Surfactant Analysis by Matrix-Assisted Laser Desorption Time-of-Flight Mass Spectrometry

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ABSTRACT: Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry was used to characterize nonionic, anionic and cationic surfactants. Rapid mass analyses can be achieved with proper choice of matrix material. The technique is suitable for development as a routine analytical tool.
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KEY WORDS: Matrix-assisted laser desorption mass spectrometry, surfactant analysis.

Surfactants are of considerable commercial importance and find use in numerous applications as detergents, dispersants and flocculants; for enhanced oil recovery and surface wetting modifications; and in paints, dyestuffs, cosmetics, pesticides and pharmaceuticals. However, many surfactants are not pure substances, and in some cases are in fact composed of a distribution of closely related species. It is therefore essential to be able to mass characterize these types of materials quickly and reliably.

The analysis of surfactants encompasses a wide range of analytical disciplines, with the choice depending on the particular aspect or property of the sample requiring elucidation. For example, the molecular composition of anionic surfactants may be determined by high-performance liquid chromatography (HPLC). The oligomer distribution of lower-molecular weight ethoxylates can be obtained by gas chromatography (GC), but to increase volatility, the analyte must first be derivatized or cleaved. The gas chromatography–mass spectrometry (GC-MS) pairing will yield the isomeric composition of a surfactant, provided that the starting material is thermally volatile and stable. For an extensive review of surfactant analysis, the text by Schmitt (1) is an excellent starting point.

The development of the matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF) branch of MS has allowed the straightforward mass characterization of nonvolatile surfactants. Karas and co-workers (2,3), who developed the technique, reported that large biomolecules could be ionized and detected without significant fragmentation ("soft" ionization) when the analyte was dispersed in a large molar excess of nicotinic acid, or other suitable chromophore. MALDI has found widespread use in the field of biochemistry (4,5) for the accurate mass determination of peptides, etc., and its application in other areas (e.g., synthetic polymers) is increasing (6–10).

The mechanism of the desorption/ionization process is far from clearly understood. For neutral analyte molecules, embedded in a large excess of an ultraviolet-absorbing matrix with an added salt present for cationization, the process begins with the pulsing of the laser at the sample. This causes analyte and matrix molecules (as well as matrix species photochemically altered by the pulse) to be launched into the gas phase, where some of the former combine with a metal cation. Typically, only one cation will associate with a sample molecule, and the resulting charged species is the directed toward the detector *via* the flight chamber by a strong electric field. The time difference between the point of sample volatilization by the laser pulse and the arrival of resulting ions at the detector is proportional to mass.

We report here the results of recent MALDI work in our laboratory concerning the following surfactant types: (i) anionic alkyl sulfate and alkylbenzene sulfonates, (ii) cationic quaternary ammonium, benzalkonium and alkylpyridinium salts and (iii) nonionic ethoxylated alkylphenols.

EXPERIMENTAL PROCEDURES

Sodium dodecyl sulfate (SDS; 98%), 2,5-dihydroxybenzoic acid (DHB), cetylpyridinium chloride monohydrate (CPCM; 98%), cetyldimethylethyl ammonium bromide (CDEAB; 85%; remainder stearyl compound) and benzalkonium chloride (BAC) were purchased from Aldrich (Milwaukee, WI). Sodium dodecylbenzenesulfonate (DS-10; 93%) and the IGEPAL nonylphenol ethoxylates were acquired from Rhône-Poulenc (Cranberry, NJ). The matrix ethylene *bis*[3-(2-naphthyl) acrylate] (EBNA) was synthesized in the course of an earlier project (11). DHB was recrystallized twice from water/ethanol before use (12); all other materials were used as received.

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The desulfonation apparatus consisted of a two-necked 500-mL round-bottomed flask, fitted with a graduated addition funnel and a graduated distillate receiver/condenser. DS-10 (20 g) and 60 mL of concentrated phosphoric acid were added to the flask, and the mixture was heated to 215°C. Water was added to the flask at a rate that maintained overall mixture volume, and the azeotrope (composed of water and the alkylbenzenes released by the cleavage reaction) was collected until the distillate was clear. Thereafter, the distillate was extracted twice with diethyl ether, washed twice with sodium hydroxide solution, twice with water, dried with sodium sulfate, and evaporated to dryness in a rotary vacuum device.

