

## Supercritical fluid chromatography-mass spectrometry of non-ionic surfactant materials using chloride-attachment negative ion chemical ionization<sup>a</sup>

HENRY T. KALINOSKI\* and LEONARD O. HARGISS

*Unilever Research U.S., Inc., 45 River Road, Edgewater. NJ 07020 (U.S.A.)*

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### SUMMARY

Capillary supercritical fluid chromatography interfaced with chemical ionization mass spectrometry (SFC-CI-MS) provides high-efficiency separations and identification for characterization of alcohol ethoxylate and other non-ionic surfactant mixtures. When using the capillary direct interface for SFC-CI-MS, however, the role of the chromatographic mobile phase during ionization must be considered. The presence of carbon dioxide or nitrous oxide in the chemical ionization source of a Hewlett-Packard 5985 gas chromatography-mass spectrometry system configured for SFC-CI-MS significantly influences the appearance of positive and negative ion chemical ionization mass spectra. Positive and negative ion mass spectra produced using methane, isobutane or ammonia all display extensive fragmentation and **adduct** ion formation in the presence of carbon dioxide or nitrous oxide. Surfactant sample fragmentation can be limited or eliminated through the use of **difluorodichloromethane** (Freon-12) as the reagent gas for chloride-attachment negative ion chemical ionization. Only the chloride-attachment **adduct** anion is produced for alkoxyated **surfactants** and free fatty acids, even with a two-fold excess of carbon dioxide present in the ion source.

With CI conditions that permit the production of only molecular species, effects due to restrictor-heater temperature and interface design and operation could be evaluated. A comparison of direct supercritical fluid injection *versus* heated probe inlet introduction for surfactant samples was also possible. Chloride-attachment negative ion CI-MS following capillary SFC may be the preferred system for obtaining molecular weight and telomer distribution information on commercial alcohol alkoxyates and other non-ionic surfactant mixtures.

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## INTRODUCTION

Non-ionic surfactants are consumed at a rate of 800 million pounds annually in the U.S.A., 75% of this in household detergent products. Supercritical fluid chromatography (SFC) provides for high-efficiency separations for the analysis of these and related materials<sup>1-3</sup>. The interface of SFC with chemical ionization mass spectrometry (CI-MS) extends the utility of the technique by providing identification information to complement the efficient separation. Information required for non-ionic surfactant characterization includes identification of hydrophobe type, usually an alkyl or alkyl-substituted aryl group, hydrophobe distribution and the type, length and distribution of the hydrophile, usually repeating ethylene or propylene ethers. Characterization using MS is often enhanced by limiting fragmentation of higher-molecular-weight species.

A probe-mounted capillary direct interface for SFC-CI-MS was developed and an initial evaluation of its performance conducted<sup>4</sup>. When the system was further evaluated for applicability to characterization of alkoxyated surfactants, the positive and negative ion CI mass spectra produced were found to be strongly influenced by the presence of the chromatographic mobile phase in the ion source. These results were contrary to results reported for other sample types and SFC-CI-MS systems<sup>5,6</sup>. The influence of the mobile phase on ionization complicated evaluation of the SFC-CI-MS interface and limited application of the system for surfactant characterization.

To determine whether observed effects were sample specific and to understand the role of mobile phase on CI following capillary SFC, conditions in the ion source of the SFCCI-MS system were studied with selected fatty acid and alkoxyated surfactant mixtures. Various sample introduction methods were employed with positive and negative ion CI performed with and without supercritical fluid solvents present. The influence of carbon dioxide and nitrous oxide on CI of non-ionic surface-active materials was evaluated and conditions defined which limited such influence. Parameters were established which allowed evaluation of interface conditions, sample transfer and system transmission independent of mobile phase. The system was finally employed to obtain average molecular weight and hydrophile distribution information on alkoxyated mixtures that had been extensively studied by other MS methods'.

## EXPERIMENTAL

All work was conducted on a Model 602 SFC system (Lee Scientific, Salt Lake City, UT, U.S.A.) consisting of a computer-controlled syringe pump for delivery of pressurized carbon dioxide or nitrous oxide (AGL, Clifton, NJ, U.S.A.), a Model 7526 helium-actuated HPLC-type injector (Rheodyne, Cotati, CA, U.S.A.) with a 0.5- $\mu$ l volume internal loop, an oven capable of isothermal or temperature-programmed operation, gas chromatography (GC)-type flame ionization detection (FID) system or a probe-mounted interface for MS<sup>4</sup>. Operation in either pressure or density programming modes was possible. Sample injections were made at ambient temperature and split using the manufacturer-supplied "T". Volumetric split ratio (usually 50:1) was controlled by flow through a length of 10- $\mu$ m I.D. fused-silica tubing or a similar length of 50- $\mu$ m I.D. tubing with a polished restriction. A 10 m  $\times$

50  $\mu\text{m}$  I.D. fused-silica open tubular column with a biphenyl-methylpolysiloxane (30:70) stationary phase (SB-Biphenyl-30) was used for chromatography. Direct fluid injection experiments were conducted at 125°C using various lengths of deactivated fused-silica tubing, both uncoated and with stationary phase. Injections were made at 100 bar followed by a 140 **bar/min** increase to 400 bar, sufficient to separate the analyte from the injection solvent. Lee Scientific porous "frit" restrictors were used for pressure (flow) restriction. Restrictors were connected to the column terminus using a zero-dead-volume union. Restrictor-heater temperatures for the FID system were from 350 to 400°C. For SFC-CI-MS the restrictor terminus was kept flush with the interface probe exit. Mobile phase linear velocity was *ca.* 2 cm/s, volumetric flow-rate was *ca.* 4  $\mu\text{l/s}$ , measured at a carbon dioxide density of 0.2 g/ml. The design and operation of the **SFC-CI-MS** interface probe has been fully described **previously**<sup>4</sup>. The interface probe was operated at SFC oven temperature and the restrictor-heater temperature was varied between 200 and 450°C.

