Identification and Quantitation of Surfactants in Consumer Products by Ion-Spray Mass Spectrometry

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ABSTRACT: Current approaches for identifying and quantitating surfactants in various product matrices require the use of wet chemical, chromatographic, and spectroscopic techniques. The primary objective of this work is to replace current multiple-technique approaches for identifying surfactants and quantitating their homologue distribution with a single rapid technique. To meet this objective, a simple preparation procedure has been developed to prepare consumer product samples for subsequent analysis by ion-spray mass spectrometry. Quantitation of linear alkylbenzene sulfonates in detergents with this technique is demonstrated.
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KEY WORDS: Anionic surfactant, cationic surfactant, conditioner, detergent, fabric softener, identification, ion-spray, mass spectrometry, nonionic surfactant, shampoo.

Identification and quantitation of surfactants have been routinely accomplished for many decades through the use of wet chemical extraction and isolation procedures, complexometric and acid-base titrations, gravimetry, and colorimetry (1–5). These approaches take time and effort, however, and do not provide information on distributions of homologues or identify unknown surfactants.

Spectroscopic approaches, such as infrared (IR) and nuclear magnetic resonance (NMR) spectrometry, provide information on the identification of surfactants (1–3,6–8). These techniques, however, are limited by the matrix and their inability to separate and quantitate homologue distribution.

Chromatographic approaches, e.g., thin-layer chromatography (TLC), gas chromatography (GC), high-performance liquid chromatography (HPLC), or supercritical fluid chromatography (SFC), have bridged this gap concerning homologue distribution measurements (9–22). These techniques are limited, however, by their inability to identify surfactant molecules, particularly in the absence of standard compounds. They are also dependent on time-consuming sample-preparation procedures.

Recent development of several mass-spectrometric interfaces has enabled the coupling of various chromatographic instruments with mass spectrometry. These systems can simultaneously provide information on the composition and quantitation of surfactants in various matrices (23–27). Extensive method development studies for analysis of surfactants in environmental matrices have been reported for these systems (28–32).

The objectives of this work were to develop a single instrumental technique without chromatography that could identify all types of surfactants in a wide variety of consumer product matrices as well as provide quantitative information on homologue distributions and surfactant concentrations. The approach, described in this paper, starts with a simple sample-preparation procedure that isolates surfactants from the product matrix, thereby eliminating potential interferences before mass-spectroscopic analysis. Different types of surfactants can generate ions with identical mass-to-charge ratios, providing misleading information for surfactant identification. The surfactants that generate these ions can be positively identified by their collisionally-activated dissociation (CAD) spectra. The use of deuterated internal standards provides quantitative information on the total concentration of the various surfactants in consumer products.

EXPERIMENTAL PROCEDURES

Reagents. HPLC-grade methanol, acetonitrile, and water, as well as reagent-grade ammonium acetate and trifluoroacetic acid, used for this research, were purchased from Wako Junyaku Kogyo Co., Ltd. (Osaka, Japan). The anion exchange solid-phase extraction (SPE) cartridges, used to remove anionic surfactants from matrices, were Sep-Pak Vac 20cc Accell plus QMA from Japan Millipore Co., Ltd. (Osaka, Japan). Deuterated internal standards, i.e., d-7 C_{10} linear alkylbenzene sulfonate (LAS), d-7 C_{12} LAS and d-7 C_{14} LAS, were synthesized in-house.

Equipment. The mass spectrometer used in this research was an API-III from PE-Sciex (Toronto, Canada). A Harvard syringe pump (Saint-Laurent, Canada) was used for direct injections into the mass spectrometer. The mass spectrometer was coupled to a Macintosh IIfx computer (Palo Alto, CA) for system control, and a Macintosh Quadra 800 computer (Palo Alto, CA) was used for data handling.

Operating conditions. The injection mode of solvents into the mass spectrometer was direct infusion, and no chromato-

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graphic separations were performed prior to the mass-spectral analysis. The orifice voltage for API-III interface was set at –90 volts for anionic surfactants, and +90 volts for cationic and nonionic surfactants.

For all surfactants, the flow rate of solvent to the interface orifice was between 5 and 10 μL/min. The solvent system used for analyzing anionic surfactants was methanol. The solvent system used for cationic and nonionic surfactants was methanol, or a mixture of methanol and water (50:50) with 0.1% wt/vol trifluoroacetic acid when surfactants were detected as protonated molecular ions. When nonionic surfactants were detected as adduct ions, a mixture of methanol and water (50:50) with 0.01 N ammonium acetate was used.

