HPLC Analysis of Quaternary Ammonium Surfactants with the Evaporative Light Scattering Detector

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A normal-phase high-pressure liquid chromatography technique has been elaborated for the separation of quaternary ammonium surfactants. The separation was achieved on a bonded polyphenol silica gel column with gradient elution and evaporative light-scattering (ELS) detection. The proposed method has been applied to the quantitative determination of low levels of monoalkyltrimethylammonium and trialkylmethylammonium chlorides in dialkyldimethylammonium chloride.

KEY WORDS: Analysis, cationic surfactants, evaporative light scattering detector, fabric softeners, HPLC, quantitation, quaternary ammonium salts, separation.

Dialkyldimethyl quaternary ammonium compounds (quats) are widely used as disinfectants, fabric softening agents, foam depressants and antistatic agents. Their properties are dependent on both the distribution of the fatty chain and the nature of the substitution at the quaternary nitrogen. Recent studies have demonstrated that the presence of certain contaminants greatly influence the performance of cationic surfactants in cosmetic and household products. The primary focus of this paper is the quantitative determination of mono- and trialkyl quats in dialkyldimethylammonium chloride.

Dialkyldimethylammonium salts are usually prepared from fatty acids or, to a lesser extent, from fatty alcohols, which are transformed into fatty amines. These amines are finally quaternized with methyl chloride to obtain predominantly dialkyldimethylammonium chloride that contains monoalkyltrimethyl and trialkylmethylammonium chloride as by-products.

Several publications have described the analysis of cationic surfactants by high-temperature gas chromatography (GC) (1), nuclear magnetic resonance (NMR) (2), thin-layer chromatography coupled with flame ionization detection (3) and high-pressure liquid chromatography (HPLC). Of the various techniques available, HPLC seems to be the most promising because the analysis is performed directly on the cationic surfactant without derivatization or modification of the quat structure, simultaneously providing information on the chainlength distribution of the fatty moieties and the nature of the quaternary substitution.

The available HPLC methods refer to refractive index (4,5) and conductivity detection (6), or to indirect photometry (7). These modes of detection, limited to isocratic elution, are not totally satisfactory for the separation of quats with a wide range of molecular weight. Recently, the mass evaporative light scattering detector (ELS) has been introduced as a universal detector compatible with gradient elution. The principle of this detector is that the eluent from the HPLC column is nebulized, the carrier solvent is evaporated in a heated column, and the eluted solutes less volatile than the carrier solvent remain as a fine cloud of particles, which is carried at high speed past a tungsten light source. Light scattered by this particle cloud is detected by a photomultiplier. The ELS detector has been employed in the analysis of carbohydrates (8), lipids (9) and, lately, to nonionic and anionic surfactants (10).

In this study, a direct HPLC technique with ELS detection designed for the separation and quantitation of mono- and trialkyl quats is described. The proposed method has been successfully applied to the analysis of quat raw materials, quat mixtures and commercial products.

EXPERIMENTAL PROCEDURES

Reagents and surfactants. The solvents were HPLC-grade from Romil Chemicals (Leics, England) or Merck (Darmstadt, Germany), and trifluoroacetic acid (reagent-grade) was purchased from Aldrich (Milwaukee, WI). Trialkylmonomethyl (T) reference material was received from the quat manufacturer. This material was assayed by both carbon-13 NMR and by two-phase titration with the mixed-indicator technique.

Dialkyldimethylammonium bromide (D) with C18 alkyl chain was purchased from The Eastman Kodak Company (Rochester, NY). Monoalkyltrimethyl ammonium bromide (M) with carbon chain C12, C14, C16, C18, monoalkyl dimethyl benzyl ammonium bromide (2MB) with carbon chain C12, C14, C16, tetramethylammonium bromide (4M) and dimethylbenzylhexadecylammonium chloride (CBDMC, used as reference standard) were purchased from Fluka (Buchs, Switzerland).

Apparatus. The liquid chromatographic system consisted of a Spectra-Physics (St. Albans, England) model SP8800-020 ternary gradient pump, model SP8780XR-021 autosampler, model SP4270-220 integrator with Winner Workstation and ACS evaporative light scattering detector model 75014.