MS was performed on a Hewlett-Packard 5985B GC-MS system operated in both positive and negative CI modes. The interface probe was inserted through the interlock used for the tuning or direct insertion probe (DIP). As with the DIP, the SFC-CI-MS interface probe mates with a tapered port on the ion source, ensuring a well confined volume, relative to the **GC-electron** impact (EI) ionization-MS configuration. The restrictor terminus was within 5 mm of the source volume entrance. Ion source temperature was 200°C, with a starting source pressure (column flow plus reagent gas) of  $1.2 \cdot 10^{-4}$  Torr. Final ion source chamber pressure at completion of density-programmed SFC was *ca.*  $2.0 \cdot 10^{-4}$  Torr. No effort was made to maintain constant mobile phase-reagent gas ratio. Methane, isobutane, ammonia and Freon-12 of the highest available purity (AGL) were used as CI reagent gases. The mass spectrometer was controlled and data were collected on a Teknivent (St. Louis, MO, U.S.A.) Vector/One MS data system, requiring manual tuning and calibration. The system was always operated at unit mass resolution to  $m/z$  614 (**perfluorotributylamine**).

All samples were used in solution in dichloromethane (Optima grade, Fisher Scientific, Fair Lawn, NJ, U.S.A.) at concentrations of 1-5 **mg/ml** for single compounds or simple mixtures or 2% (w/w) for complex mixtures. Non-ionic alcohol ethoxylate samples were obtained from numerous sources at Unilever Research. "OXYPRUF" alkoxyated pyrazoles (Olin Chemical) were obtained from Dr. Kenneth L. Busch. Homogeneous dodecanol ethoxylate samples were purchased from Nikko Chemical (Tokyo, Japan). Fatty acid mixtures were obtained from commercial sources or from the Chem Services Surfactant Chemicals Kit (Chem Services, West Chester, PA, U.S.A.).

## RESULTS AND DISCUSSION

The applicability of the SFC-CI-MS interface for characterization of **surfactant** materials was first tested by comparing the results produced using FID with those produced using CI-MS detection. Fig. 1 shows the SFC-FID chromatogram and the SFC-CI-MS reconstructed total ion chromatogram (ammonia CI from  $m/z$  150 to 1000) obtained for a **poly(ethylene glycol)** methyl ether sample. Comparisons between FID and MS detection for **these and** related **poly(ethylene glycol)** (PEG) and

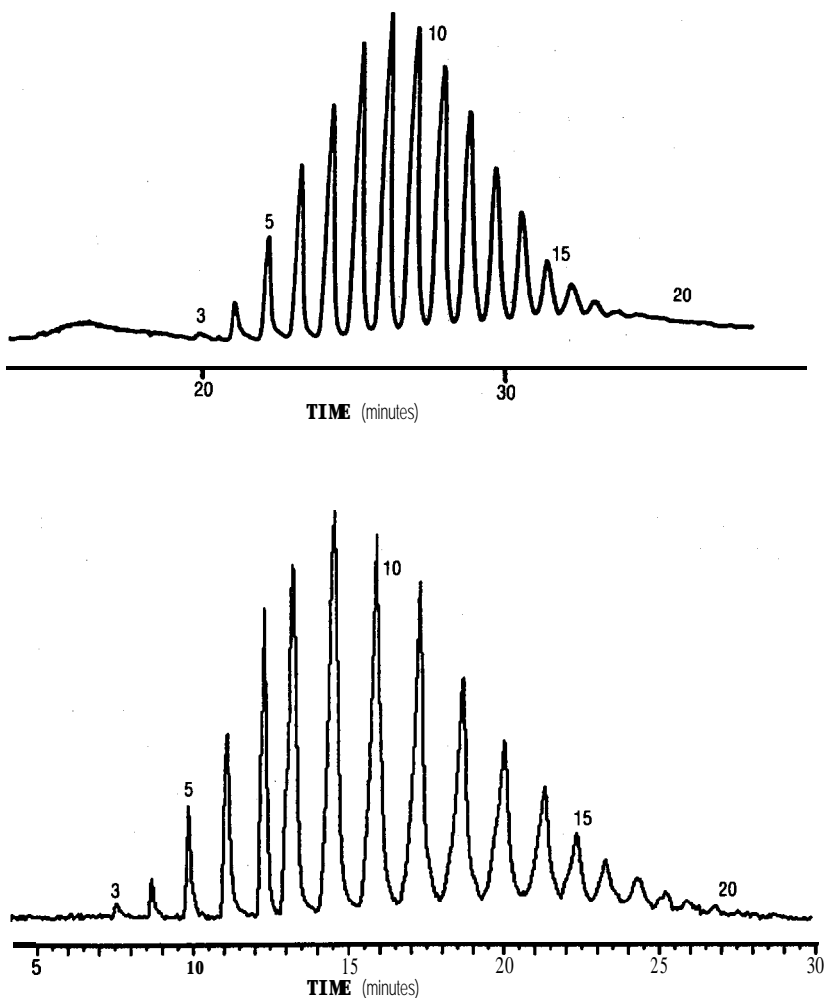


Fig. 1. Capillary supercritical fluid chromatographic separations of a poly(ethylene glycol) methyl ether sample (average molecular weight 550) using flame ionization (top) and ammonia positive ion CI-MS (bottom) for detection. Separations were conducted at 125°C, isothermal, using carbon dioxide as the mobile phase. A two-step density program, from 0.2 g/ml to 0.52 g/ml at 0.033 g/ml/min followed by a 0.009 g/ml/min increase to 0.69 g/ml was used to obtain separation. Numbers indicate moles of ethylene oxide per molecule.

poly(propylene glycol) (PPG) samples all displayed comparable separations with baseline resolution and narrow peak widths and efficient transfer and detection of higher molecular weight species. Samples were chosen to fall within the mass range of the HP5985 quadrupole mass spectrometer, 1000 dalton. In all cases, conditions developed for separation with FID could be directly transferred to SFC-CI-MS<sup>4</sup>. One difference found in the use of SFC-CI-MS was shorter dead times and shorter retention times for all analytes when the same restrictor was used in both SFC-FID and SFCCI-MS. This increase in mobile phase velocity, due in part to expansion

into the CI ion source vacuum, was not found to adversely affect the separations of PEG, PPG and PEG methyl ether samples.