Internal standard solution. The internal standard solution was prepared by weighing 0.0500 g pure-chainlength deuterated surfactant into a 100-mL volumetric flask and diluted with methanol. In the research presented here, d-C_{10} LAS, d-7 C_{12} LAS, and d-7 C_{14} LAS were used as internal standards for quantitation of total LAS in consumer products.

Sample preparation. About 0.1–0.5 g of granular or liquid detergent, fabric softener, shampoo, or conditioner samples are weighed into 100-mL volumetric flasks, diluted with ethanol, and mixed until the surfactants are dissolved. The ethanol solution is then centrifuged to remove insoluble inorganic materials that may interfere with mass spectrometry.

For simple identification of surfactants, 1.0 mL ethanol supernatant is diluted to 100 mL with the methanol or methanol/buffer solution. Then, 1 mL of this solution is further diluted to 10 mL with methanol or methanol/buffer solution and analyzed by ion-spray mass spectrometry (IS/MS). When quantitation is needed, 1.0 mL ethanol supernatant and 1.0 mL internal standard solution are added to a 100-mL volumetric flask, mixed, and diluted with methanol or methanol/buffer solution. Then, 1 mL of this solution is further diluted to 10 mL with methanol or methanol/buffer solution, prior to infusion into the IS/MS.

For analysis of nonionic surfactants in formulations that contain large amount of anionic surfactants, the ethanol supernatant is passed through an anion-exchange SPE cartridge, then diluted with methanol or methanol/buffer solution, prior to infusion into the IS/MS.

RESULTS AND DISCUSSION

The key to success of this single technique for identification and quantitation of surfactants is that the ion-spray interface is a soft ionization technique, providing strong parent ion signals for polar surfactant molecules while reducing the background noise from the ionization of nonpolar organic compounds in consumer products. Excellent studies on direct analysis of surfactants with the soft ionization technique, such as fast atom bombardment (FAB), have been reported for the same purposes (33–36). It is reported that FAB does not provide good reproducibility because the sensitivity changes with time due to the evaporation of matrices and the depletion of the more surface-active species (34).

Another key to the successful development of this work is the injection system into the mass spectrometer. The ion-spray interface is unique in its ability to reproducibly introduce aqueous samples into the mass spectrometer. This ability to handle aqueous samples means that polar or ionic compounds, such as surfactants, can be introduced into the mass spectrometer without difficulty (37,38).

Anionic surfactants. Under the conditions specified in the Experimental Procedures section, anionic surfactants are detected as singularly charged sulfonate, sulfate, or carboxylate ions in the negative ion detection mode of the mass spectrometer. Figure 1 is a spectrum of a typical commercial granular detergent formulation. This spectrum contains ion signals that were generated from alkyl carboxylate, alkyl benzene sulfonate, and alkyl sulfate ions. Positive identification of all ions in this spectrum could not be made, however, because different types of anionic surfactants can generate ions with the same *m/z* ratio.

These ions can be positively identified from their CAD spectra. CAD spectra are also known as daughter ion spectra. Figure 2 shows the differences between CAD spectra of tetradecyl sulfate and hydroxy tetradecyl sulfonate. Both surfactants give a deprotonated parent ion with the same mass of *m/z* 293. When these two surfactants are fragmented with collision gas, however, the daughter ions are different. The sulfonated surfactant gives a daughter ion with a mass of *m/z* 80, while the sulfated surfactant gives a daughter ion with a mass of *m/z* 96. The CAD spectrum of hydroxy alkane sulfonate also provides information on the existence of a hydroxy group in the molecule due to an ion formed by the loss of a neutral water molecule.

Linear and branched isomers of the same surfactant species generate the same deprotonated parent ions by simple

