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Fabric softeners: nearly instantaneous characterization and quality control of cationic surfactants by easy ambient sonic-spray ionization mass spectrometry

Sérgio A. Saraiva[1], Patrícia V. Abdelnur[1], Rodrigo R. Catharino[1,2], George Nunes[3] and Marcos N. Eberlin[1]*

[1]ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, University of Campinas, UNICAMP, Campinas, SP, 13083-970, Brazil
[2]Department of Clinical Pathology, School of Medical Sciences, University of Campinas, UNICAMP, Campinas, SP, 13083-887, Brazil
[3]Clariant Corporation – Industrial & Home Care Division, Charlotte, NC 28216, USA

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A tiny droplet of typical samples of fabric softeners from different commercial brands placed on a smooth paper surface was subjected to easy ambient sonic-spray ionization mass spectrometry (EASI-MS). With no need for sample-preparation or pre-separation procedures, EASI-MS and EASI-MS/MS identify nearly instantaneously the main surfactants and the homologous series employed in their formulations. Adulterated and low quality samples containing no or less efficient softeners are also easily recognized. Copyright © 2009 John Wiley & Sons, Ltd.

Fabric softeners first appeared on the market in the 1950s, after the introduction of automatic washing machines and more powerful synthetic detergents. Today, these products are used worldwide to provide enhanced softness of washed textile goods.[1,2] The major active ingredient in fabric softeners is normally the salt of a cationic surfactant such as a quaternary ammonium compound (QUAC). The positive charge on the nitrogen atom combined with the relatively long alkyl chains ensures the adsorption of the cation and provides the soft feel of the fabric. Fabric softeners also act as anti-static agents helping to prevent fibers from becoming entangled.[1]

A large number of surfactants have been patented but the main commercial surfactants used (Fig. 1) are dialkyldimethylammonium, esterquat, and diethylenetriamine derivatives (diamidoamine ethoxylated quaternaries and imidazolinium quaternaries).[2]

Commercial softeners often fail to contain a detailed description of their composition and some products are labeled solely as containing 'cationic surfactants'. Counterfeit fabric softeners are also common and these illegal products are normally of quite poor quality. Ingestion accidents involving fabric softeners of unknown and potentially dangerous compositions are a subject of even greater concern since clinical treatment cannot rely on the knowledge of the chemical composition of the product.

For forensic analysis, quality control and emergency clinical procedures, it is important to develop a fast method to characterize the surfactants in fabric softeners. Surfactants have been analyzed, after derivatization to volatile compounds owing to their lack of volatility, mostly by gas chromatography (GC) and GC coupled to mass spectrometry (GC/MS).[3,4] Hofmann elimination, in which the long-chain quaternary ammonium salt is heated in an alkaline solution to yield the respective long-chain alkenes, is normally employed to analyze QUACs. Cationic surfactants may also be characterized after extraction and isolation and with no pre-separation by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy.[4,5] High-performance liquid chromatography (HPLC)[6–8] and capillary electrophoresis (CE)[9,10] of the non-derivatized surfactants are also employed.

Mass spectrometry, owing to its speed, sensitivity and selectivity, has also provided a powerful tool to characterize surfactants in different matrices.[11–14] For instance, Ayorinde and co-workers[15] analyzed QUACs in oral rinses and disinfectants by MALDI-MS and Ogura *et al.*[16] used direct infusion ESI-MS to identify anionic, cationic and non-ionic surfactants in samples of detergents, shampoos, conditioners and fabric softeners as well as linear alkylbenzene sulfonates in detergents.

Recently, new ambient mass spectrometric techniques,[17] such as DESI,[18] DART,[19] ELDI,[20] MALDESI,[21] ASAP,[22] EESI,[23] DAPPI,[24] and EASI,[25] have been introduced. These techniques allow MS analysis with great speed directly for samples placed on original or auxiliary matrices under ambient conditions. Among these techniques, easy ambient sonic-spray ionization (EASI, originally termed DeSSI)[25] is simple, gentle and easily implemented. An EASI source can be constructed from a few simple MS laboratory parts (see Fig. 2) and is assisted only by compressed N_2 or air. EASI uses super-sonic spray ionization (SSI)[26] to create very minute droplets which end up being charged due to statistically imbalanced distribution of charge (cations and anions). The dense stream of the super-sonic charged droplets causes analyte pickup from the surface, ionization of neutral molecules, and transfer to the gas phase. EASI has already been applied with success to different analytes in

