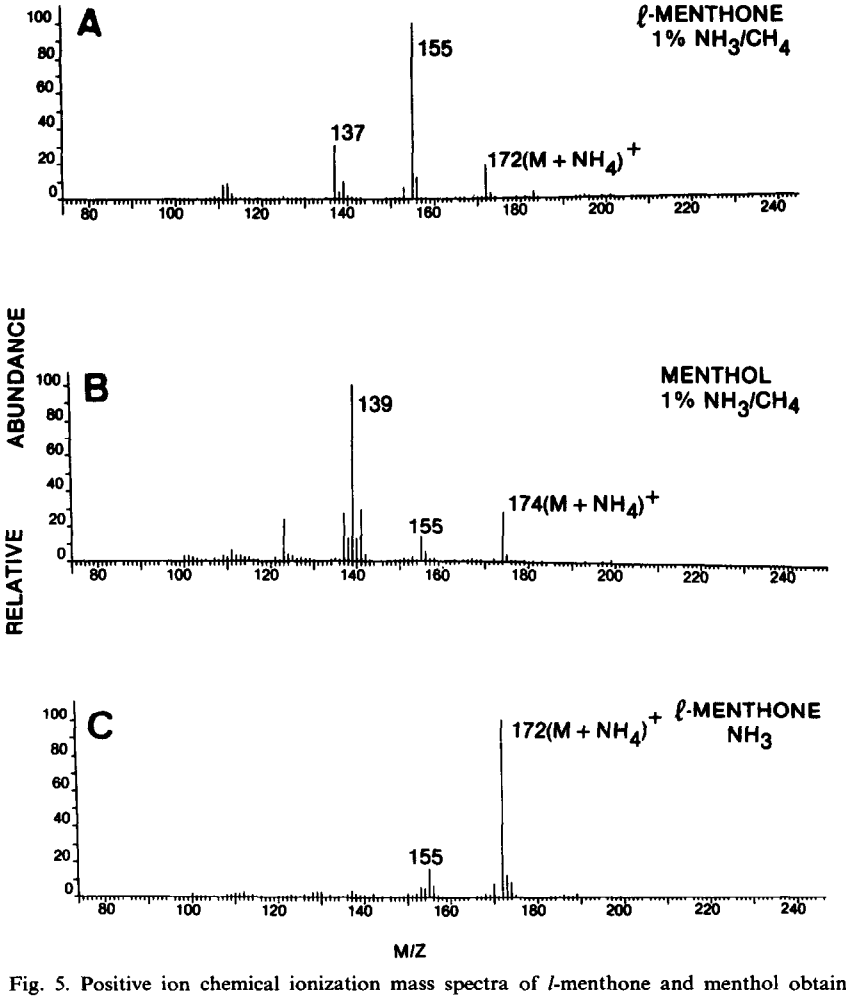

Fig. 5. Positive ion chemical ionization mass spectra of *l*-menthone and menthol obtained following capillary carbon dioxide SFC separation using 1% ammonia mixed in methane (A and B) and ammonia (C) as the reagent gases.

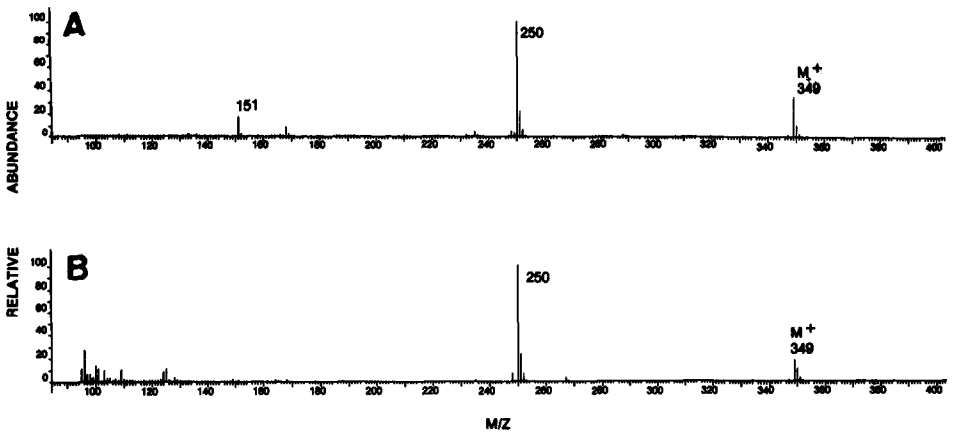

Fig. 6. Probe inlet 70 eV electron ionization (A) and 180 eV charge exchange CO_2–Ar chemical ionization mass spectra (B) of a sample of chromium(III) acetyl acetonate. The sample for CE ionization was introduced using carbon dioxide SFC.

reagent, ammonia (Fig. 5C) clearly gives weight information, in the form of ammonium adduct ions $(M + NH_4)^+$. The use of a mixed reagent gas, in this case 1% ammonia in methane, produces both molecular weight and useful structural information.