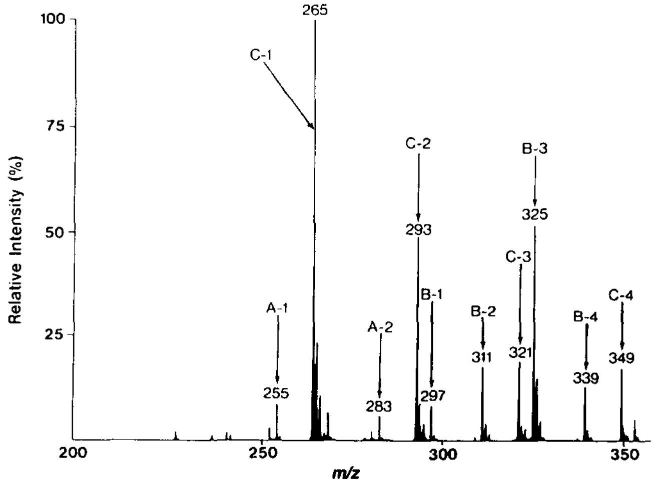

FIG. 1. Ion-spray/mass spectrometry spectrum for a typical commercial granular detergent in negative ion detection mode: A-1, C_{16} alkyl carboxylate; A-2, C_{18} alkyl carboxylate; B-1, C_{10} linear alkylbenzene sulfonate; B-2, C_{11} linear alkylbenzene sulfonate; B-3, C_{12} linear alkylbenzene sulfonate; B-4, C_{13} linear alkylbenzene sulfonate; C-1, C_{12} alkyl sulfate; C-2, C_{14} alkyl sulfate; C-3, C_{16} alkyl sulfate; C-4, C_{18} alkyl sulfate.

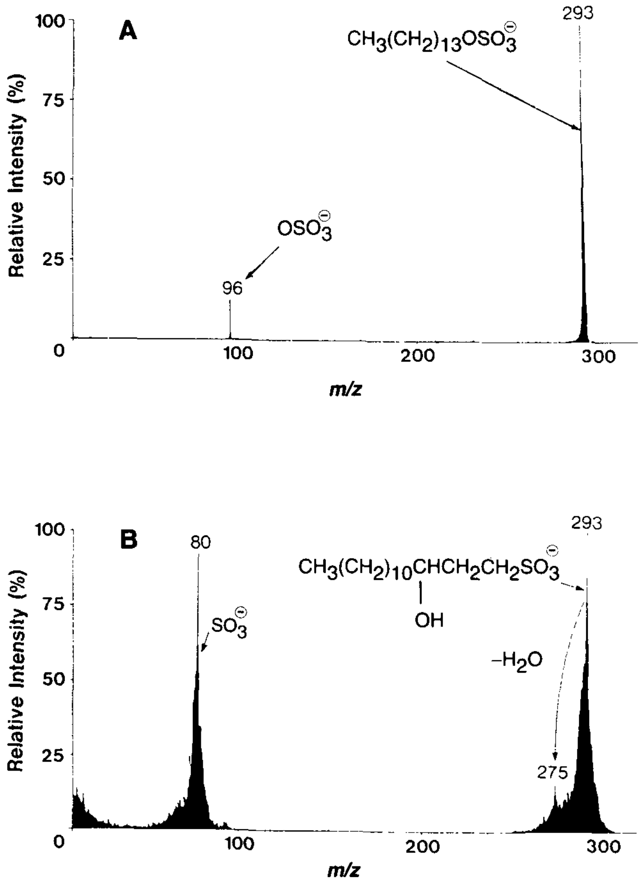

FIG. 2. Collisionally-activated dissociation spectra of alkyl sulfate and hydroxy alkane sulfonate in the negative ion detection mode.

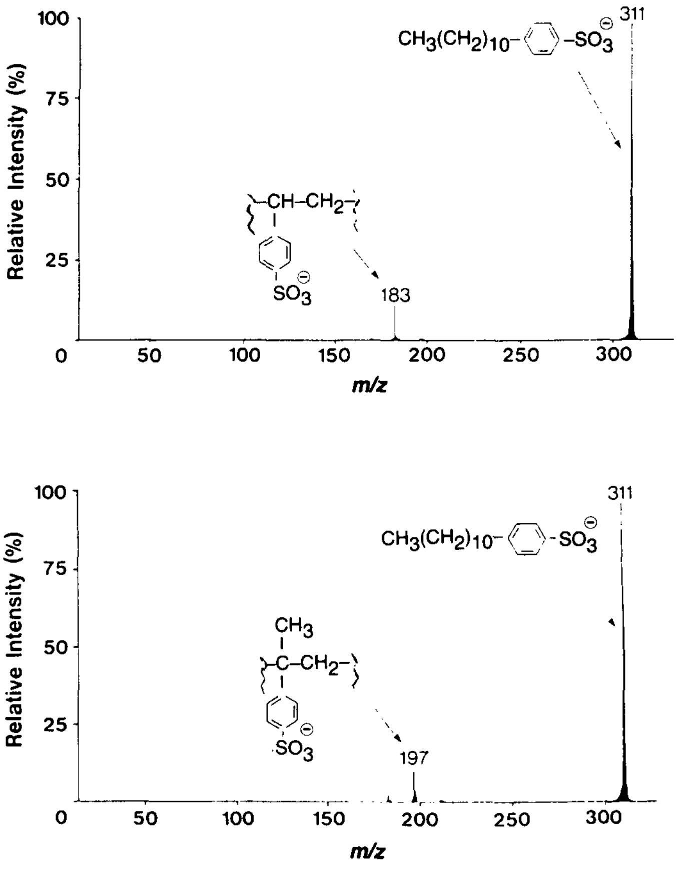

FIG. 3. Collisionally-activated dissociation spectra of linear alkylbenzene sulfonate and branched alkylbenzene sulfonate in the negative ion detection mode.

mass spectral techniques. They can also be distinguished by CAD spectra, however. Figure 3 compares the CAD spectra for linear alkylbenzene sulfonate and branched alkylbenzene sulfonate. Distinctive daughter ions are generated by CAD at *m/z* 183 and 197, respectively.