A model HP5890 gas chromatograph coupled to an HP5971A mass spectrometer was used to analyze the mass and chainlength of the alkylbenzenes obtained by the desulfonation procedure (Hewlett-Packard, Palo Alto, CA). GC conditions: 0.31 mm × 25 mm silica capillary column, ramped from 180 to 220°C at 2°C/min, with total ion current (TIC) detection.

The mass spectrometer used was a TofSpec (VG/Fisons Instruments, Manchester, United Kingdom) in which samples were irradiated with a nitrogen laser (wavelength 337 nm; 4-ns pulse duration) under high vacuum. All spectra were recorded with an accelerating voltage of 25,000, a detector voltage of 1,800, and were the averaged result of between 30 and 60 laser shots. Instrument control was provided by a DEC VAX station (DEC, Maynard, MA) with software provided by VG. DHB or EBNA was employed as the matrix. For neutral samples, either sodium or potassium chloride was added to provide the cation source. The routine involved making stock solutions of the matrix, salt and surfactant and using these to make up pre-mixtures. In this way, the concentration of salt and sample could easily be varied to optimize spectral quality. There is no "correct" level of analyte or salt, and acceptable spectra can be collected over a wide range of concentrations. Analyte levels in the nanomole or picomole (per μL of pre-mix solution) are sufficient for effective analysis, and only 2 μL of such solutions are actually applied to the probe surface. The number and weight average molecular weights (M_n and M_w) are easily calculated by entering the relevant masses and peak areas into a commercial spreadsheet.

RESULTS AND DISCUSSION

An aqueous solution of SDS was cast onto the metal probe surface and allowed to dry. The resulting negative ion MALDI spectrum, shown in Figure 1a, is dominated by a sharp signal at mass 265, corresponding to the dodecyl sulfate anion. Weak peaks at approximately 80 and 96 mass units are probably due to sulfonate and sulfate anions, respectively, and may be indicative of some fragmentation. Spectra can also be obtained (at lower laser energy levels) by dispersing the SDS in DHB, but in the low mass region, matrix signals of indeterminate origin invariably clutter the spectrum and interfere with interpretation.

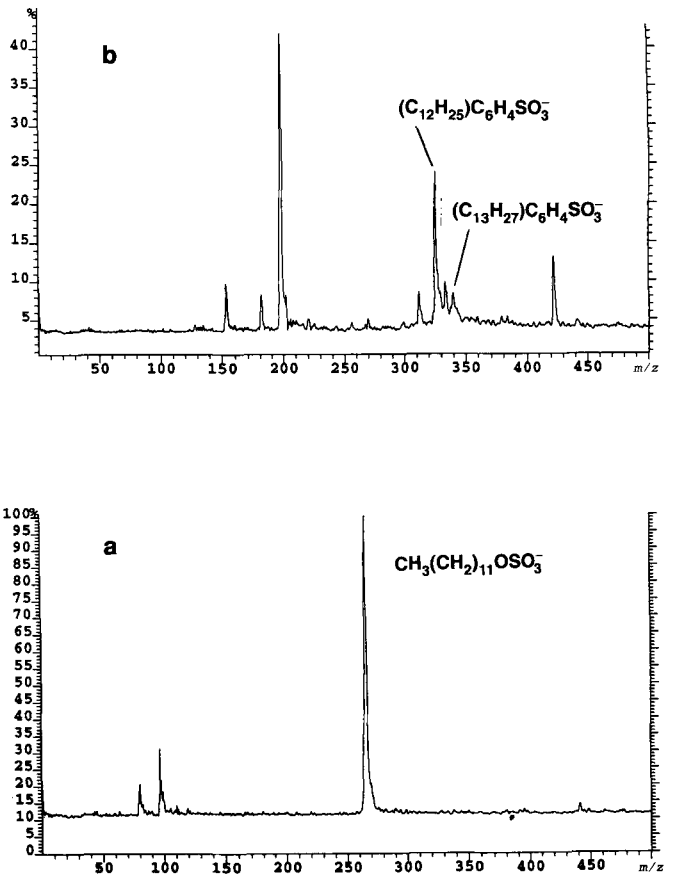

FIG. 1. Negative-ion matrix-assisted laser desorption/ionization time-of-flight spectra of (a) neat sodium dodecylsulfate and (b) sodium dodecylbenzenesulfonate dispersed in ethylene *bis*[3-(2-naphthyl)acrylate].

