Potentialities of Field Desorption Mass Spectrometry Using Emitter Current Programmer for Direct Analysis of Multicomponents

Hiroaki Shiraishi,* Akira Otsuki, and Keiichiro Fuwa

Department of Chemistry and Physics, National Institute for Environmental Studies, Yatabe, Ibaraki 300-21

(Received February 26, 1979)

The influence of emitter current on field desorption (FD) mass spectra was examined with use of an emitter current programmer (ECP). Reproducibility of FD mass spectra measured by electronic detection is improved with ECP and the integration of stored spectra on the computer. The FD mass spectra of some surfactants are shown as an example of complex mixture. The FD mass spectra of poly(oxyethylene) alkylphenyl ethers show that the distribution pattern of molecular ion peaks depends upon emitter current. The fractional desorption also occurs in the FD mass spectra of α-hydro-ω-(octadecylamino)poly(oxyethylene) measured with a constant emitter current. The emitter current required for desorption of hexadecyltrimethylammonium chloride is greatly affected by coexisting with another ammonium salt. Use of ECP supplies information on the analysis of multicomponents.

Field desorption mass spectrometry (FDMS) has been found to be useful for analysis of thermally labile and non-volatile compounds. However, the formation of ions in FD-MS is affected by various parameters such as electric field strength, emitter temperature, morphology and surface properties of the emitter needles and kind of sample loading.[1,2] Maine *et al.*[3] found that automatic control of the emitter temperature is essential for obtaining reproducible results from successive analysis of the same sample. They suggested that the most important factors are the emitter temperature and the use of an emitter current programmer, which provides precise control of the magnitude and rate of change of current in the emitter wire, for obtaining reproducible FD mass spectra.

Several emitter current control devices[3-5] were reported; they are not yet available commercially. In an attempt to develop a method for identification and analysis of several types of surfactants, an emitter current programmer was constructed with a slight modification of that by Maine *et al.* The possibility for separation and analysis of multicomponents using the ECP has been examined.

Experimental

Apparatus. Mass spectrometry was performed on a JEOL JMS-OlSG double focusing mass spectrometer with a combined field desorption/field ionization/electron impact ion source, connected to JMS-2000 mass data analysis system (Japan Electronic and Optics laboratory). FD-emitter used was 10 μm tungsten wire with carbon needles grown at high temperature.[6] An anode potential of 10 kV and cathode potential of −3 kV were applied. Emitter curent was increased linearly by use of a modified emitter current programmer during the course of repetitive magnet scanning. The emitter was loaded with 0.2—1 μg samples from stock solutions (*ca.* 1 μg/μl) using microsyringe technique.[7]

Figure 1 shows a block diagram of the modified ECP. Operation modes are the same as those described by Maine *et al.* The current programming rate can be set at a desired value in the range 1–100 mA/min. The emitter current is regulated within 0.05 mA at any level between 0 and 60 mA. Initial and final current values can be controlled within this range.

Initial focussing was done on acetone introduced *via* the batch inlet. After measurements of each sample the emitter current was increased to 60 mA in order to clean the emitter.

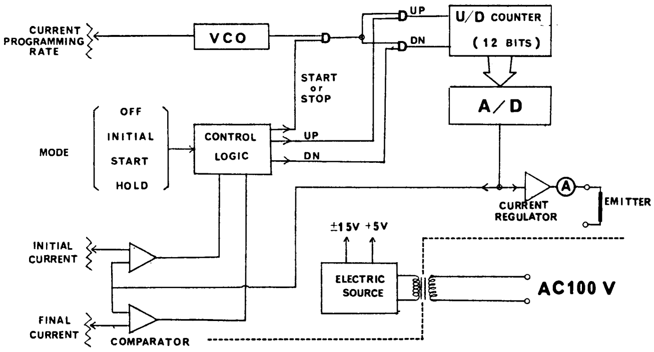


Fig. 1. The block diagram of ECP.

Materials. Poly(oxyethylene) octylphenyl and dodecylphenyl ethers supplied by Gasukuro Kogyo Co., Ltd. and Daiichi Seiyaku Co., Ltd., respectively, and other surfactants from Wako Pure Chemical Industries, Ltd. were used.