Cationic surfactants. Molecular ions of quarternary amines and protonated ions of tertiary amines are detected in the positive ion detection mode of the mass spectrometer. In the same manner as for anionic surfactants, structural information can be obtained from CAD spectra of individual surfactant ions. Figure 4 is a mass spectrum of a commercial fabric softener that contained a protonated dialkyl tertiary amine as the key cationic surfactant. Protonated parent ions of the homologues can be observed.

Figure 5 is the CAD spectrum from the parent ion with a mass of *m/z* 637. The cleavage of the parent ion occurs on either side of the tertiary amine. This cleavage occurs with the loss of an electron from the alkyl chain, the tertiary amine disappears from the spectra as a neutral fragment, and the alkyl chain is observed as a charged fragment.

Nonionic surfactants. Interference from other surfactants, especially anionic surfactants, can cause problems with the reproducible identification and quantitation of nonionic surfactants in detergent products that contain both anionic and nonionic surfactants. Removal of anionic surfactants *via* anion exchange resin cartridges eliminates this interference. In addition, unless the proper buffer is added, a mixture of protonated ions, sodium adducts, and ammonium adducts may be formed. This mixture of ions unnecessarily complicates the surfactants' spectra. The buffer systems, specified in

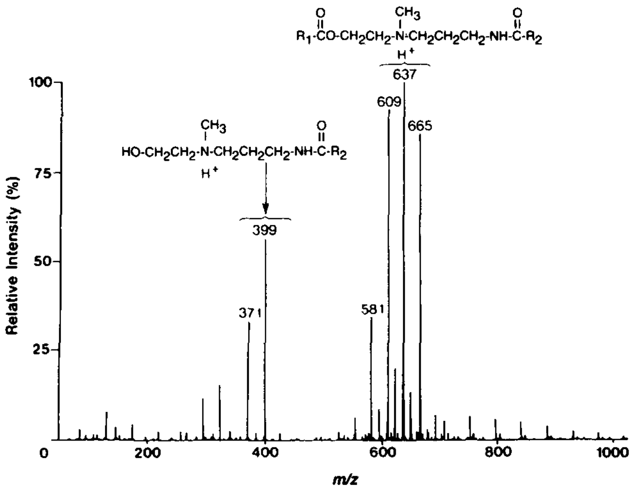

FIG. 4. Ion-spray/mass spectrometry spectrum of a commercial fabric softener in the positive ion detection mode.

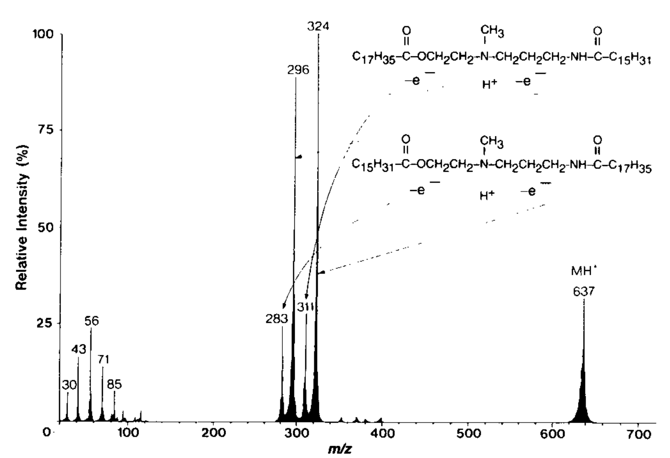

FIG. 5. Collisionally-activated dissociation spectrum of dialkyl tertiary amine in the positive ion detection mode.

the Experimental Procedures section, minimize problems due to multiple ion types.

Figure 6 is a spectrum of the cationic and nonionic surfactants in a light-duty liquid detergent product. The ions with masses at *m/z* 284 and 312 are parent ions for cetyltrimethylammonium and stearyltrimethylammomium ions. The ions with masses at *m/z* 338 and 366 are ammonium adduct parent ions for decylmonoglycoside and dodecylmonoglycoside. The ions with masses at *m/z* 500 and 528 are ammonium adduct parent ions for the diglycoside series of the same surfactant species, i.e., alkylpolyglycoside (APG).