Integration of the SDS ^1H nuclear magnetic resonance (NMR) spectrum gave a relative intensity ratio for the RCH_2R', $RCH_2OSO_3^-$ and CH_3 protons of 81.1:7.7:11.2. From the chemical formula, the equivalent ratio was calculated to be 80:8:12. The small difference between these two sets suggests that the SDS analyzed is reasonably pure, and structurally linear.

Figure 2 shows the GS–MS chromatogram of the alkylbenzene product obtained by the desulfonation of DS-10, from which the following homologous mixture composition (as percent of TIC) was found: C_6–C_{11} (10%), C_{12} (89%), C_{13} (1%). The same chromatogram also reveals that the C_{12} alkylbenzene fraction is composed of more than two dozen isomers. From the integrated intensities of the aromatic and methyl proton signals of the ^1H NMR spectra (not shown), we estimate that there are 3.8 methyl groups per molecule of both the original surfactant and the desulfonated product. NMR results are therefore in good agreement with the GC–MS analysis, which uncovered a large number of stereoisomers, the consequence of the highly branched nature of this surfactant.

Of all the materials analyzed by MALDI in this project, DS-10 proved to be the most challenging. It will fly when cast

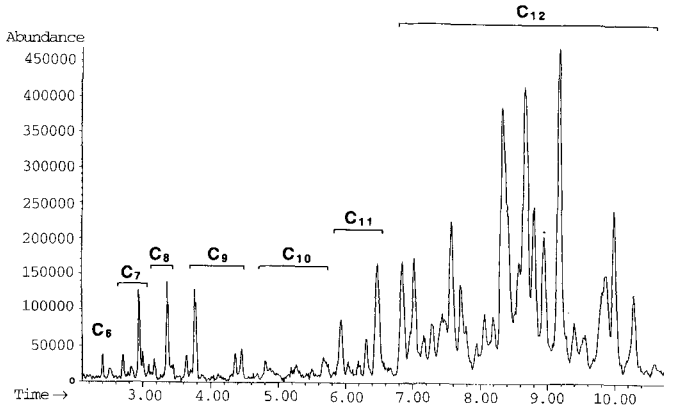

FIG. 2. Gas chromatography–mass spectrometry chromatogram of desulfonated sodium dodecylbenzene sulfonate. The labels indicate the size of the alkyl chain attached to the benzene ring.

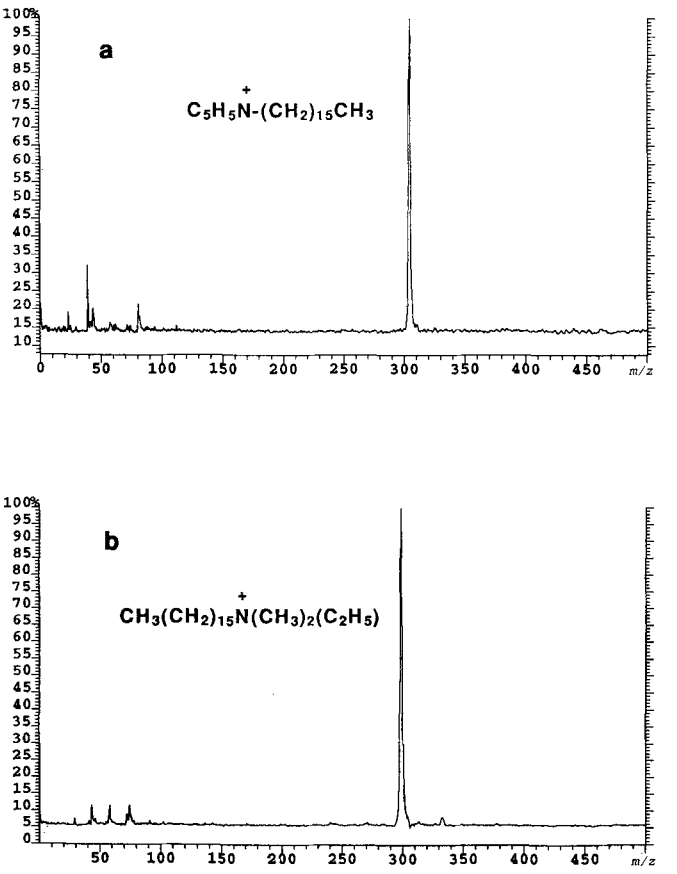

FIG. 3. Positive-ion matrix-assisted laser desorption/ionization time-of-flight spectra of (a) neat cetyldimethylethylammonium bromide and (b) cetylpyridinium chloride monohydrate dispersed in 2,5-dihydroxybenzoic acid.