Ammonia positive ion mass spectra of PEG methyl ether telomers were characterized by ammonium **adduct** ions ( $M + \text{NH}_4$ )<sup>+</sup> as the base peaks and minor contributions from fragment ions. Isobutane positive ion mass spectra displayed **protonated** molecules ( $M + \text{H}$ )<sup>+</sup> as the base peaks and limited amounts of fragment ions. These spectra correspond to the type of CI spectra for alcohol ethoxylates reported by Rudewicz and Munson<sup>8</sup>. Fragmentation, to aid in structural characterization of unknowns, could be increased by using methane or argon as the reagent **gas**<sup>4</sup>.

### Mobile phase effects

Alkoxyated pyrazoles, manufactured by Olin Chemical under the OXYPRUF tradename, provided a more rigorous test of the SFC-CI-MS interface. Ethoxylated (OXYPRUF-E) and propoxylated (OXYPRUF-P) **dimethyl** pyrazoles are highly viscous liquids with vapor pressure low enough to allow for direct introduction into the source of a mass spectrometer. They are stable and of relatively low mass, amenable to many forms of sample introduction and mass analysis. For these reasons the OXYPRUFs were used to develop a comprehensive comparison of various **desorption ionization techniques**<sup>7,9</sup>.

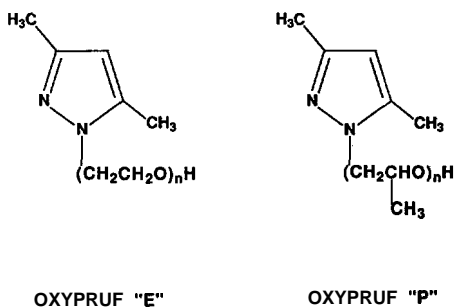


Fig. 2 shows the carbon dioxide capillary SFC separation of OXYPRUF E and P mixtures using FID. These alkoxyated antioxidants were found to be readily amenable to analysis using capillary SFC and of sufficiently low volatility to test the SFC-CLMS interface. The ability to compare SFC-CI-MS results with mass spectral results using desorption ionization techniques permitted evaluation of possible mass discrimination effects. The **number-( $M_n$ )** and **weight-( $M_w$ )** average molecular weights for these samples obtained from SFC-FID and desorption MS data are summarized in Table I. The results from SFC-FID characterization agreed quite well with data from gel permeation chromatography (GPC) (within about 5%), used in the study of desorption ionization as the non-MS "standard".

Unlike results with PEG and PPG, SFC-CI-MS of alkoxyated pyrazole samples did not correspond to SFC-FID results. Fig. 3 shows averaged mass spectra, positive ion ammonia CI, obtained for OXYPRUF P and E following direct **super-critical** fluid injection (no chromatography). Direct supercritical fluid injection was employed in an effort to minimize differences in source conditions over the course of a chromatographic separation<sup>10</sup>. All of the OXYPRUF mixture components were ionized under the same interface and CI source conditions (temperatures, pressures,

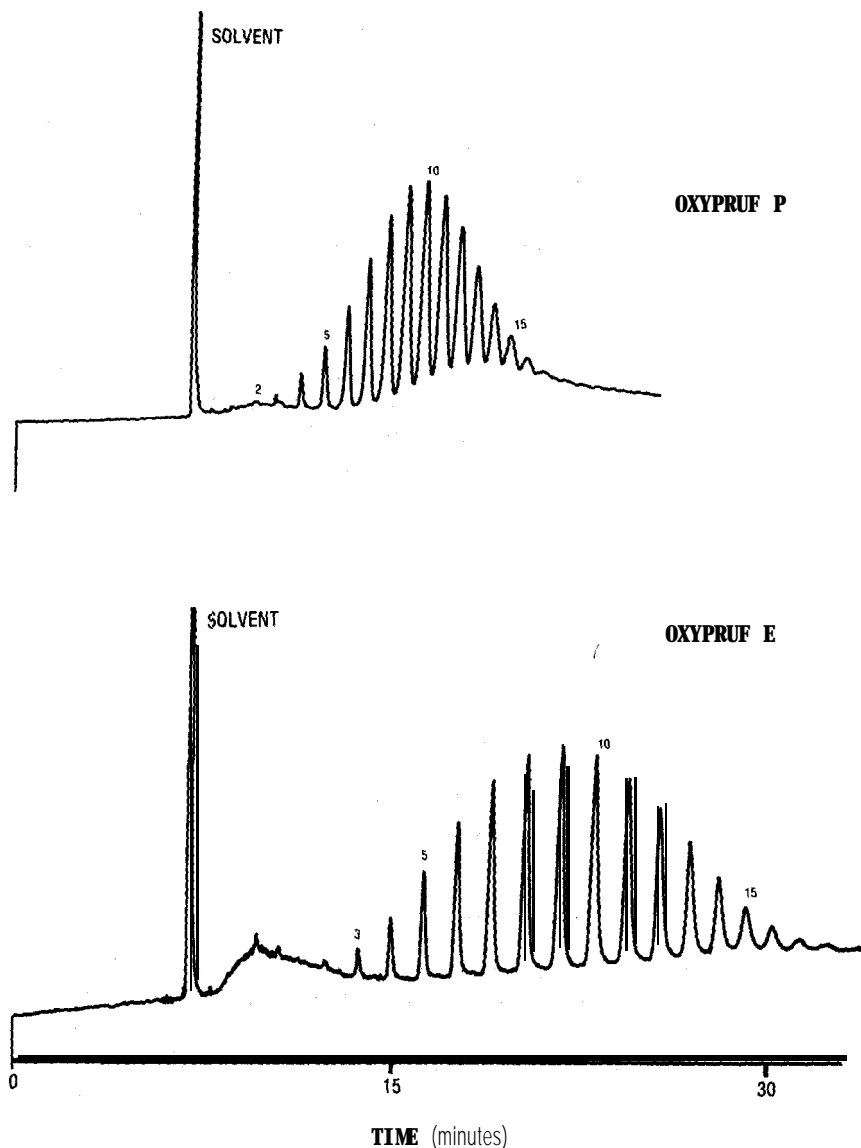


Fig. 2. Capillary supercritical fluid chromatographic separations of propoxylated (OXYPRUF "P", top) and ethoxylated (OXYPRUF "E", bottom) dimethylpyrazole obtained using FID. Carbon dioxide was used as the mobile phase with the same chromatographic conditions as described for Fig. 1 used for both samples. Restrictor-heater temperature was 375°C. Numbers indicate moles of ethylene or propylene oxide per molecule (n).