Results and Discussion

The FD mass spectrum of sodium dodecylbenzenesulfonate (DBS), a typical anionic surfactant, was measured by repetitive magnet scanning at 11 s intervals, the emitter current increasing linearly at a rate of 3 mA/min. Integration of all the spectra collected on the computer showed *m*/*e* 719 $(2M+Na)^+$, 371 $(M+Na)^+$, and 348 $(M)^+$ ion peaks (Fig. 2). Each coefficient of variation calculated from seven measurements of the same sample was ±4% for the intensity of the base peak $(M+Na)^+$ to the total intensity of all peaks, ±30% and ±20% for those of M^+ and $(2M+Na)^+$ peaks, respectively. FD mass spectra obtained with a single magnet scan and electric detection gave less reproducible spectra due to the fluctuation of ion current. FD mass spectrum of DBS was considerably affected by emitter current (Fig. 2(b)). In general, $(2M+Na)^+$ ion has a relatively high intensity at lower emitter current, but at higher emitter current the intensity of this cluster ion rapidly decreased whereas $(M)^+$ and $(M+Na)^+$ peaks increased. Emission controlled FD mass spectra of some sulfonates were studied by Schulten and Kummler.[8] They used a vacuum evaporated AgBr plate for photographic detection and found that $(nM+Na)^+$ cluster ion with $n=1$ is mostly prominant, molecular ion having

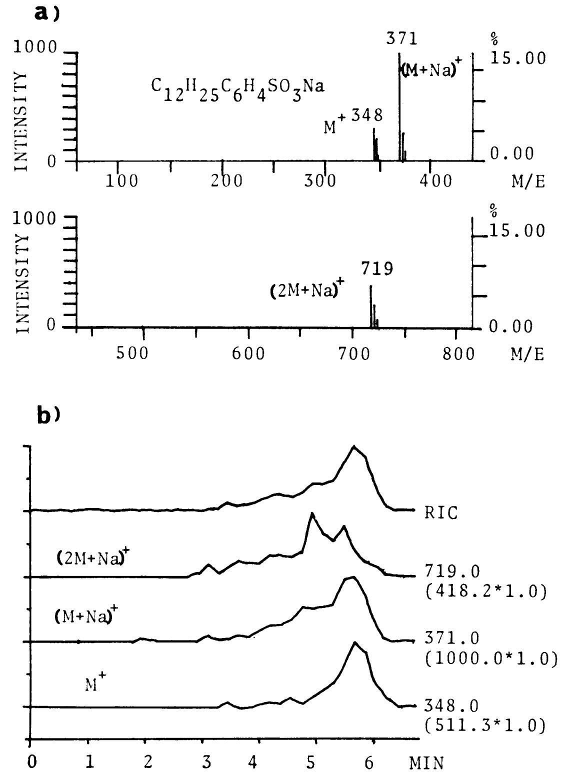


Fig. 2(a). The FD mass spectrum of DBS; initial current 0 mA, current programming rate 3 mA/min, sum of the stored spectra.

(b). Reconstructed mass chromatogram; RIC (reconstructed ion current): sum of ion intensities between *m/e* 50 to 800. ion intensities are plotted on ordinate and full scales are designated in parentheses.

relatively smaller intensity. The integration of spectra, obtained by electric detection and linear current program, gives reproducible spectra consisting of the spectrum obtained by Schulten and Kummler by potographic detection and emission controlled time/current program.

Figure 3 shows the integrated FD mass spectrum (a) of hexadecyltrimethylammonium chloride (CA), a typical cationic surfactant, and the reconstructed mass chromatogram (b) obtained under the same conditions as those of DBS except for the initial current value. The ion peaks at *m/e* 284, 603, and 269 were assigned to salt cation (molecular ion minus chloride ion), cluster ion of the type, molecular ion plus cation portion, and fragment ion peak $(M-Me)^+$, respectively. The intensities of these ion peaks were also dependent upon emitter current. Reconstructed mass chromatogram (Fig. 3(b)) indicates that the intensity of cluster ion $(M+C)^+$ decreases at higher emitter current, while the intensities of salt cation and fragment ions increase. Disappearance of the cluster ion at the higher emitter current can be attributed to weak binding of the cluster ion that thermally decomposes. Figures 4(a) and (b) show the FD mass spectra of equimolar mixture of hexadecyltrimethylammonium chloride(CA)and benzylhexadecyldimethylammonium chloride (BA). Lower emitter current gave ion peaks of two salt cations (*m/e* 284, 360) and relatively high intensities of three cluster ions (*m/e* 603, 679, 755) of the type $(M+C)^+$. The ion peak at *m/e* 679 demonstrates the production of a mixed cluster ion consisting of both cation portions and chloride ion. A similar phenomenon has been observed by Veith,[9] who used simple ammonium salts. On the