neat onto the probe surface, but the resulting spectra tend to be weak and noisy. When dispersed in either DHB or EBNA, the desorption process is greatly enhanced, and the collection of higher-quality spectra becomes possible; again, however, matrix signals are a nuisance. The number of matrices and co-matrices suitable for the MALDI technique is growing, and some may offer a signal-free region over which low-mass surfactants can be confidently analyzed without fear of encountering peaks of dubious origin. In the MALDI spectrum of DS-10, dispersed in EBNA (Fig. 1b), the major surfactant spike at 325 mass units represents the C_{12} sulfonate anions. The C_{11} signal stands alone at 311, and the C_{13} peak is visible at 339. Between the 325 and 339 peaks lies one at approximately 334. The latter appears in the spectrum of pure matrix (not shown) and is thus assigned as an interfering matrix signal. Other peaks in the spectrum are also due to the matrix, with the parent anion located near 422 mass units. Overlap with the 334 matrix response and poor resolution over the 320 to 350 mass range means that the DS-10 peak areas give only a rough estimate of the alkylbenzene chain distribution. The $C_{11}/C_{12}/C_{13}$ ratio is 19:74:7, broadly in line with that determined by GC–MS. A more meaningful analysis awaits a better matrix.

In the absence of a matrix, the three cationic surfactants studied desorbed from the probe surface far more readily than the above two anionic materials. Figure 3a shows the positive ion spectrum of a neat cast film of CDEAB. The peak at 299 is that of the CDEA cation. According to the bottle label, 15% of the sample is the stearyl compound (i.e., C_{18} chain). If so, we would expect to observe a medium intensity signal at 327 mass units. No such signal was detected in any of the numerous neat and matrix-containing samples that we examined. However, a peak at 333 appears in all spectra, although it is generally more intense than shown in Figure 3a. The origin of this signal is not known as yet, but clearly it does not represent the stearyl derivative.

The MALDI spectrum of CPCM, dispersed in DHB, is displayed in Figure 3b. The major peak represents the CP cation, with a mass of approximately 304.5 units. Weak sodium and potassium ion signals (probably present as impurities in the DHB) are visible, along with a small peak near 80 mass units. The latter may represent the pyridinium radical cation, again indicating minor amounts of fragmentation. Matrix peaks are nonexistent; only a small amount of DHB was actually used to assist cation desorption. In accordance with the claim of the supplier, this surfactant appears to be pure.

The positive ion spectrum of BAC, mixed with a small quantity of DHB, is shown in Figure 4a. The two intense spikes at 304 and 332 correspond to BA cations with major alkyl substituents of length C_{12} and C_{14}, respectively. An extremely feeble signal at 360 is probably that of the C_{16} derivative. The bottle label cites an alkyl chain distribution of C_8H_{17} to $C_{18}H_{37}$ for the contents, an assertion at odds with our MALDI analysis. We have observed evidence of significant fragmentation with this material, especially in the absence of matrix. Two medium-intensity peaks appear in the neat film spectrum (Fig. 4b), having the same mass separation as the major signals, but displaced from the latter by 91 mass units. The rise of a sharp peak at 91 confirms that the loss of the benzyl substituent is responsible for the observed fragments. The 213 and 241 peaks appear when the C-N bond undergoes homolytic cleavage to yield the tertiary amine rad-