**Correspondence to*: M. N. Eberlin, ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, University of Campinas, UNICAMP, Campinas, SP, 13083-970, Brazil.
E-mail: eberlin@iqm.unicamp.br

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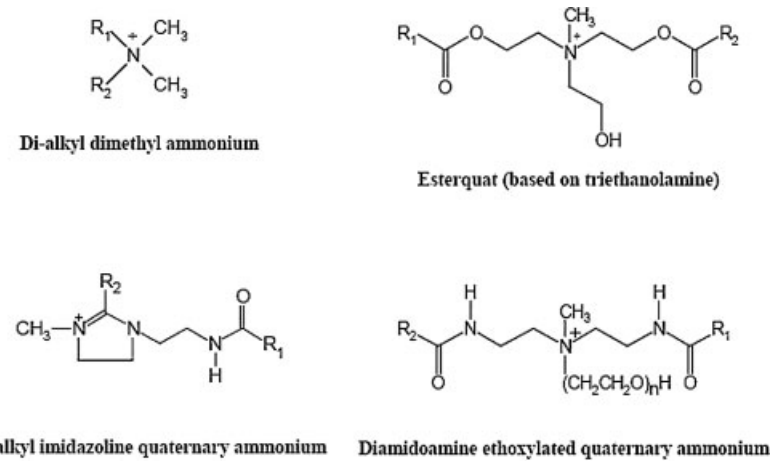

Figure 1. Four representative quaternary ammonium surfactants employed in fabric softeners.

matrices such as drug tablets,[25] oils,[27] perfumes[28] and biofuels,[29] and it has been recently coupled to membrane introduction mass spectrometry (EASI-MIMS)[30] and thin-layer chromatography (EASI-TLC-MS).[31]

We report herein our investigation of the suitability of EASI-MS for fast and direct characterization of surfactants in fabric softeners.

EXPERIMENTAL

Reagents and samples

All reagents used were of analytical grade. Formic acid and methanol (HPLC grade) was purchased from Merck SA (Rio de Janeiro, Brazil). Deionized water was obtained from a MilliQ purification unit (Millipore, Bedford, MA, USA). Twenty samples of fabric softeners of various trademarks were analyzed, including some that were purchased from street vendors.

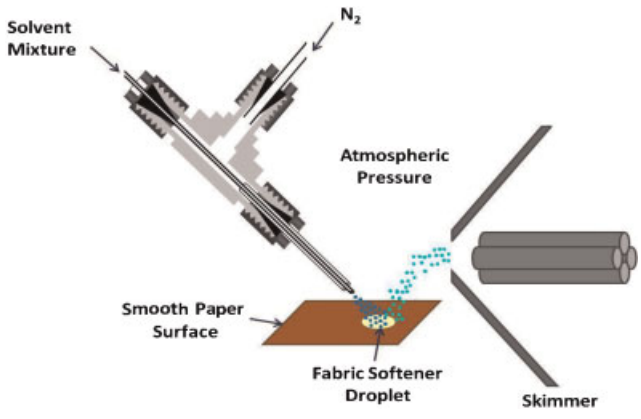

Figure 2. Schematic of the nearly instantaneous EASI-MS characterization of surfactants in fabric softeners. A droplet of the sample (yellow circle) is placed on a smooth paper surface. The surfactant ions are then desorbed by minute charged droplets (blue dots) and transferred to the gas phase (green dots) followed by MS detection. Sonic-spray ionization is assisted only by compressed N_2, and EASI uses a simple Swagelok T-element with appropriate ferrules and tubings for the gas flow and a fused-silica capillary at the supersonic spray exit. This figure is available in color online at www.interscience.wiley.com/journal/rcm.

General experimental procedure

Experiments were performed on both a Q-Trap® hybrid triple-quadrupole linear ion trap mass spectrometer (Applied Biosystems, Foster City, CA, USA) and a quadrupole time-of-flight (QToF) mass spectrometer (Waters/Micromass, Manchester, UK) using home-made EASI sources described in detail elsewhere.[25] The mass spectrometers were operated in the positive ion mode and the fabric softener samples (one tiny droplet) were deposited on a smooth paper surface. The EASI operational conditions were as follows: flow rate of the 1:1 acidic (0.1% formic acid) water/methanol solution of $20\,mL \cdot min^{-1}$, nebulizing gas back-pressure of ca. 30 bar, curtain gas pressure of 10 bar, declustering potential of 10 V, tip-paper and tip-entrance distances of ca. 2 mm, and capillary-paper surface-entrance angle of ca. 30° (Fig. 2). Tandem mass spectrometric experiments were performed using collision energies ranging from 10 to 50 eV, as required to obtain good yields of product ions. Mass spectra were acquired over the *m/z* 100–1000 range.