mobile phase flow-rate and reagent gas composition). Although protonated molecules are the most abundant ions in the spectra, abundance of fragment ions is greater than was seen for PEG or PPG samples and the average molecular weights and telomer distributions do not correspond with the SFC-FID data (Table I). The greater abundance of unresolved material present in OXYPRUF "E" (Fig. 2, bottom) may

TABLE I

NUMBER-AVERAGE ( $M_n$ ) AND WEIGHT-AVERAGE ( $M_w$ ) MOLECULAR WEIGHTS OF ALKOXYLATED PYRAZOLE MIXTURES OBTAINED FROM CHROMATOGRAPHIC AND MASS SPECTROMETRIC DATA

GPC and desorption ionization mass spectral data from ref. 7. FAB = fast atom bombardment; NICI = negative ion chemical ionization; PICI = positive ion chemical ionization; SF-DFI = direct supercritical fluid introduction; SIMS = secondary-ion mass spectrometry. For other abbreviations, see text.

Method	OXYPRUF "E"		OXYPRUF "P"	
	$M_w$	$M_n$	$M_w$	$M_n$
SFC-FID	582	556	747	710
SF-DFI				
NH, PICI-MS	420	390	506	473
CI - NICI-MS	545	535	617	585
FAB	512	471	603	549
SIMS	538	501	642	601
Electrospray	587	562	665	630
EI	375	360	423	390
GPC	617	570	735	681

account for part of the apparent difference in the amount of fragmentation in the mass spectra in Fig. 3. Some physical changes have been noted in the source stocks of this sample and further MS studies of this material are currently in progress". These results were also found when the samples were analyzed using complete chromatographic separations<sup>12</sup>. These spectra correspond to the type described by Pinkston *et al.*<sup>13</sup> obtained in SFC-CI-MS. Attempts to minimize production of fragment ions through control of restrictor-heater temperature or use of another mobile phase (nitrous oxide) were unsuccessful. Influence of ion source temperature and role of mobile phase modifiers are currently under study.

One drawback of the OXYPRUF samples was the inability to analyze isolated telomers under a variety of conditions. Mass spectra obtained as single telomers were eluting from the SFC column indicated lower-molecular-weight, components were transferred and ionized intact, as evidenced by production of only protonated molecules. Higher-molecular-weight species were found to produce less abundant protonated molecules and extensive fragmentation<sup>12</sup>. The same behavior was found for ethoxylated n-alcohol surfactants, although not to the same extent. Homogeneous alcohol ethoxylates were available and used to study the effect of various source and introduction conditions and reagent gases and ion source gas mixtures.

Ethoxylated dodecanols, containing an ethoxylated chain from one to ten units long, were analyzed using both direct supercritical fluid injection and heated DIP introduction. DIP introduction allowed evaluation of the effect of thermal decomposition on the samples. Positive and negative ion CI mass spectra were obtained using a variety of reagent gases and source gas pressure combinations. Complete details of the study of alcohol ethoxylate surfactants by SFC-CI-MS are described elsewhere<sup>14</sup>. Briefly, results of the study indicated samples up to the dodecanol decaethoxylate species ( $C_{12}H_{25}[OCH_2CH_2]_{10}OH$ ) -produced predominantly protonated molecules or ammonium adduct ions when introduced from the heated DIP (ca. 280°C) using