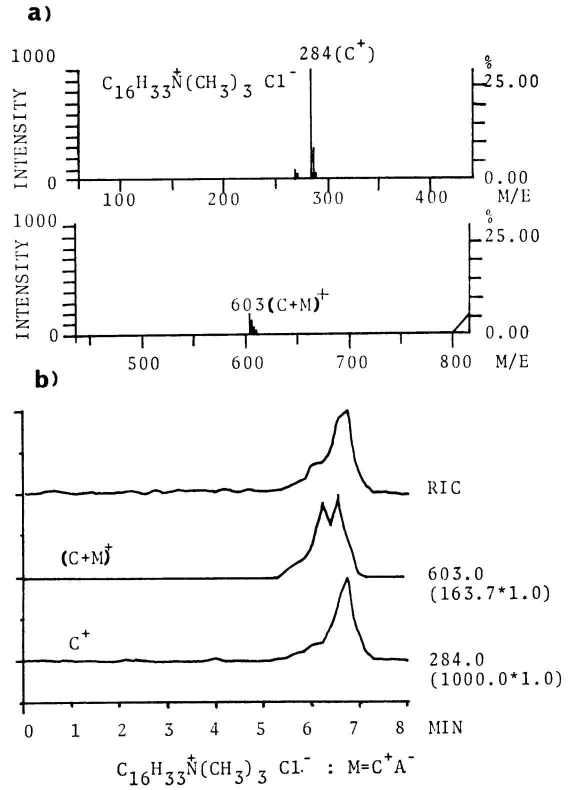
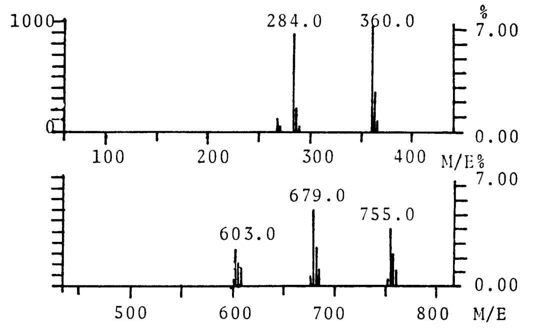


Fig. 3. The FD mass spectrum of CA (a) and reconstructed mass chromatogram (b). Initial current 10 mA, current programming rate 3 mA/min, sum of the stored spectra.

a) lower emitter current



b) higher emitter current

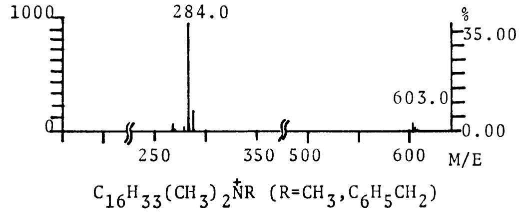


Fig. 4. The FD mass spectra of equimolar mixture of CA and BA. Emitter current: (a) 17 mA, (b) 19 mA.

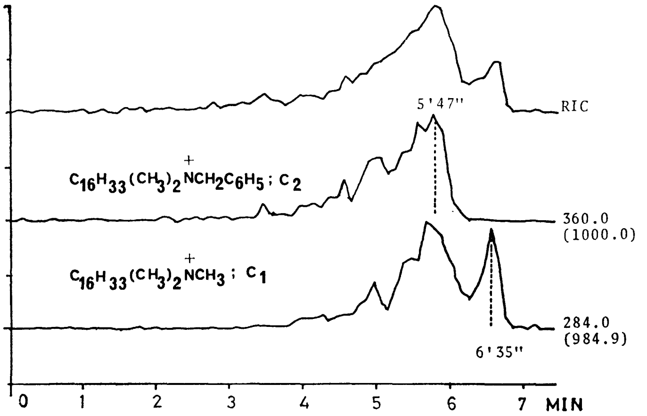


Fig. 5. Reconstructed mass chromatogram of equimolar mixture of CA and BA.
Current programming rate 3 mA/min.