RESULTS AND DISCUSSION

Figure 3 exemplifies three typical EASI-MS fingerprints of liquid fabric softeners. Despite being commercial formulations analyzed directly without pre-separation or sample-treatment procedures, good spectra, indicating the different compositions of the cationic surfactants, were obtained. For each sample, the type and distribution of homologue surfactants can be recognized via characteristic sets of diagnostic surfactant cations for each class. As expected, we detect ions with odd *m/z* values for the QUACs due to the odd number of nitrogen atoms (N_1 or N_3) in their structures. These surfactants bear different combinations of alkyl chains since hydrogenated and non-hydrogenated tallow are both used in their preparation.[2,32] The fatty acid nature of such surfactants is recognized by the $(C_2H_4)_n$ homologous series

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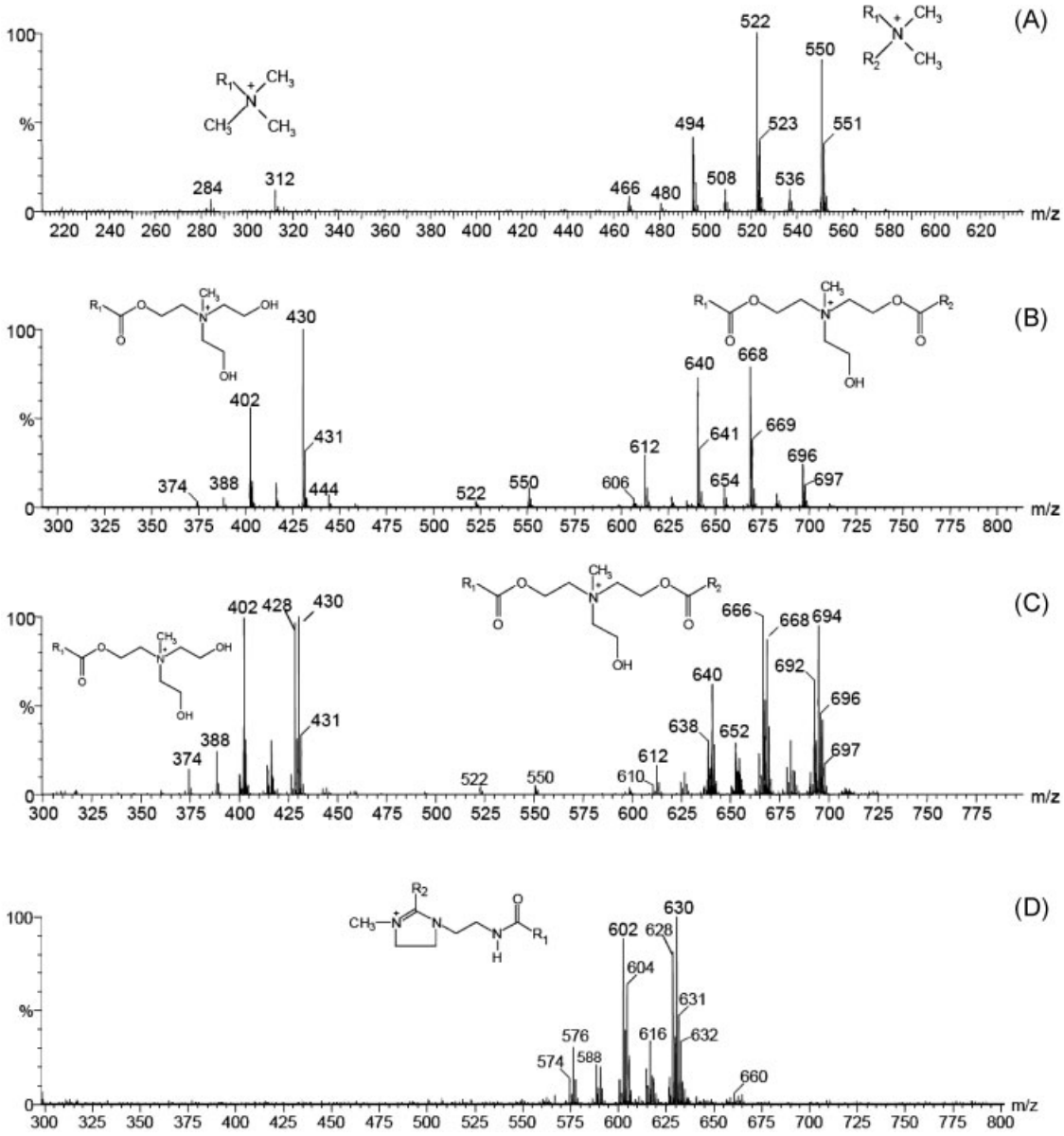