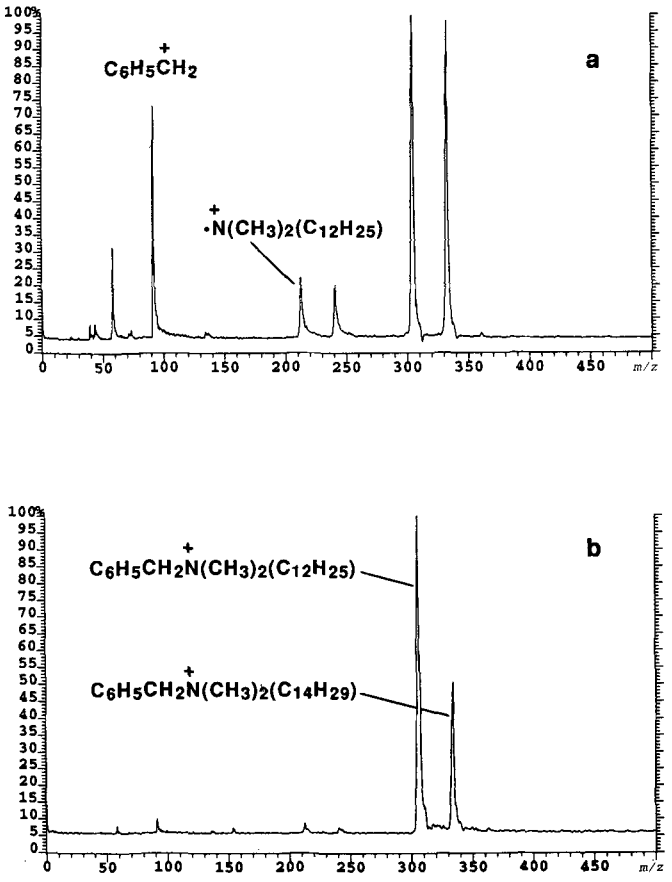

FIG. 4. Positive-ion matrix-assisted laser desorption/ionization time-of-flight spectra of (a) benzalkonium chloride (BAC) mixed with 2,5-dihydroxybenzoic acid and (b) neat BAC.

ical cation (detected) and a benzyl radical (not detected). It would appear that the laser pulse is the cause of this fragmentation. For samples dispersed in DHB, the effect is less widespread or nonexistent, depending on the portion of the sample at which the laser is aimed. Presumably, in situations where no fragmentation is observed, surfactant chains are surrounded by matrix molecules, which offer protection from the energy pulse. Chains in more exposed positions are at the mercy of the incoming radiation and, being unable to effectively dissipate the laser energy, divide in a manner that will yield the most stable fragments. The benzyl–nitrogen bond is the obvious candidate for annihilation under these circumstances, with the aromatic ring providing resonance stabilization for the resulting benzyl cation.

IGEPAL CO-850, CO-880 and CO-890 are commercial nonionic surfactants of a class known as nonylphenol ethoxylates, which have the general formula $C_9H_{19}C_6H_4O(CH_2CH_2O)_nH$. These chains contain no charged group, and a salt must therefore be added prior to analysis by MALDI–MS. The dopant (usually NaCl or KCl for PEG-type materials) provides a source of cations for attachment to the neutral analyte chains, enabling them to be directed into the flight tube and on to the detector. Figures 5 and 6 show, respectively, the positive ion MALDI spectra on IGEPAL CO-850 and CO-880, recorded from a DHB matrix laced with NaCl. In both spectra, the major series of peaks represent surfactant molecules that carry a single sodium ion, with the peak separation of 44 units equal to that of the ethylene oxide repeat. The minor distribution in each spectrum is displaced from the dominant series by +16 mass units and corresponds to surfactant chains associated with a potassium ion. The lowest mass region is not shown; it is invariably complex and contains irrelevant signals due to matrix ions, matrix adducts with salt, etc.

With accurate peak masses in hand, the composition of the species they represent can be straightforwardly deduced. Consider, for example, the 1255 peak in Figure 5. Subtracting from this number (i) the sodium ion mass [23], (ii) the mass of the hydroxyl end group [17], and (iii) the mass of the nonylphenol chain end [203], leaves a value of 1012. Division of this by the repeat unit mass yields the number of ethylene oxide groups that comprise the chain. The 1255 peak