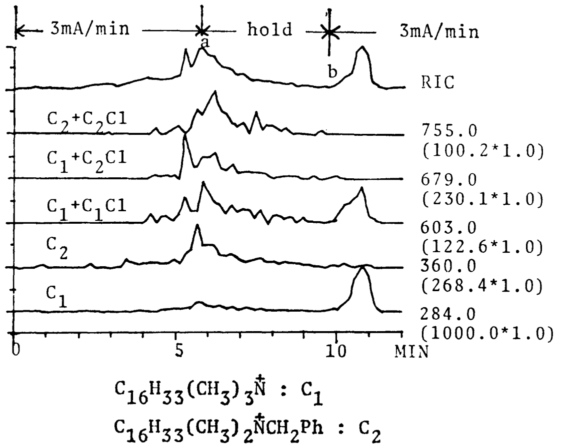


Fig. 6. Reconstructed mass chromatogram of equimolar mixture of CA and BA.

other hand, higher emitter current gave only the spectrum of CA due to the disapperance of BA at lower emitter current. Figure 5 shows the reconstructed mass chromatogram of two salt cations during the course of a linear emitter current programming, suggesting that the part of CA on the emitter wire can be desorped at lower emitter current when BA coexist, compared with that in Fig. 3(b), but further increase in emitter current is required for the desorption of the remaining part of CA after all BA was desorped. The results indicate that emitter current required for desorption of CA is greatly affected by the presence of BA, *viz.*, emitter current required for field desorption changes with not only the properties of individual compounds but also the interaction of each component loaded on emitter wire. When emitter current was increased to 17 mA at a rate of 3 mA/min and kept constant for 4 min, a mixture of CA and BA was found to be separated by fractional desorption (Fig. 6). This suggests that the use of ECP producing programmed thermal gradients makes the separation and analysis of multicomponents in complex mixtures by mass chromatograpy or selected ion monitoring techniques possible.

The FD mass spectra of poly(oxyethylene) alkylphenyl ethers, nonionic surfactants, were measured. The results indicate only molecular ions with different polymerization degree of ethylene oxide unit.[10] Single scan FD mass spectra of poly(oxyethylene) octhylphenyl ethers (PO) obtained during the course of a linear emitter current programming are shown in Fig. 7. The distribution pattern of molecular ion peaks is also dependent upon emitter current, *viz.*, at lower emitter current the distribution pattern of ions is weighted for low mass region, whereas at higher emitter current it is weighted for high mass region, suggesting that fractional desorption occurs. The integrated FD mass spectrum of PO and the reconstructed mass chromatogram of selected ions are shown in Figs. 8(a) and (b). Figure 8(b) shows that the fractional desorption of mixtures occurs by thermal gradient. A similar fractional desorption was observed in the FD mass spectra