All experiments were performed on a 250 × 4.6 mm stainless steel column packed with 5-micron RSil polyphenol (Bio-Rad RSL, Eke, Belgium) and a guard column (50 × 3.2 mm) packed with the same material. All the separations were obtained by gradient elution with a flow rate of 1.5 mL/min and were carried out at ambient temperature. The gradient elution program is summarized in Table 1. Detector conditions were air pressure, 1 bar; evaporation temperature, 95°C; time constant, 5 seconds; and photomultiplier setting, 1. After each run, the mobile phase was reset to the initial conditions, and 15 min were allowed for column equilibration. Quantitation was ef-

TABLE 1

Gradient Elution Program

Time (min)	Solvent A[a]	Solvent B[b]
0	90	10
20	10	90
25	10	90

[a]5mM Trifluoroacetic acid (TFA) in n-hexane.
[b]5mM Trifluoroacetic acid in THF/methanol (3:1).

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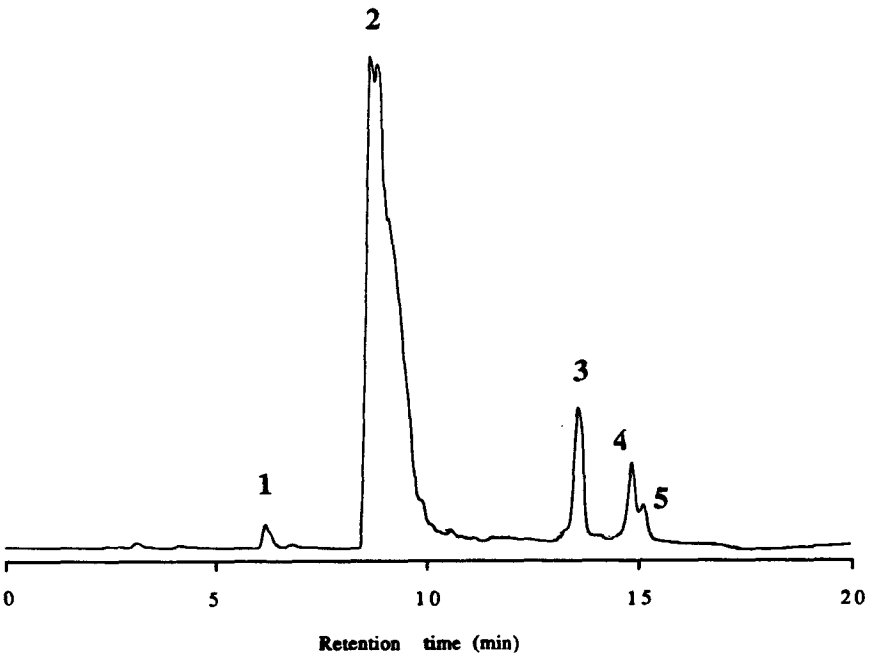

FIG. 1. HPLC analysis of dialkyldimethyl quat (technical grade). Peaks: 1, trialkyl quat; 2, dialkyl quat; 3, CBDMC; 4, monoalkyl quat (C18); and 5, monoalkyl quat (C16).