The most interesting part of the spectrum in Figure 6 is the ammonium adduct parent ions for the lauryl alcohol ethoxylate series. The series reaches a maximum with 11 ethoxylates and continues to about 20 ethoxylate units. GC has been used to routinely measure ethoxylate distributions but can only see out to about 14 or 15 ethoxylate units. SFC is also used for the analysis and is reported to see out to about 30 ethoxylate units (7). The method developed here provides the information on the distribution of ethoxylation much more quickly without chromatography.

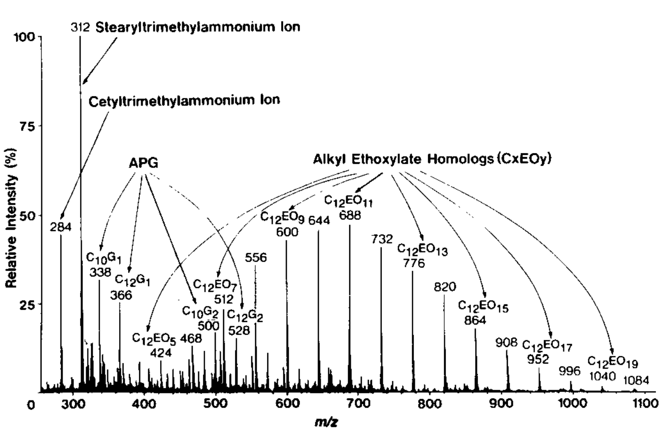

FIG. 6. Ion-spray/mass spectrometry spectrum of a commercial light-duty liquid detergent in the positive ion detection mode; APG, alkylpolyglycoside.

Scope. This quick identification method was applied to other surfactants in various matrices. Especially, anionic surfactants, such as α-sulfo fatty acid esters, alkyl amide sulfonates and alkyl ether sulfate, were identified and quantitated in detergents and shampoos. Cationic surfactants, such as monoalkyl quaternary amines, were identified, and their homologue distributions were satisfactorily obtained from conditioner products with this method.

Quantitation. Bias among homologues has been the major problem for quantitation with mass spectrometric techniques. This bias is mainly the result of differences in relative surface activity between ions. Homologues of shorter chainlength are more efficiently ionized than longer-chainlength ions with IS/MS. Bias can be minimized through optimization of the sample preparation procedure and the conditions used for IS/MS. Optimization of buffer systems and orifice voltage helped reduce bias found between homologues of the same surfactant series, though some bias still exists.

Figure 7 is a mass spectrum of a commercial liquid detergent that contained LAS homologues and three d-7 internal standards. The consumer product was prepared so that the final surfactant concentration from detergents in the solution was about 1.5 ppm (parts per million). Each internal standard was added to the solution so that their final concentrations were about 0.5 ppm.

Table 1 compares the ion intensities among LAS homologues. There is a noticeable drop in the signal intensities of the internal standards as their alkyl chainlength increases. The mass spectrometer responds on a mole basis, not a mass basis. Therefore the intensity of homologues with the longer chainlengths should be lower than the shorter ones when compared on a mass basis. When the ratios of ion intensity are compared on a mole basis, however, the longer ones still give lower responses.

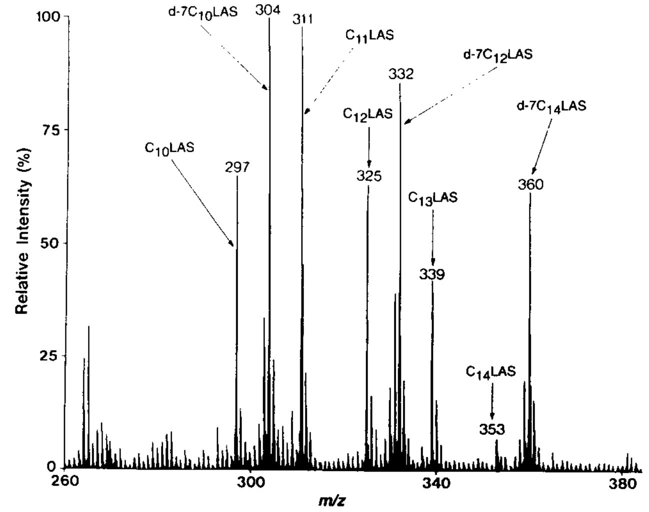

FIG. 7. Ion-spray/mass spectrometry spectrum of a commercial liquid detergent containing linear alkylbenzene sulfonate homologues and three d-7 internal standards.