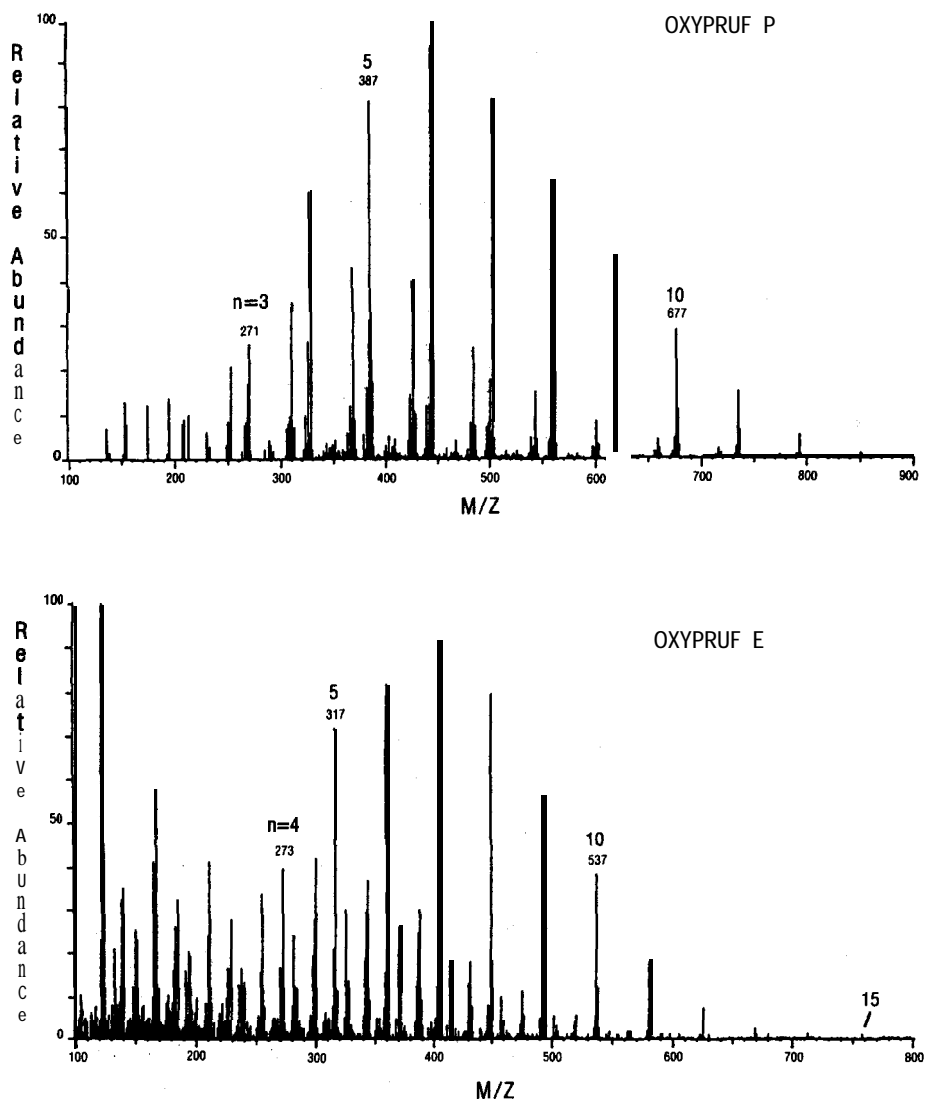


Fig. 3. Positive ion ammonia chemical ionization mass spectra of OXYPRUF "P" and OXYPRUF "E" mixtures obtained following direct **supercritical** carbon dioxide injection. Injection and interface conditions, described in the Experimental section, were similar for both samples. Restrictor-heater temperature was 385°C.

isobutane or ammonia as the reagent gas, up to a source pressure of  $2 \cdot 10^{-4}$  Torr. Thermal decomposition did not contribute to these mass spectra. When carbon dioxide or nitrous oxide was introduced along with CI reagent gas, the relative abundance of fragment ions increased. The results for dodecanol-pentaethoxylate ionized using isobutane in the presence of carbon dioxide are summarized in Table II. An increase in the relative concentration of carbon dioxide or nitrous oxide resulted in an increase



TABLE II

RELATIVE ABUNDANCE OF THE  $m/z$  133 FRAGMENT ION FROM THE PROTONATED MOLECULE OF PENTAETHYLENEGLYCOL DODECYL ETHER ( $m/z$  407) OBTAINED AT VARIOUS ION SOURCE GAS COMPOSITIONS

<i>Isobutane pressure (Torr)</i>	<i>Carbon dioxide pressure (Torr)</i>	<i>% Relative abundance <math>m/z</math> 133 ion<sup>a</sup></i>
$1.0 \cdot 10^{-4}$	0	17.5
$1.0 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$	19.2
$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$	27.1
$0.5 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$	39.8
$0.5 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$	34.1

<sup>a</sup> Protonated molecule,  $m/z$  407, was the base peak in all cases.

in the abundance of fragment ions. Only one fragment ion,  $m/z$  133, is listed but similar changes were found for many fragment ions. The relative abundance of the molecular ion ( $M^+$ ) did not appear to change but the role of charge exchange with carbon dioxide could not be discounted from these data.

Chlorinated hydrocarbons and chlorofluorocarbons as reagent gases for CI have been employed in the analysis of **polysaccharides**<sup>15</sup>. The mild chloride-attachment negative ionization was tried with ethoxylated alcohols and found to yield only chlorine **adduct** ions ( $M + Cl$ )<sup>-</sup> even with a two-fold excess of carbon dioxide **present**<sup>12,14</sup>. The negative ion CI mass spectrum (averaged) of a mixture of OXYPRUF "P" and PPG produced using dichlorodifluoromethane following supercritical carbon dioxide direct fluid injection is shown in Fig. 4. The mass spectrum is composed primarily of ( $M + Cl$ )<sup>-</sup> **adduct** ions for the OXYPRUF and PPG samples. The expected chlorine isotope abundance is found in all cases for the OXYPRUF species. The chlorine isotope ratios for the PPG species are shifted due to water loss ions from OXYPRUF materials. This effect is more noticeable for the higher  $m/z$  value ions. The calculated average molecular weights (Table I) compare quite favorably with the FAB, SIMS and electrospray ionization data. Production of water loss ions and possible discrimination against higher molecular weight materials might account for the discrepancy between SFC-CI-MS (chloride attachment) and SFC-FID data. Results with OXYPRUF "E" were similar (Table I) and results from propoxylated hydrazines (OXYPRUF "6") also agreed well with other **methods**<sup>7,9</sup>.

### *Interface parameter effects*

With conditions that produce solely molecular species, the role of various interface and source parameters could be studied. One variable studied was the direction of CI reagent gas introduction. The present design of the SFC-CI-MS interface permits CI reagent gas introduction coaxially along the SFC pressure restrictor. Alternatively, reagent gas is introduced through the GC-MS interface, the conditions used for capillary GC-CI-MS on this system. Coaxial CI reagent gas introduction was found to permit more stable temperature control of the SFC-CI-MS restrictor heater but no measurable change in the mass spectra produced. Positive and negative ion CI mass spectra produced were of slightly greater intensity, but no statistically