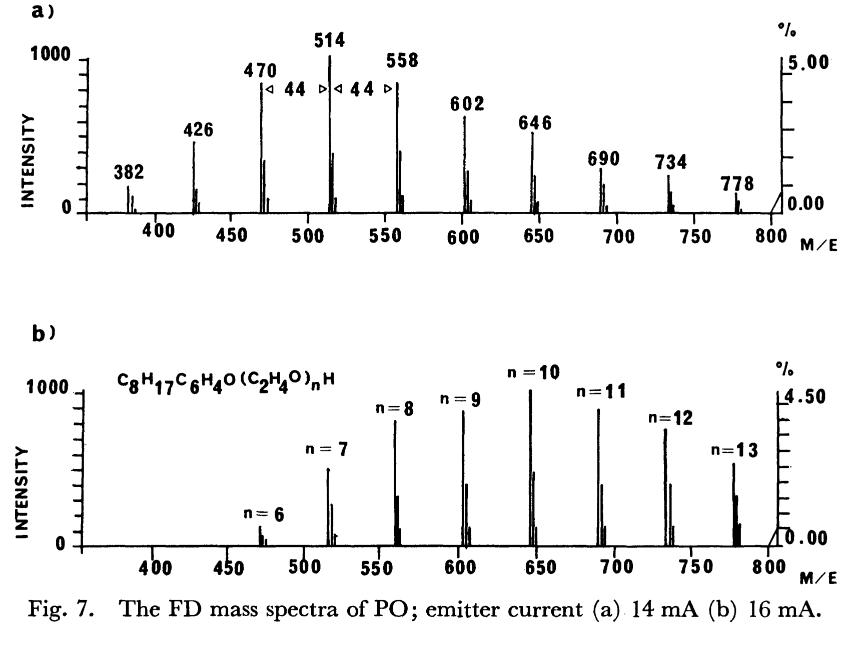


Fig. 7. The FD mass spectra of PO; emitter current (a) 14 mA (b) 16 mA.

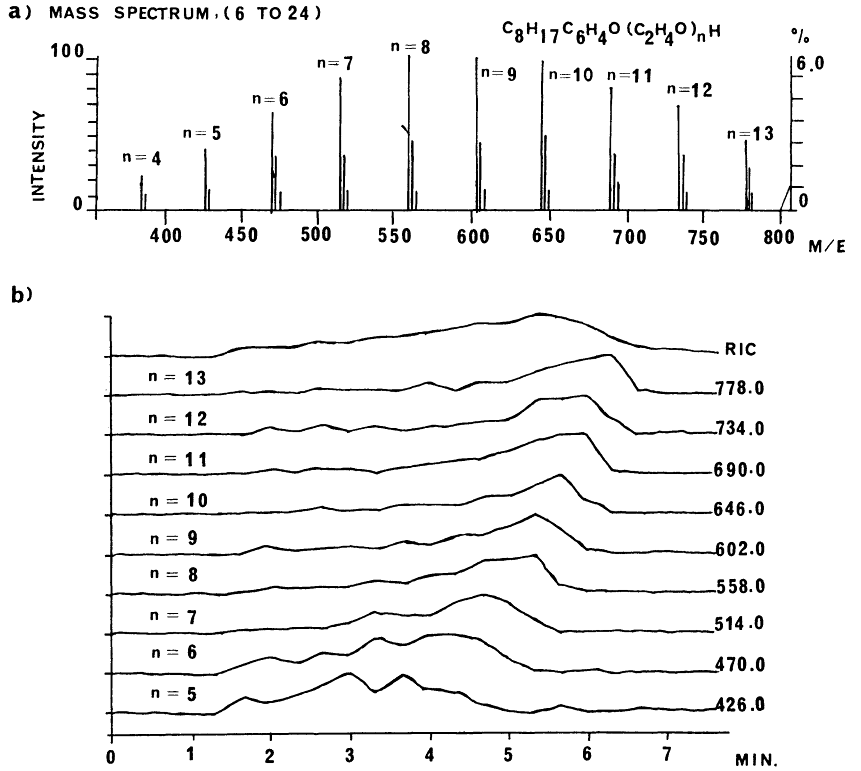


Fig. 8. (a) The FD mass spectrum of PO; sum of the stored spectra, small peaks are neglected. (b) Reconstructed mass chromatogram; current programming rate 3 mA/min.

of poly(oxyethylene) nonylphenyl and dodecylphenyl ethers. The result suggests that the true distribution of multicomponents in the original sample can be estimated at least from an integration of stored spectra during the course of slow increase in emitter current or photographic detection. The series of weak peaks found at *m/e* 14 lower and higher than the major ion peaks exhibit the existence of impurities having different alkyl side chains. The impurities correspond to poly(oxyethylene)nonylphenyl and hexylphenyl ethers. The FD mass spectra of α-hydro-ω-(octadecylamino)poly(oxyethylene) obtained under the following conditions are shown in Figs. 9(a) and (b): initial emitter current was set at 14 mA and kept constant during repetitive magnet scanning at 18 s intervals. Integration of the spectra of first 20 scans (a) and next 30 scans (b) indicates different distribution pattern of protonated molecular ions, suggesting that a similar fractional