TABLE 1
Relative Ion Intensity of Linear Alkylbenzene (LAS) Homologues

Chainlength of LAS	Relative ion intensity (mass basis)	Relative ion intensity (mole basis)
d-7 C_{10} LAS	1.00	1.00
d-7 C_{12} LAS	0.85	0.93
d-7 C_{14} LAS	0.58	0.69

Bias between longer- and shorter-chain homologues has also been recognized with another soft ionization mass spectrometry, FAB. Wernery and Peake (34) reported that the abundance of C_{14} LAS was enhanced relative to the shorter-chain homologues with FAB at lower total LAS concentrations, as expected from the higher surface activity of C_{14} LAS, though the trend reversed as LAS concentration increased. The IS/MS detector response slowly changes with time, and different surfactant species will have some bias due to their ion evaporation efficiency in matrices. The only way to compensate for these biases and provide quantitative results on surfactant concentrations is to develop calibration curves by using appropriate internal standards. Deuterated standards are routinely used as internal standards in mass spectrometry.

Table 2 and Figure 8 show the data of the variation and the correlation coefficient of this IS/MS method by using deuterated internal standards. A solution of 0.5 ppm wt/vol d-7 C_{10} LAS was used as an internal standard. Because pure LAS standards were not available, a consumer product, containing LAS homologues, was spiked into the solution of deuterated internal standards. The consumer product was diluted to between 5 and 30 ppm wt/vol before mixing so that the ion intensity of LAS homologues was similar to that of the internal standard. It was found that both the correlation coefficient and variation were satisfactory when samples were appropriately diluted. For LAS and alkyl sulfate, the spike and recovery results were greater than 90%.

The results in Table 3 compare the analytical results on alkyl benzene sulfonates in a commercial liquid detergent between IS/MS and colorimetric titration methods. Because the correlation coefficient of the IS/MS method was reasonable, the concentration of alkyl benzene homologues in the product was calculated based on the relative ion intensity to the d-7 C_{10} LAS internal standard. The IS/MS method provided both the homologue distribution and the total LAS level, while the titration method provided only the total LAS level. The comparison of the total level between both methods demonstrates that IS/MS is effective for providing reasonable accuracy in quantitating surfactant levels in commercial product formulations.

When multiple species with identical molecular ions are present in the same formulation, the use of selected ion monitoring of the CAD spectra is effective to quantitate individual species. The mass spectrometer is set to monitor the characteristic daughter ions generated by CAD for both the internal standard and analyte species. Calibration can be performed based on daughter ion peak areas of standard solutions.

TABLE 2
Data of Variation and Correlation Coefficient of Ion-Spray/Mass Spectrometry Internal Standard Method

Chainlength of LAS[a]	% Relative standard deviation (n = 3)	Correlation coefficient
C_{10} LAS	4.0	0.9993
C_{11} LAS	5.3	0.9995
C_{12} LAS	3.3	0.9997
C_{13} LAS	1.1	0.9999
C_{14} LAS	4.4	0.9997

[a] Abbreviation as in Table 1.

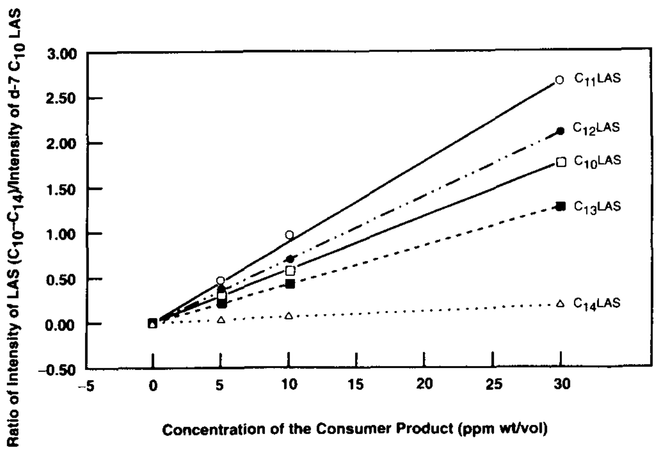

FIG. 8. Study on correlation coefficient of ion-spray/mass spectrometry internal standard method; LAS, linear alkylbenzene sulfonate.

TABLE 3
Comparison of the Analytical Results Between Titration Method (ISO 2271) and Ion-Spray/Mass Spectrometry (IS/MS) Internal Standard Method[a]

Chainlength of LAS	Titration method (%)	IS/MS method (%)
C_{10} LAS	—	3.0
C_{11} LAS	—	5.1
C_{12} LAS	—	4.3
C_{13} LAS	—	3.1
C_{14} LAS	—	0.8
Total LAS	13.7	16.3

[a] Abbreviation as in Table 1.