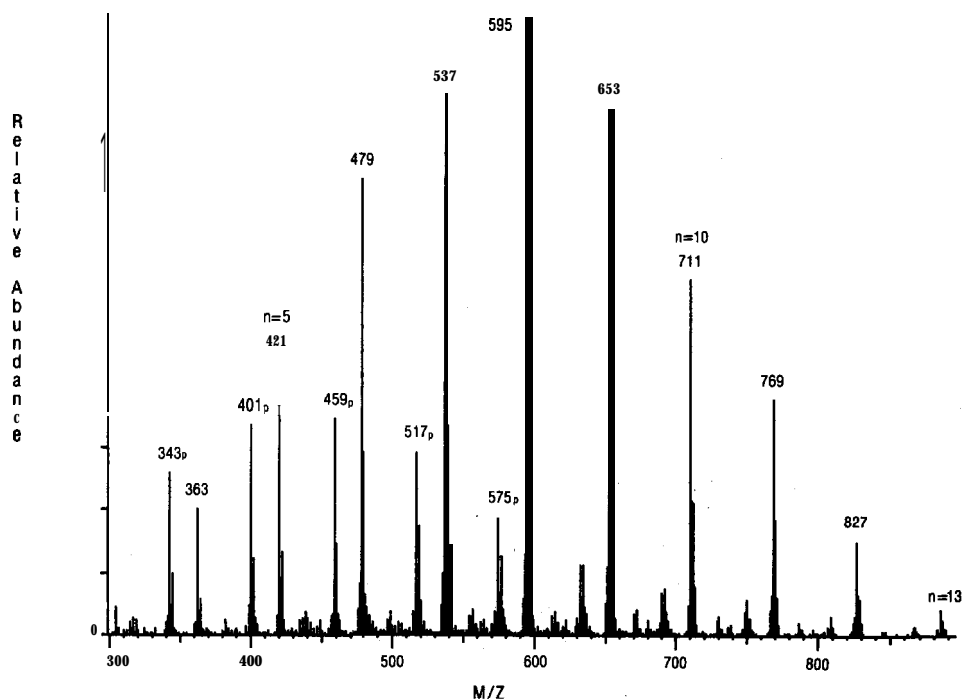


Fig. 4. Negative ion dichlorodifluoromethane (Freon-12) chemical ionization mass spectrum of a mixture of OXYPRUF "P" and poly(propylene glycol) obtained following supercritical carbon dioxide direct injection. Poly(propylene glycol) chloride adduct ions are marked with a "P". Injection and interface conditions were similar to those used for positive ion ammonia chemical ionization.

significant change has been found. There was no change in the ions produced in the mass spectra.

The effects of restrictor-heater temperature were probed using underivatized ("free") fatty acids. In preliminary evaluation<sup>4</sup> and analysis of OXYPRUF materials, restrictor-heater temperature was found to have little effect. Temperatures determined as applicable for SFC-FID were directly transferred to SFC-CI-MS. It was not apparent whether restrictor-heater temperature strongly influenced production of water loss ions for the OXYPRUF samples. Results with free fatty acids were noticeably different.

Fig. 5 shows the reconstructed total ion chromatogram for the SFC-NICI-MS analysis of a mixture of fatty acids from a marine fish oil (521, Chem Services). Separation was achieved using a linear 140-bar/min pressure program on the 10 m × 50 μm biphenyl phase column. Advantages of fast pressure program rates for rapid separations on small bore fused-silica columns have been clearly described<sup>16,17</sup>. The separation shown in Fig. 5 was conducted at a restrictor-heater temperature of 250°C. The chloride attachment negative ion mass spectra of the C<sub>18</sub> and C<sub>22</sub> acids from the mixture are shown in Fig. 6. The mass spectra are characterized by the production of the chloride adduct ion, (M + Cl)<sup>-</sup>. The ion at m/z 291 in the C<sub>18</sub> mass spectrum is from the "tail" of the C<sub>16</sub> acid chromatographic peak about 12 s earlier, and the m/z

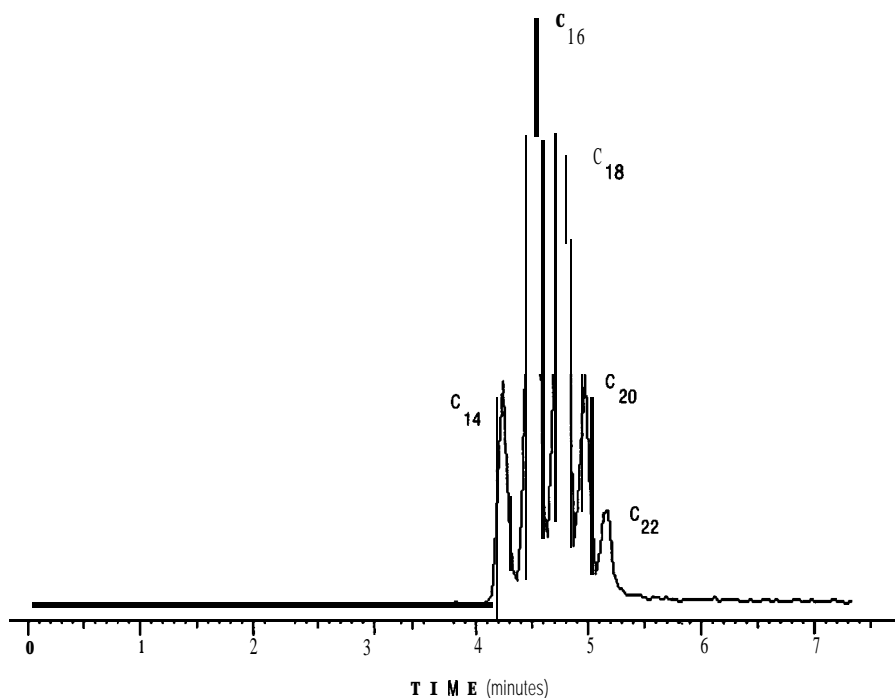


Fig. 5. Reconstructed total ion chromatogram of the rapid capillary carbon dioxide supercritical fluid separation of a hydrogenated marine fish oil fatty acid mixture produced using dichlorodifluoromethane negative chemical ionization mass spectrometry detection. A linear **140-bar/min** pressure program was used to produce this separation at **125°C**, isothermal, on a **10 m × 50 μm** SB-Biphenyl-30 open tubular column. Full scan (**100–400** dalton) mass spectra were obtained at 0.7 s/scan.

353 ion corresponds to an  $(M - H + Cl_2)^-$  species. The  $m/z$  155 ion in the  $C_{22}$  spectrum is a cluster ion due to the reagent gas. When produced at the restrictor-heater temperature used for SFC-FID, **333°C**, the chloride-attachment mass spectra in Fig. 7 are obtained. These spectra show extensive fragmentation and the formation of ions which correspond in mass to unusual **adduct** ions,  $(M + CH_2Cl)^-$  and  $(M + C_2H_4Cl)^-$ . As analytes are chromatographically separated from higher homologues, these ions could not be produced from coeluting species (Figs. 5 and 6). Further, there are no  $C_{19}$  fatty acids present in the fish oil sample that could yield the  $m/z$  333 ion. The **adduct** ions may be formed from reaction of the thermally degraded materials with intact molecules. What is not clear is where in the system thermal decomposition may be occurring. It may be that analyte molecules contact hot surfaces in the interface restrictor heater and decompose (pyrolyze) prior to introduction to the CI ion source<sup>18</sup>. This type of pyrolysis-SFCCI-MS interface has been proposed as a means of extending SFC-CI-MS to very involatile materials<sup>5</sup>. It is also possible that reactions are occurring on or near ion source surfaces in close proximity to the interface probe<sup>19</sup>.