Figure 3. Characteristic EASI-MS fingerprints of fabric softeners formulated with salts of: (A) dihydrogenated tallow dimethylammonium; (B) esterquat from hydrogenated tallow; (C) esterquat from non-hydrogenated tallow; and (D) dialkyl imidazoline ammonium.

separated by 28 *m*/*z* units; for instance, the ions of *m*/*z* 522 and 550 in Fig. 3(A) and those of *m*/*z* 640 and 648 in Fig. 3(B). The use of saturated (Fig. 3(B)) or unsaturated tallow as feedstock (Fig. 3(C)) is also easily recognized. Further characterization of these cationic surfactants can be obtained by EASI-MS/MS.

In Fig. 3(A), the EASI-MS characterizes a softener formulated with a dihydrogenated tallow dimethylammonium salt, and Table 1 summarizes the identification of the most relevant ions. Others ions, such as those of *m*/*z* 284 and 312, represent, respectively, cetyltrimethylammonium and stearyltrimethylammonium (mono-tallow trimethylammonium

Table 1. Ions characterized via EASI-MS in fabric softeners containing di-tallow dimethylammonium (Fig. 3(A))

		Alkyl groups		
m/*z*	Composition	R_1	R_2	Name
466	$C_{32}H_{68}N^+$	C14	C16	Myristyl cetyl dimethyl ammonium
494	$C_{34}H_{72}N^+$	C16	C16	Dicetyl dimethyl ammonium
		C14	C18	Myristyl stearyl ammonium
522	$C_{36}H_{76}N^+$	C16	C18	Cetyl stearyl dimethyl ammonium
550	$C_{38}H_{80}N^+$	C18	C18	Distearyl dimethyl ammonium