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REFERENCES

1. Kariyone, T., *Kaimenkasseizai Bunsekiho*, edited by Kaimenkasseizai Bunseki Kenkyu-kai, Saiwai Shobo, Tokyo, 1987.

2. *Kaimenkasseizai no Bunseki to Shikenho,* edited by Kitahara, F., S. Hayano, and I. Hara, Kodan-sha, Tokyo, 1989, p. 123.
3. *Kaimenkasseizai Handbook,* edited by Yoshida, T., S. Shindo, T. Ohgaki, and K. Yamanaka, Kogaku Tosho, Tokyo, 1987, p. 562.
4. Lin, J.T., D.G. Cornell, and T.J. Micich, Cobaltothiocyanate Colorimetric Analysis for Homologous Polyoxyethylated Alkyl Amides, *J. Am. Oil Chem. Soc. 63*:1575–1579 (1986).
5. Wang, C.N., L.D. Metcalfe, J.J. Donkerbroek, and A.H.M. Cosijn, Potentiometric Titration of Long Chain Quaternary Ammonium Compounds Using Sodium Tetraphenyl Borate, *Ibid. 66*:1831–1833 (1989).
6. Carminati, G., L. Cavalli, and F. Buosi, Application of ^{13}C NMR to the Identification of Surfactants in Mixture, *Ibid. 65*:669–677 (1988).
7. Kalinoski, H.T., and A. Jensen, Characterization of Nonionic Surfactants Using Supercritical Fluid Chromatography and Carbon-13 Nuclear Magnetic Resonance Spectroscopy, *Ibid. 66*:1171–1175 (1989).
8. Nakamura, M., K. Tanaka, S. Yamamura, and T. Takeda, C 13-NMR ni yoru hi-ion kaimenkasseizai no kozo kaiseki, *Kagaku-to-Kogyo, 64*:114–120 (1990).
9. Osburn, Q.W., Analytical Methodology for Linear Alkylbenzene Sulfonate (LAS) in Waters and Wastes, *J. Am. Oil Chem. Soc. 63*:257–263 (1986).
10. Sato, T., Y. Saito, and I. Anazawa, Polyoxyethylene Oligomer Distribution of Nonionic Surfactants, *Ibid. 65*:996–999 (1988).
11. Nakamura, K., Y. Morikawa, and I. Matsumoto, Rapid Analysis of Ionic and Nonionic Surfactant Homologs by High Performance Liquid Chromatography, *Ibid. 58*:72–77 (1981).
12. Allen, M.C., and D.E. Linder, Ethylene Oxide Oligomer Distribution in Nonionic Surfactants via High Performance Liquid Chromatography (HPLC), *Ibid. 58*:950–957 (1981).
13. Johannessen, R.O., W.J. Dewitt, R.S. Smith, and M.E. Tuvell, High Pressure Liquid Chromatography of Alpha Olefin Sulfonates, *Ibid. 60*:858–861 (1983).
14. Garti, N., E. Wellner, A. Aserin, and S. Sarig, Analysis of Sorbitan Fatty Acid Esters by HPLC, *Ibid. 60*:1151–1154 (1983).
15. Aserin, A., M. Frenkel, and N. Garti, HPLC Analysis of Nonionic Surfactants. Part IV. Polyoxyethylene Fatty Alcohols, *Ibid. 61*:805–809 (1984).
16. Maruyama, K., and C. Yonese, Separation and Quantitative Determination of Monoacylglycerol Mixtures by Reversed Phase HPLC, *Ibid. 63*:902–905 (1986).
17. Kanesato, M., K. Nakamura, O. Nakata, and Y. Morikawa, Analysis of Ionogenic Surfactants by HPLC with Ion-Pair Extraction Detector, *Ibid. 64*:434–438 (1987).
18. Schmitt, T.M., M.C. Allen, D.K. Brain, K.F. Guin, D.E. Lemmel, and Q.W. Osburn, HPLC Determination of Ethoxylated Alcohol Surfactants in Wastewater, *Ibid. 67*:103–109 (1990).
19. Kubeck, E., and C.G. Naylor, Trace Analysis of Alkylphenol Ethoxylates, *Ibid. 67*:400–405 (1990).
20. Geissler, P.R., Quantitative Analysis of Ethoxylated Alcohols by Supercritical Fluid Chromatography, *Ibid. 66*:685–689 (1989).
21. Johnson, A.E., P.R. Geissler, and L.D. Talley, Determination of Relative Ethoxylation Rate Constants from Supercritical Fluid Chromatographic Analysis of Ethoxylated Alcohols, *Ibid. 67*:123–131 (1990).