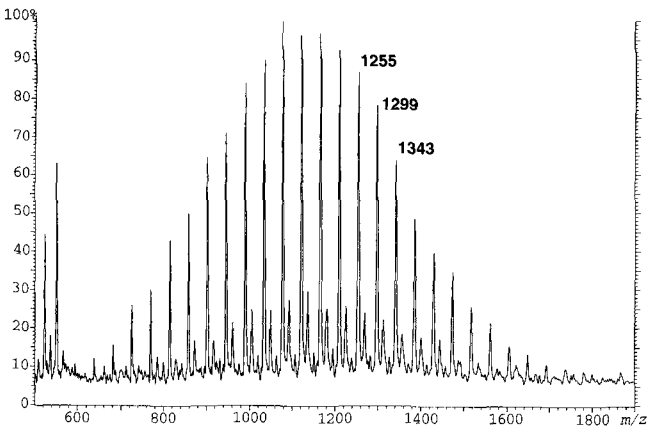

FIG. 5. Positive-ion matrix-assisted laser desorption/ionization time-of-flight spectra spectrum of IGEPAL CO-850 (Rhône-Poulenc, Cranberry, NJ); the matrix is 2,5-dihydroxybenzoic acid, the added salt is NaCl.

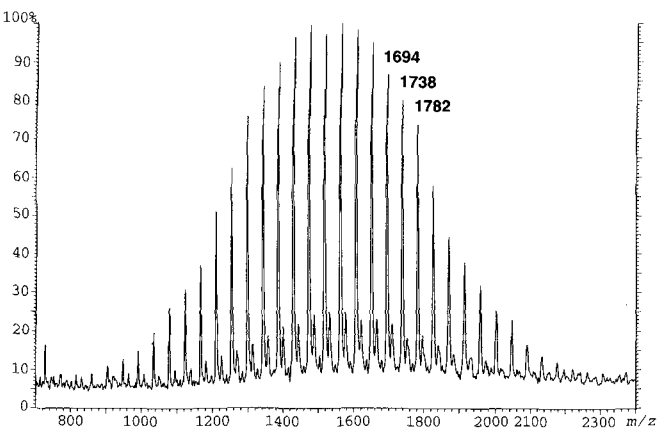

FIG. 6. Positive-ion matrix-assisted laser desorption/ionization time-of-flight spectra spectrum of IGEPAL CO-880; the matrix is 2,5-dihydroxybenzoic acid, the added salt is NaCl. See Figure 5 for company source.

TABLE 1
Mass Characterization of Nonylphenol Ethoxylates by MALDI–MS[a]

		MALDI Mass Information			
IGEPAL[b]	Salt	n[c]	M_n[d]	M_w[e]	PD[f]
CO-850	NaCl	8–36	1120	1162	1.037
CO-850	KCl	9–35	1117	1155	1.034
CO-880	NaCl	12–47	1515	1559	1.029
CO-880	KCl	16–44	1482	1519	1.025
CO-890	KCl	13–54	1769	1833	1.036
CO-890	KCl	13–53	1773	1833	1.034

[a]MALDI–MS, matrix-assisted laser desorption/ionization mass spectrometry.
[b]Rhône-Poulenc (Cranberry, NJ).
[c]Range of n-mers detected.
[d]$M_n = \Sigma A_i M_i / \Sigma A_i$, where A_i = area of peak i, M_i = mass of peak i.
[e]$M_w = \Sigma A_i M_i^2 / \Sigma A_i M_i$.
[f]Polydispersity = M_w/M_n.

therefore epitomizes species with the formula $C_9H_{19}C_6H_4(CH_2CH_2O)_{23}H$. The calculated mass distributions of two samples of the three IGEPALs are listed in Table 1. All are narrowly distributed, and the CO-850 and CO-880 have average numbers of moles of ethylene oxide as stated by the manufacturer; 20 for CO-850 and 30 for CO-880. IGEPAL CO-890 is generally listed as having an average of 40 such units, but the MALDI analysis reveals that, for this particular batch, the median is closer to 35.

In conclusion, this work demonstrates that MALDI–TOF–MS can be used for the rapid mass analysis of low-molecular weight surfactants. Although several MALDI instruments are on the market, the technique is still in its infancy, particularly in regard to the chemistry occurring during the desorption/ionization phase of the experiment. Nevertheless, for low-molecular weight substances, or mixtures thereof, molecular weight distribution information can easily be extracted and used to complement data obtained from analytical methods that are structure sensitive. Furthermore, while samples need not be derivatized, they must either carry a charged group or be capable of associating with a cation; in practice, few surfactants will be excluded on these grounds. As the cost of MALDI technology falls, the day approaches when it will be employed as a routine analytical tool by the surfactant industry.

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