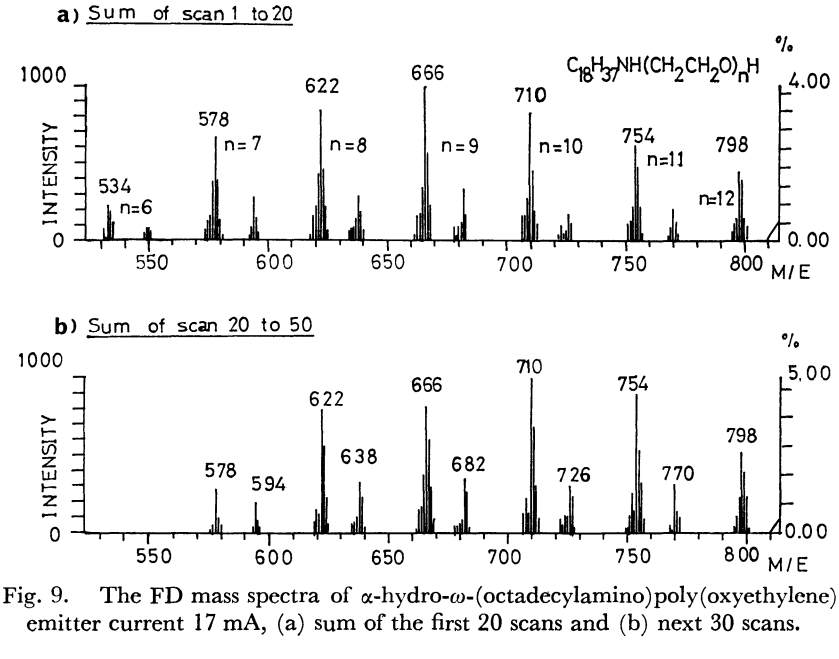


Fig. 9. The FD mass spectra of α-hydro-ω-(octadecylamino)poly(oxyethylene); emitter current 17 mA, (a) sum of the first 20 scans and (b) next 30 scans.

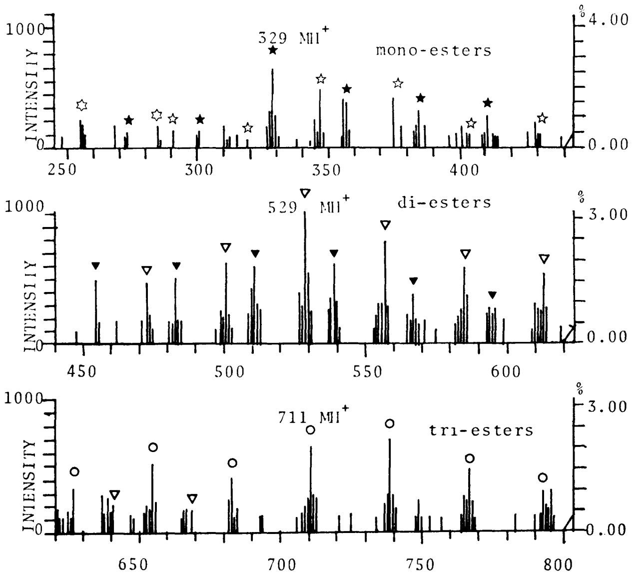


Fig. 10. The FD mass spectrum of "Span 20", Current programming rate 3 mA/min, sum of 20 scans, ☆, ▽ and ○ indicate mono-, di- and tri-esters of sorbitans respectively. ★ and ▲ indicate mono- and di-esters of sorbid respectively, ✩ indicates unreacted fatty acids.

desorption was taking place. The series of minor ion peaks found at 28 mass lower than the protonated molecular ion peaks correspond to the protonated molecular ions of α-hydro-ω-(hexadecylamino)poly(oxyethylene) contained in the commercial samples as impurities.