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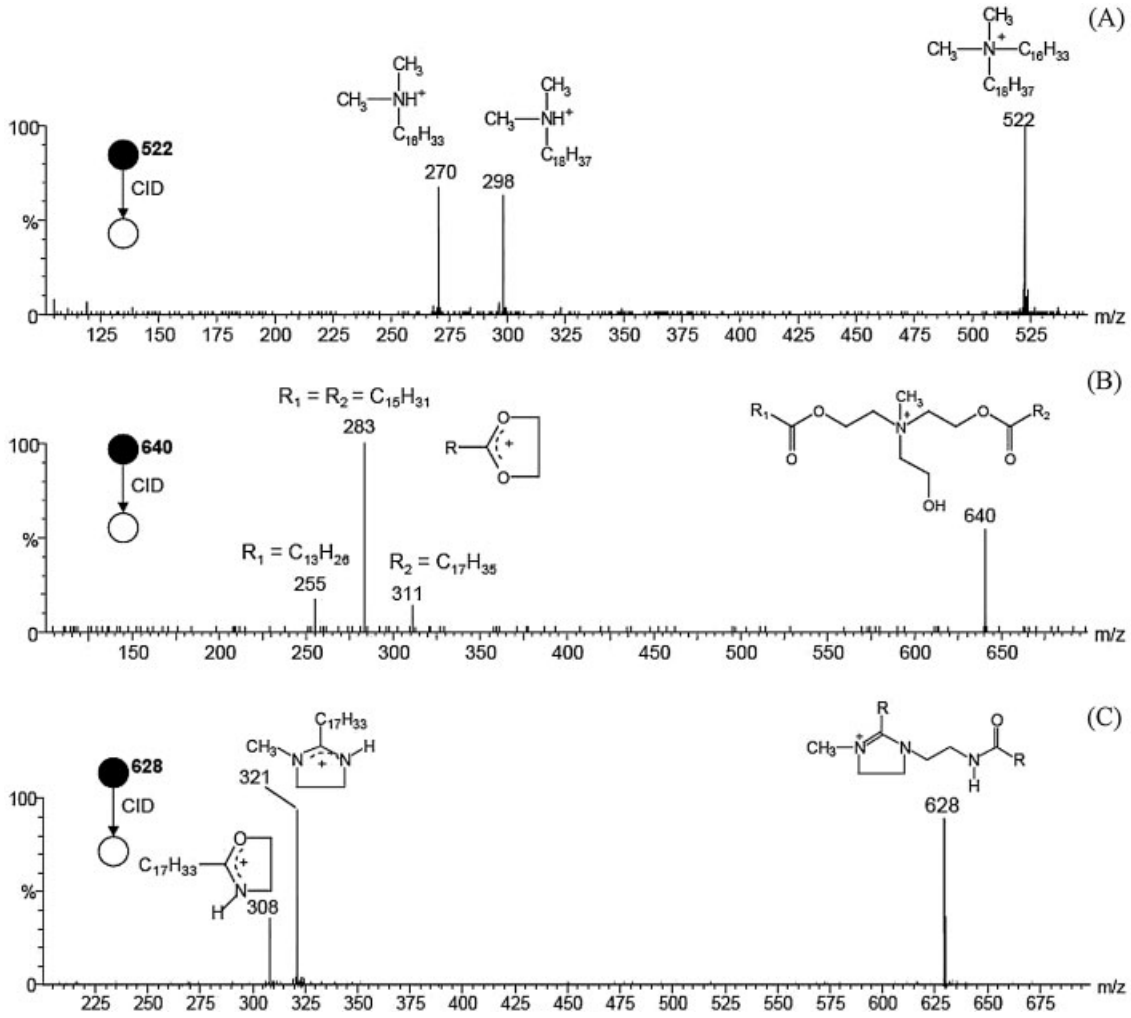

Figure 4. EASI(+)-MS/MS of representative surfactant ions: (A) a di-tallow dimethylammonium ion of *m/z* 522; (B) an esterquat ion of *m/z* 640; and (C) a di-tallow imidazoline ammonium of *m/z* 630.

ions), which are probably present as side products. Other impurities are residual tertiary amines, which are detected in their protonated forms: dioctadecyl methylamine (*m/z* 536), hexadecyl octadecylamine (*m/z* 508), dihexadecyl methylamine and tetradecyl octadecyl methylamine (*m/z* 480).

EASI-MS/MS spectra of the di-tallow dimethylammonium ions are also characteristic and structurally diagnostic since dissociation occurs via the loss of the alkyl chains as the respective alkenes (Fig. 4(A)). EASI-MS/MS confirms therefore the structural assignments and provides detailed information on the alkyl chains. For example, the C16 + C18 QUAC mixture of isobaric ions of *m/z* 522 (Fig. 4(A)) yields two main product ions due to either hexadecene (*m/z* 298) or octadecene loss (*m/z* 270).

Figures 3(B) and 3(C) show EASI-MS fingerprints that characterize two samples of fabric softeners employing esterquat surfactants (Table 2), which are mixtures of fatty acid mono- and diesters of triethanolamine quaternized with dimethyl sulfate.

Note that the surfactant class identified in the EASI mass spectra shown in Figs. 3(B) and 3(C) is the same (esterquat), but there is an important difference. Figure 3(B) indicates an esterquat made from hydrogenated tallow (*m/z* 668 for the C18:0: stearic acid for instance) whereas Fig. 3(C) indicates an esterquat made from the non-hydrogenated natural tallow (note, for instance, the various doublets of ions such as those of *m/z* 668 for C18:0: stearic acid and *m/z* 666 for C18:1: oleic acid).

Table 2. Ions characterized via EASI-MS from fabric softeners containing esterquat (Figs. 3(B) and 3(C))

	Fatty acids[a]		*m/z*
Monoester	C14	—	374
	C16	—	402
	C18:1	—	428
	C18	—	430
Diester	C14	C16	612
	C14	C18:1	638
	C14	C18	640
	C16	C16	640
	C16	C18:1	666
	C16	C18	668
	C18:1	C18:1	692
	C18	C18:1	694
	C18	C18	696

[a] C14 = myristic acid; C16 = palmitic acid; C18 = stearic acid; C18:1 = oleic acid.