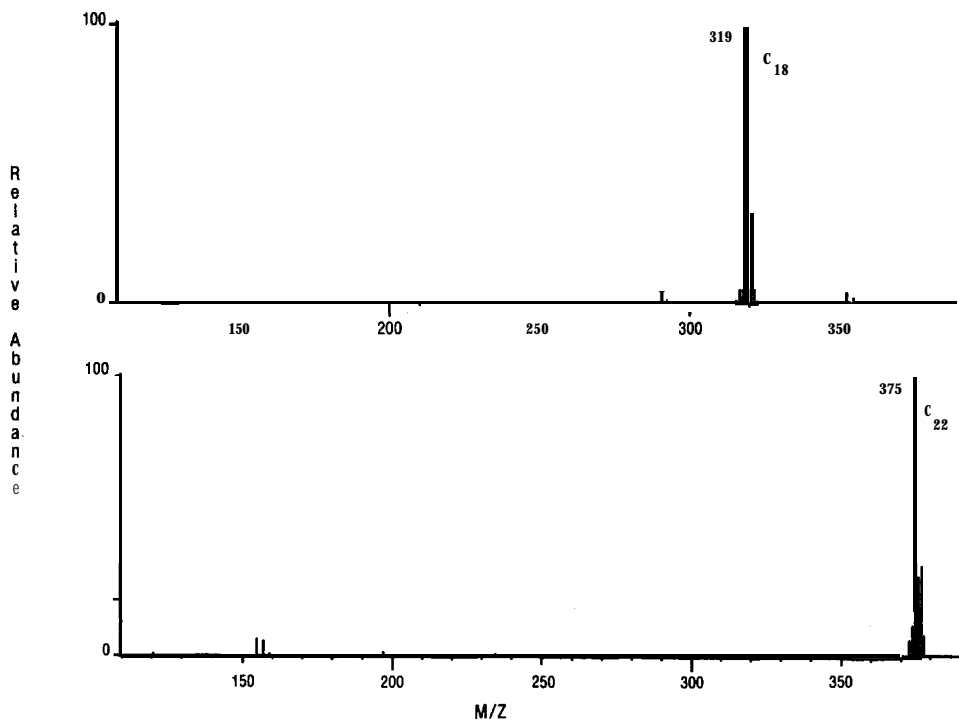


Fig. 6. Dichlorodifluoromethane negative ion chemical ionization mass spectra of the C<sub>18</sub> and C<sub>22</sub> saturated fatty acids from the marine fish oil mixture separated in Fig. 5. These mass spectra were obtained at an ion source temperature of 200°C and a restrictor-heater temperature of 250°C.

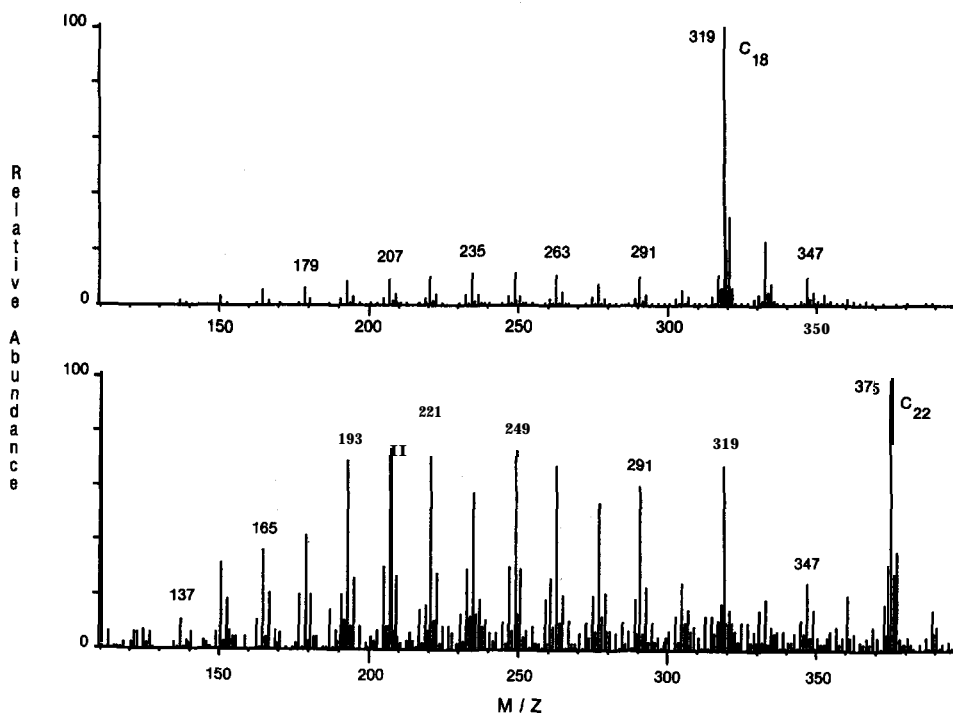


Fig. 7. Dichlorodifluoromethane negative ion chemical ionization mass spectra of the C<sub>18</sub> and C<sub>22</sub> fatty acids from the fish oil mixture. Supercritical fluid chromatographic conditions were similar to those used for Fig. 6, with the restrictor heater operated at 333°C.