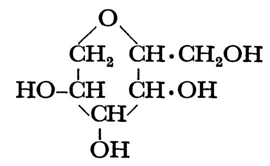
The FD mass spectra of a group of nonionic surfactant, called "Span" known as a complex mixture of mono-di-, tri-, and tetra-esters of 1,5- and 1,4-sorbitans and mono- and di-esters of 1,4: 3,6-sorbid were measured. Figure 9 shows the integrated FD mass spectra of "Span 20" as an example of complex mixtures, showing many protonated molecular ion peaks of the esters and molecular ion peaks of unreacted fatty acids and fragment ions at m/e 183, 211, 239, and 269 $(RCO)^+$ in low mass region. The protonated molecular ions of esters of sorbitan and sorbid observed in the FD mass spectra of various "Span"s are given in Table 1. Since these ions might consist of some isomers, the total carbon number of acyl groups ($l+n$, $l+n+m$) can be calculated. The composition of acyl groups in the samples can be estimated from the distribution of protonated molecular ion peaks of mono-esters. With linear increase in emitter current, desorption of di-esters occurs before that of tri-esters, the esters of sorbid being generally desorped prior to the esters of sorbitans. Because of fractional desorption, an integration of single scan spectra was needed to identify all the components in the mixtures.

The present study and others[11] indicate that there are two types of FD mass spectrum, one obtained from single scanning at near the best anode temperature and the other an integrated FD mass spectrum obtained from repetitive magnet scanning or photoplate detection, the latter being much more reproducible than the former when the cluster and fragment ions are produced.

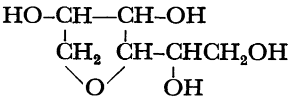
Table 1. PROTONATED MOLECULAR IONS OF ESTERS OBSERVED IN THE FD MASS SPECTRA OF "Span"s

Mono-esters			Di-esters			Tri-esters	
n	A	B	$n+m$	A	B	$l+m+n$	A
8	291	273	20	473	455	28	599
10	319	301	22	501	483	30	627
12	347	329	24	529	511	32	655
14	375	357	26	557	539	34	683
16	403	385	28	585	567	36	711
18	431	413	30	613	595	38	739
$18F_1$	429	411	32	641	623	40	767
			34	669	651	42	795
			36	697	679		

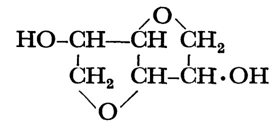
A and B indicate esters of sorbitans and sorbid, respectively. l, m, and n indicate carbon numbers of each fatty acid.



1,5-Sorbitan



1,4-Sorbitan



1,4:3,6-Sorbid

The present study also suggests that the compounds, from which cluster and fragment ions will be produced, and a complex mixture sample in which fractional desorption occurs, should be measured with ECP as an integrated FD mass spectrum. It seems that when the integrated FD mass spectrum is taken, the effect of the difference in morphology of emitter needles on the reproducibility of FD mass spectrum can be reduced. In FD-MS, the thermal gradient produced by ECP has become a powerful means for analysis of complex mixtures.

References

1) H. D. Beckey and H.-R. Schulten, *Angew. Chem.*, **87**, 425 (1975); *Angew. Chem. Int. Ed. Engl.*, **14**, 403 (1975).

2) H. D. Beckey, "Principles of Field Ionization and Field Desorption Mass Spectrometry," Pergamon, Oxford (1977).

3) J. W. Maine, B. Soltmann, J. F. Holland, N. D. Young, J. N. Gerber, and C. C. Sweeley, *Anal. Chem.*, **48**, 427 (1976).

4) H.-R. Schulten and N. M. M. Nibbering, *Biomed. Mass Spectrom.*, **4**, 55, (1977).

5) H. U. Winkler, W. Neumann, and H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, **21**, 57 (1976).

6) H. D. Beckey, E. Hilt, and H.-R. Schulten, *J. Phys. E: Sci. Instr.*, **6**, 1043 (1973).

7) H. D. Beckey, A. Heindrichs, and H. U. Winkler, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 9 (1970).

8) H.-R. Schulten and D. Kummler, *Z. Anal. Chem.*, **278**, 13 (1976).

9) H. J. Veith, *Org. Mass Spectrom.*, **11**, 629 (1976).

10) A. Otsuki and K. Fuwa, *Talanta*, **24**, 584, (1977).

11) H. Budzikiewicz and M. Linscheid, *Biomed. Mass Spectrom.*, **4**, 103 (1977).