22. Marcomini, A., and W. Giger, Simultaneous Determination of Linear Alkylbenzenesulfonates, Alkylphenol, Polyethoxylates, and Nonylphenol by High-Performance Liquid Chromatography, *Anal. Chem. 59*:1709–1715 (1987).
23. Rockwood, A.L., and T. Higuchi, Liquid Chromatography/Mass Spectrometry (LC/MS) Analysis of Non-Ionic Surfactants Using the FRIT-FAB Method, *Tenside Surfactants Deterg. 29*:6–12 (1992).
24. Lawrence, D.L., The Application of Normal Phase Liquid Chromatography/Mass Spectrometry By Using Coaxial Continuous Flow Fast Atom Bombardment, *J. Am. Soc. Mass Spectrom. 3*:575–581 (1992).
25. Matsumoto, K., S. Tsuge, and Y. Hirata, Analysis of Non-Ionic Surface Active Agents by Supercritical Fluid Chromatography/Mass Spectrometry, *Mass Spectroscopy 35*:15–22 (1987).
26. Takeuchi, T., S. Watanabe, N. Kondo, M. Goto, and D. Ishii, Liquid Chromatography/Fast-Atom-Bombardment Mass Spectrometry of Nonionic Detergents, *Chromatographia 25*:523–525 (1988).
27. Kalinoski, H.T., and L.O. Hargiss, Supercritical Fluid Chromatography-Mass Spectrometry of Non-Ionic Surfactant Materials Using Chloride-Attachment Negative Ion Chemical Ionization, *J. Chrom. 505*:199–213 (1990).
28. Rivera, J., J. Caixach, I. Espadaler, J. Romero, F. Ventura, J. Guardiola, and J. Om, New Mass Spectrometric Techniques in the Analysis of Organic Micropollutants in Water: Fast Atom Bombardment and HPLC/MS, *Water Supply 7*:97–103 (1989).
29. Schröder, H.F., Surfactants: Non-Biodegradable, Significant Pollutants in Sewage Treatment Plant Effluents, *J. Chrom. 647*:219–234 (1993).
30. Schröder, H.F., Pollutants in Drinking Water and Waste Water, *Ibid. 643*:145–161 (1993).
31. Field, J.A., T.M. Field, T. Poiger, and W. Giger, Determination of Secondary Alkane Sulfonates in Sewage Wastewaters by Solid-Phase Extraction and Injection-Port Derivatization Gas Chromatography/Mass Spectrometry, *Environ. Sci. Technol. 28*:497–503 (1994).
32. Evans, K.A., S.T. Dubey, L. Kravetz, I. Dzidic, J. Gumulka, R. Mueller, and J.R. Stork, Quantitative Determination of Linear Primary Alcohol Ethoxylate Surfactants in Environmental Samples by Thermospray LC/MS, *Anal. Chem. 66*:699–705 (1994).
33. Lyon, P.A., F.W. Crow, K.B. Tomer, and M.L. Gross, Analysis of Cationic Surfactants by Mass Spectrometry/Mass Spectrometry with Fast Atom Bombardment, *Ibid. 56*:2278–2284 (1984).
34. Wernery, J.D., and D.A. Peake, The Effect of Surface Activity on Quantitation of Linear Alkylbenzenesulfonates by Fast-Atom Bombardment Mass Spectrometry, *Rapid Communications in Mass Spectrometry 3*:396–399 (1989).
35. Facino, R.M., M. Carini, P. Minghetti, G. Moneti, E. Arlandini, and S. Melis, Direct Analysis of Different Classes of Surfactants in Raw Materials and in Finished Detergent Formulations by Fast Atom Bombardment Mass Specrometry, *Biomedical and Environmental Mass Spectrometry 18*:673–689 (1989).
36. Simms J.R., T. Keough, S.R. Ward, B.L. Moore, and M.M. Bandurraga, Quantitative Determination of Trace Levels of Cationic Surfactants in Environmental Matrices using Fast Atom Bombardment Mass Spectrometry, *Anal. Chem. 60*:2613–2620 (1988).
37. Ikonomou, M.G., A.T. Blades, and P. Kebarle, Electrospray-Ion Spray: A Comparison of Mechanisms and Performance, *Ibid. 63*:1989–1998 (1991).
38. Kebarle, P., and L. Tang, From Ions in Solution to Ions in the Gas Phase, The Mechanism of Electrospray Mass Spectrometry, *Ibid. 65*:972–986 (1993).

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