### Application to surfactant characterization

The free fatty composition of a soap bar will influence the physical properties and performance of the product. The analysis of free fatty acids from soap bars is currently performed by GC of methyl esters (FAMES) derived from the soap bar acids. This widely accepted technique provides a suitable standard against which SFC-NICI-MS methods can be measured. Fig. 8 shows the averaged chloride-attachment negative ion CI mass spectrum of a fatty acid mixture from a soap bar separated using fast capillary SFC. The average mass spectrum presents data on all fatty acids present in the most concise form. Unlike FAME analysis by GC, there was no need to derivatize the acids prior to SFC-CI-MS analysis. Chloride adduct ions were found for the  $C_6$  through  $C_{18}$  even carbon number normal saturated fatty acids, the  $C_{15}$  and  $C_{17}$  saturated fatty acids and  $C_{16}$  and  $C_{18}$  fatty acids with one and two unsaturation sites ( $C_{16:1}$ ,  $C_{18:1}$  and  $C_{18:2}$ ). The composition of this mixture, as determined from SFC-NICI-MS data, is given in Table III. The data indicate that this acid composition was prepared from a mixture of coconut oil and tallow fatty acids, a common combination in commercial soap bars. Also given Table III are weight percentages for this same sample as determined by the GC-FID method (FAMES). The results from SFC-NICI-MS correspond quite well with GC data, confirming the applicability of the SFC method for analysis of surfactant materials. Some of the discrepancies between data sets may result from the need to deconvolute isotope signals for unsat-

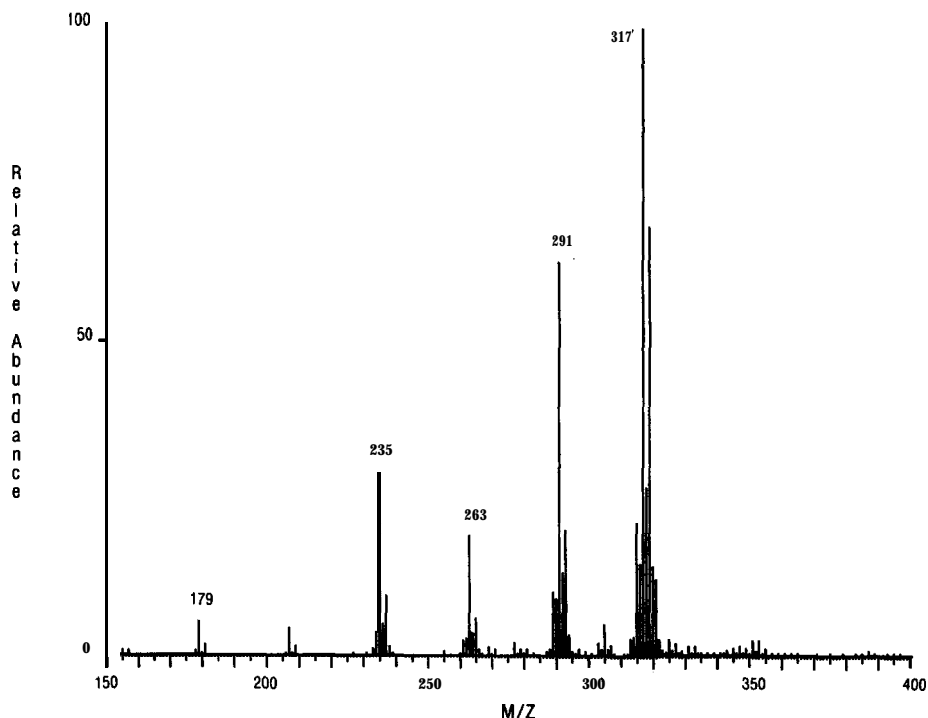


Fig. 8. Averaged dichlorodifluoromethane negative ion chemical ionization mass spectrum of a fatty acid mixture, derived from a soap bar, obtained following capillary supercritical fluid chromatography using a carbon dioxide mobile phase and the conditions described for Fig. 5.

TABLE III

COMPOSITION OF FATTY ACID MIXTURE FROM SOAP BAR OBTAINED FROM GC AND SFC-NICI-MS DATA

Fatty acid, carbon number:degree of unsaturation	Composition (% w/w)	
	GC-FID (FAMES)	SFC-NICI-MS
8:0	0.6	1.1
10:0	0.9	1.1
12:0	7.8	7.5
14:0	5.9	5.6
15:0	0.4	0.8
16:1	3.6	3.5
16:0	21.6	21.2
17:0	1.2	2.0
18:2	3.6	8.0
18:1	35.6	35.0
18:0	16.4	14.4

urated fatty acids ( $C_{18:0}$ ,  $C_{18:1}$  and  $C_{18:2}$ ) where the  $^{37}\text{Cl}$  isotope of the unsaturated species and the  $^{35}\text{Cl}$  isotope of the saturate species are isobaric. There may also be some loss of the more volatile  $C_6$  and  $C_8$  acids during sample pretreatment and derivatization for GC(FAMES) analysis. Efforts are in progress to evaluate other fluorocarbon reagent gases for negative CI to produce monoisotopic **adduct** ions, ( $M + F$ )<sup>-</sup>, for analysis of mixtures of saturated and unsaturated materials.

## CONCLUSIONS

Presence of the mobile phase gas in the CI source of a system configured for SFC-CI-MS can strongly influence the appearance of the positive and negative ion CI mass spectra obtained. This condition can be used to produce desirable results, such as library-searchable "ET-like" carbon dioxide charge exchange mass spectra<sup>4</sup> or using the mobile phase as a buffer gas for electron-capture negative CI<sup>20,21</sup>. The materials used as mobile phase modifiers can also be used to such **advantages**<sup>5,14</sup>. For evaluation of an SFC-CI-MS interface and for analyses that require optimum production of parent species, the ion source and reagent gas mixture conditions must be properly chosen. The use of chlorofluorocarbons as negative ion CI reagent gases was found to yield solely chloride **adduct** ions for surfactant materials containing at least one hydroxyl function. This type of ionization was not influenced by the presence of mobile phase gases, even when the mobile phase was present in large excess. Production of only parent species following capillary SFC allowed the study of alkoxyated surfactants, free fatty acids and SFC-CI-MS interface conditions affecting analyses of such materials. The SFC-NICI-MS method compares well with other MS techniques for analysis of surfactant materials and GC techniques for fatty acid analyses.

Still to be studied is the effect of ion source temperature on the production of CI mass spectra of materials transported using supercritical fluids. In progress is an evaluation of the effect of mobile phase modifiers on CI mass spectra following

capillary SFC. Concurrently, the role of restrictor type, frit, integral or tapered, on the effects noted here is under investigation. Finally, the ability to fully utilize the deliberate pyrolysis of very low volatility analytes in SFC-CI-MS requires further study.

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