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Table 3. Ions characterized via EASI-MS from a fabric softener containing dialkyl imidazoline (Fig. 3(D))

	Fatty acids[a]		*m/z*
Quaternary ammonium	C16	C16:1	574
	C16	C16	576
	C16:1	C18	602
	C16	C18:1	602
	C16	C18	604
	C18:1	C18:1	628
	C18	C18:1	630
	C18	C18	632

[a] Fatty acids that originated from the alkyl groups R_1 and R_2: C16:1 = palmitoleic acid; C16 = palmitic acid; C18 = stearic acid; C18:1 = oleic acid.

As Fig. 4(B) shows, the esterquat ions also dissociate in a structurally diagnostic fashion, i.e., by the loss of the respective tertiary amine to yield cyclic fatty dioxolanylium ions. The *m/z* values of such ions reveal therefore the nature of the fatty acids used for their production. For instance, the three product ions of *m/z* 255, 283 and 311 indicate that the precursor ion of *m/z* 640 is constituted of a mixture of esterquat ions made mainly from two palmitic acid molecules ($R_1 = R_2 = C_{15}H_{31}$) and to a lesser extent from both stearic ($R_1 = C_{17}H_{35}$) and myristic acid ($R_2 = C_{13}H_{26}$).

Figure 3(D) illustrates an EASI-MS fingerprint of a fabric softener based on dialkyl imidazoline ammonium quaternary salt, whose main cations are identified in Table 3.

As in the previous case, the fingerprint of Fig. 3(D) shows that the surfactant was manufactured from unsaturated raw material (ions of *m/z* 630, 628, 602 and 574 that have an alkyl chain derived from oleic or palmitoleic acid). It is also possible to detect the free fatty amines via the ions of *m/z* 588, 590, 614 and 616.

EASI-MS/MS of the dialkyl imidazoline ions (Fig. 4(C)) is also structurally diagnostic since it shows two competing dissociation channels involving the formation of characteristic cyclic dihydrooxazolium (NO) or imidazolium (NN) ions.

Low quality and adulterated softeners

As Fig. 5 illustrates, EASI-MS fingerprints are also useful in identifying counterfeit fabric softeners. The main surfactant in the sample of Fig. 5 is identified as a monoalkyl ammonium ion, that is, the hexadecyltrimethylammonium ion of *m/z* 284, known commercially as cetyltrimethylammonium. Minor ions of *m/z* 310 (octadecenyltrimethylammonium) and 312 (octadecyltrimethylammonium) are also detected. Satisfactory softness properties in fabrics are associated with QUACs bearing two (not just one) fatty acid chains.[1,32] Monoalkyl quaternary ammonium salts such as those of cetyltrimethylammonium are used mostly in lubricants and as anti-statics in hair conditioners;[33] hence their use in fabric softener formulations detected for the sample of Fig. 5 characterizes a low quality softener. Monoalkyl salts are cheaper than salts of dialkyldimethylammonium or esterquat.

Figure 6 illustrates the EASI-MS fingerprint of an adulterated sample of fabric softener. For this sample, the label indicated the use of a dialkyl imidazoline chloride as the surfactant. However, the EASI-MS fingerprint reveals a different composition of surfactants. The ions of *m/z* 403, 431 and 459 and their respective EASI-MS/MS product ion spectra (Fig. 7 for the ion of *m/z* 459) indicate the use of a monoalkyl (hydrogenated tallow), i.e., an amidopropyldimethylbenzylammonium salt.

Alkyl amidopropyl dimethylbenzylammonium salts are not commonly used in fabric softeners but are encountered as anti-static agents in cosmetic formulations.[34] Figure 6 also shows other major ions of *m/z* 285, 313, 341 and 369, which

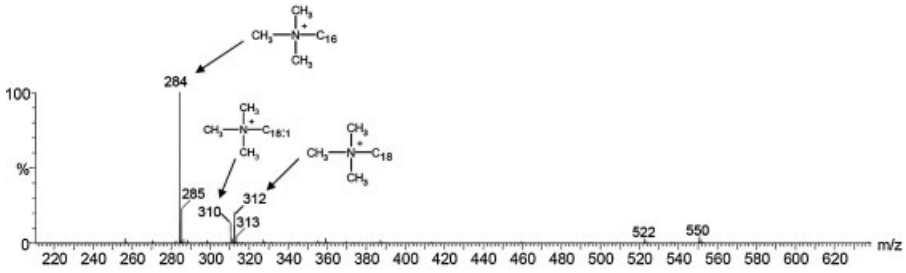

Figure 5. EASI(+)-MS fingerprint of a low quality sample of fabric softener formulated with a monoalkyltrimethylammonium salt. C16 = cetyl chain; C18 = stearyl chain; C18:1 = oleic chain.