Fig. 6 gives a comparison of charge exchange CI and EI ionization to obtain similar information from a sample[17]. Again, the analyte is amenable to GC–MS, but in this example there needs to be an independent means of sample introduction for EI. The analyte, chromium(III) acetyl acetonate used as a spin-relaxation reagent for ^{13}C NMR, may be present in samples submitted for SFC analysis. Charge exchange (CE) CI mass spectra were obtained using the carbon dioxide mobile phase and an additional amount of argon to maintain ion source pressure at about $1.2 \cdot 10^{-4}$ Torr. Methane and isobutane CI mass spectra of metal acetyl acetonates produced on this instrument generally show extensive fragmentation and little to no parent ion production. Metal acetyl acetonates are quite amenable to EI, yielding molecular ions M^+, m/z 349 in Fig. 6A, and ions due to the loss of one and two ligands with reduction of the charge on the metal. The same types of ions are found with argon–carbon dioxide charge exchange with the exception of the m/z 350 ion $(M + H)^+$ being of greater relative abundance in the CE mass spectrum. In contrast to the intentional use of the carbon dioxide mobile phase as the CI reagent gas, the occurrence of CE ionization by carbon dioxide (as evidenced by M^+ ions) when other reagent gases were used was not found to be significant.

Industrial application

Analysis of ethoxylate alcohol (non-ionic) surfactants is one application for which SFC is particularly well-suited[18,19]. Usually the samples, although complex, are composed only of the starting alcohol and telomers of the surfactant of the structure $R–O–(CH_2CH_2O)_n–H$, (n = 1–100 or more). In such instances characterization, comprised of R group identification, average molecular weight calculation and ethoxylate distribution, can be accomplished by SFC–FID[18,19]. Samples can, at

times, contain additional components and FID offers no means of identification. Other methods of characterization which do not contain a separation step may not reveal the additional materials[19,20]. The coupled SFC–MS technique is invaluable for such samples. Fig. 7 shows the total ion chromatogram of a carbon dioxide SFC–MS separation of an ethoxylated stearyl alcohol with an average of 13 moles of ethylene oxide. Telomers of up to 1238 daltons (n = 22) are illustrated here (the MS data system was filled to capacity and ceased acquisition) which directly compares with SFC–FID results of this sample[19]. Such an example illustrates the ability of the interface to transport and ionize materials of higher molecular weight (greater than the mass range of the mass spectrometer, in fact) and lower volatility.

A reportedly similar ethoxylated alcohol was found to contain a second distribution of components centered between the n = 4 and 5 telomers of the alcohol ethoxylate[19]. Positive ion chemical ionization mass spectra of these components, obtained during the carbon dioxide SFC–MS separation of the mixture, are shown in Fig. 8. The mass spectra indicate the identity of the second distribution to be poly (ethylene glycol), at times present in ethoxylated surfactants. The mass spectra are characterized by abundant protonated molecules of the oligomers and characteristic fragment ions, at m/z 133 and m/z 177. SFC–FID and SFC–MS of standard poly (ethylene glycol) samples confirmed the identification of the second distribution and aided in an average molecular weight calculation[19]. The separation power of SFC combined with the ability to obtain molecular weight and structural information through MS is shown to provide a fast, efficient means of identifying unknown materials.

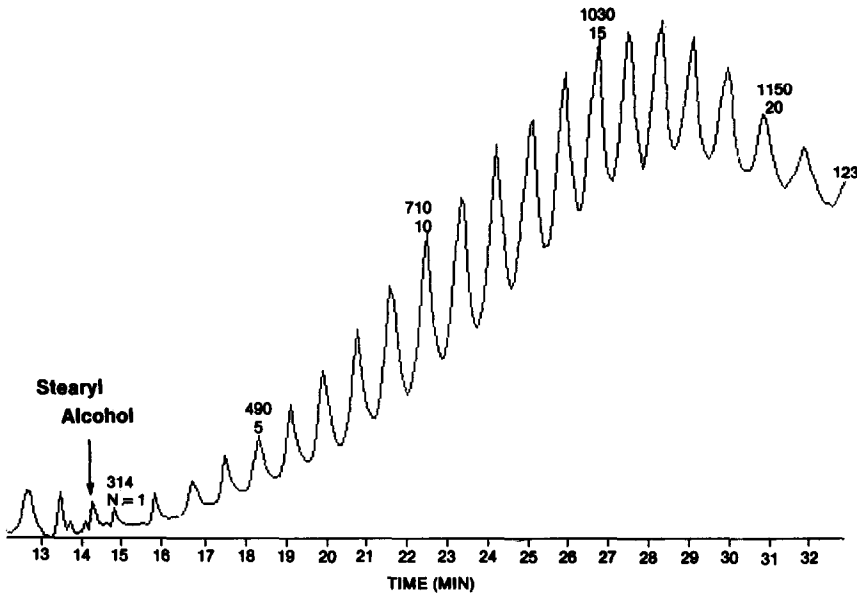

Fig. 7. Total ion chromatogram of the capillary SFC–MS separation of a sample of stearyl alcohol ethoxylate obtained using methane negative ion chemical ionization. The data system ceased acquiring at just under 33 min (prior to the end of sample elution).

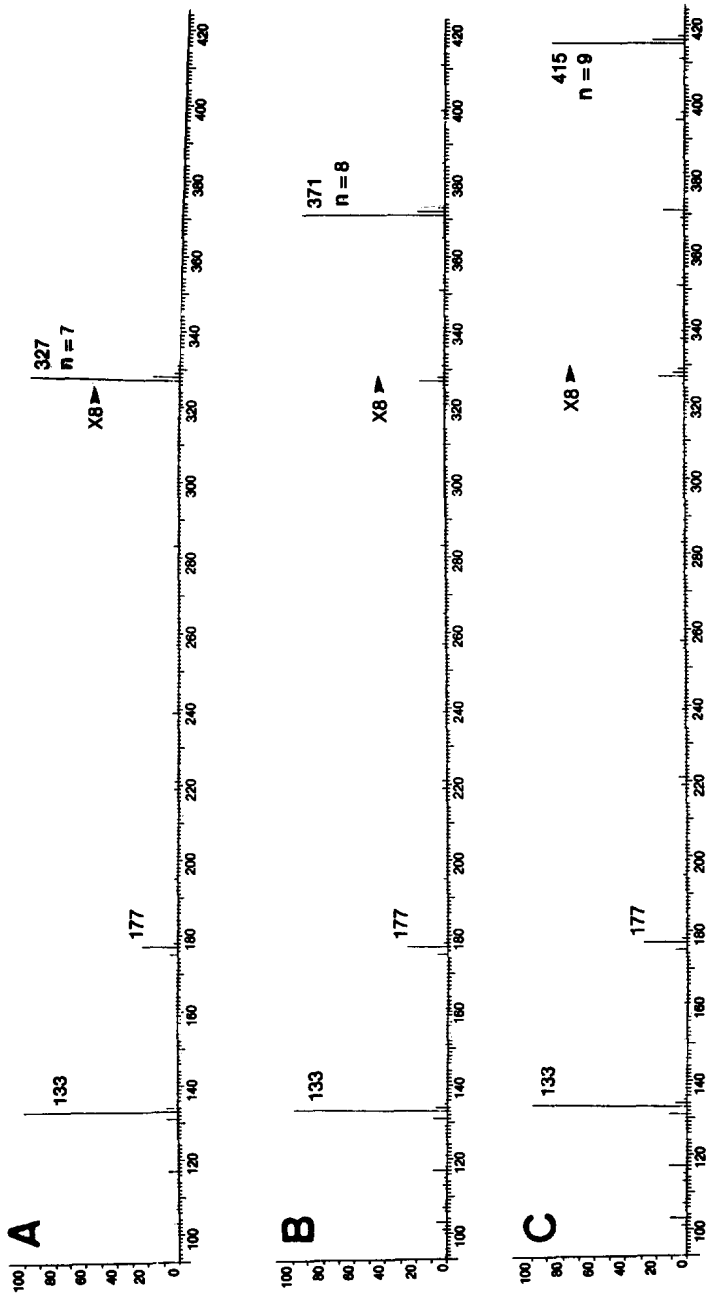

Fig. 8. Methane positive ion chemical ionization mass spectra of the n = 7, 8 and 9 oligomers of poly(ethylene glycol) obtained during the carbon dioxide capillary SFC–MS separation of a stearyl alcohol ethoxylate sample found to contain a second distribution of components.

CONCLUSION

A probe-mounted, capillary-direct interface has been assembled to allow a commercial GC–MS system to operate in the SFC–MS mode. The design required no custom machining and no modifications to either the chromatograph or the mass spectrometer. The design incorporated a heated zone for the SFC flow restrictor and three of the most widely applied types of SFC flow restrictor were used with comparable ease. All components and conditions used for SFC–FID were directly transferable to the SFC–MS system. This permitted separations to be optimized using SFC–FID with a rapid change to SFC–MS for complete analyte characterization, including abundant structural information. Changeover from GC–MS (or DIP–MS) to SFC–MS required only a few minutes. This permitted the system to be tuned and calibrated using the procedures applied for GC–MS or for direct comparison of SFC–MS introduction with other forms of sample introduction. Chromatographic performance of the SFC–MS system was only slightly less efficient than SFC–FID. This comparison was made using the identical column, splitter, restrictor and conditions and results obtained without compromising the MS system operating parameters. The one sacrifice from standard GC–MS capabilities made was the loss of electron ionization, but information usually contained in EI spectra was available through charge exchange chemical ionization. SFC has previously been shown to be broadly applicable in consumer products research and SFC–MS augments and extends the utility of SFC for solving analytical problems in this industry.

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