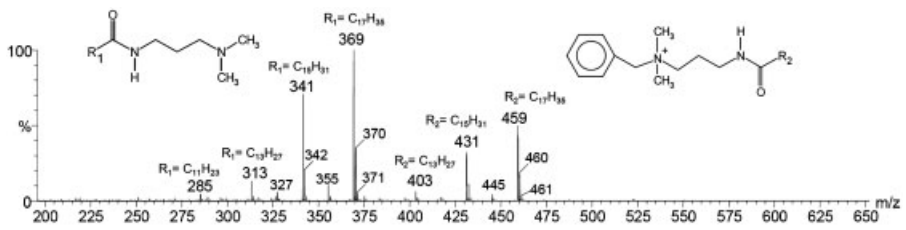

Figure 6. EASI(+)-MS fingerprint of an adulterated fabric softener formulated with alkyl amide propyldimethylbenzylammonium salts and alkyl amide propyldimethylamine.

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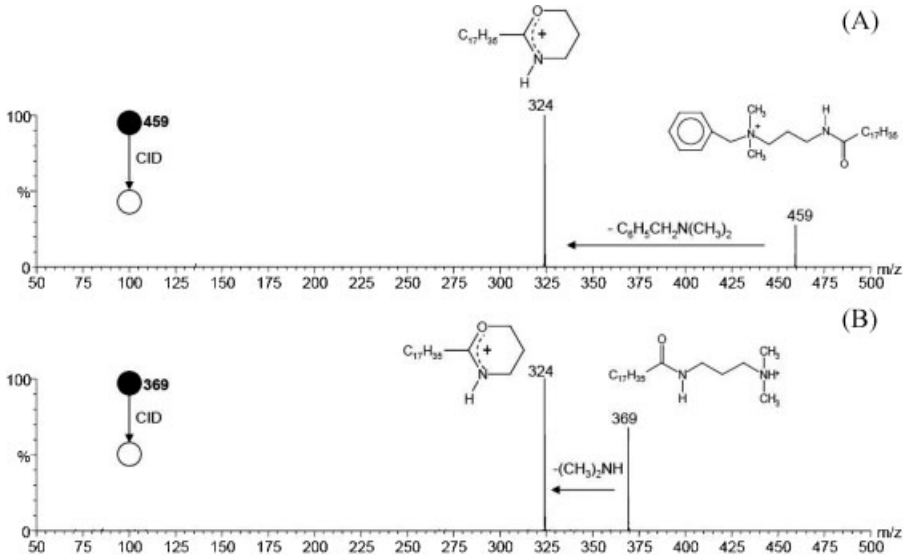

Figure 7. EASI(+)-MS/MS of the ions of *m/z* 459 and 369 detected in Fig. 6.

correspond to alkyl amide propyl dimethylamines detected in their protonated forms (Fig. 7(B)). These amidoamines have minor conditioning effects, comparable with those of a quaternary ammonium salt with a single fatty chain, and are employed normally in hair conditioners to reduce matted after-feel effects.[35] These amidoamines are also the precursors of the quaternary ammonium salt used in the formulation.

CONCLUSIONS

EASI-MS allows nearly instantaneous fingerprinting of fabric softeners via the characterization of the main ionic surfactants and the patterns of their homologous series. Adulteration and low quality formulations are therefore also readily detected. EASI-MS/MS of characteristic surfactant ions and impurities may be also used to provide more secure characterization and detailed structural analysis.

EASI-MS may also be used for the real-time monitoring of the fabric softener production process since most residual reactants, sub-products and intermediates should be readily detected. Reliable quantitation seems also possible via spiking the sample with the same known amount of an analogous, reference surfactant, and this possibility has been tested with success (precision of ca. 10%) in our laboratory.

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