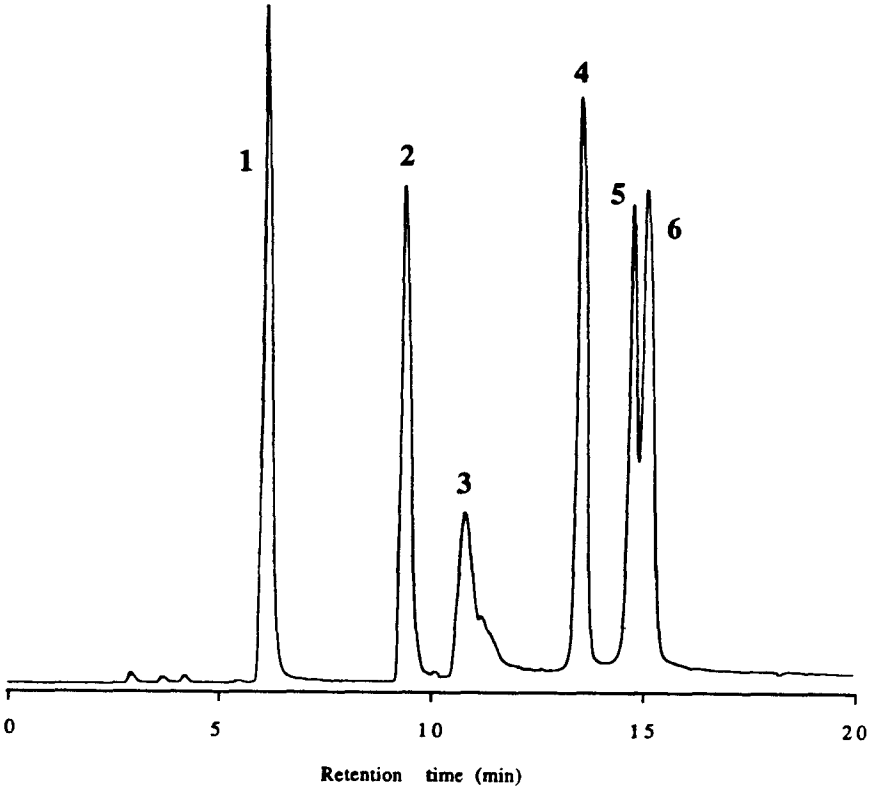

FIG. 2. HPLC analysis of quaternary ammonium salt mixture. Peaks: 1, trialkyl quat; 2, dialkyl quat; 3, imidazolinium salt; 4, CBDMC; 5, monoalkyl quat (C18); and 6, monoalkyl quat (C16).

TABLE 2

Retention Data of Quaternary Ammonium Ions

Quat	MW	k′	RT (min)
T (C18)	788	2.16	6.0
D (C18)	546	4.3	10.0
M (C18)	310	7.26	15.7
M (C18)	310	7.26	15.7
M (C16)	284	7.5	16.1
M (C14)	256	7.8	16.7
2MB (C16)	360	6.7	14.7
2MB (C14)	332	7.0	15.1
2MB (C12)	304	7.3	15.7
4M	74	11.4	23.5

fected by peak area integration with respect to a response factor determined with an internal standard technique.

RESULTS AND DISCUSSION

HPLC analysis of quaternary ammonium salts. The separation of the quaternary ammonium salts was performed with hexane in a high percentage of methanol/tetrahydrofuran rather than with the more usual solvents such as diethyl ether and chloroform with a much smaller amount of modifier. This type of solvent mixture gives better retention time stability than traditional normal-phase solvent systems (11).

Trifluoroacetic acid was added as ion-pairing agent to improve peak shape, to reduce tailing and to avoid column contamination with amines (often present in quaternary ammonium salts), which may form complexes with phenolic groups and thus modify retention times (12). Figures 1 and 2 are typical chromatograms of a commercial dimethyl-di- (hydrogenated) tallow ammonium chloride and a quaternary ammonium salt mixture, respectively. Some of the peaks in Figure 1 are unsymmetrical, which is due to the chainlength distribution of the tallow fatty acid starting material. A chainlength distribution of a typical hydrogenated beef tallow fatty acid would yield approximately 65% C18 and 30% C16 alkyl chainlengths (the negligible contributions from C12, C14 and C20 alkyl chainlength totalling less than 5% have been ignored for convenience). In the case of trialkyl quat (peak 1), four species are co-eluting and we observe one unsymmetrical peak. For dialkyl quat (peak 2), three species are co-eluting; however, we observe some separation. Finally, with monoalkyl quat, which has only one species per alkyl chainlength, a separation is effected (peaks 4 and 5). This separation is well illustrated in Figure 2, where pure reference quats were used to prepare the mixture. To demonstrate the applicability of this procedure to other quats, an imidazolinium-type quaternary ammonium salt (technical grade) was included.

The simultaneous determination of dialkyl quat by this

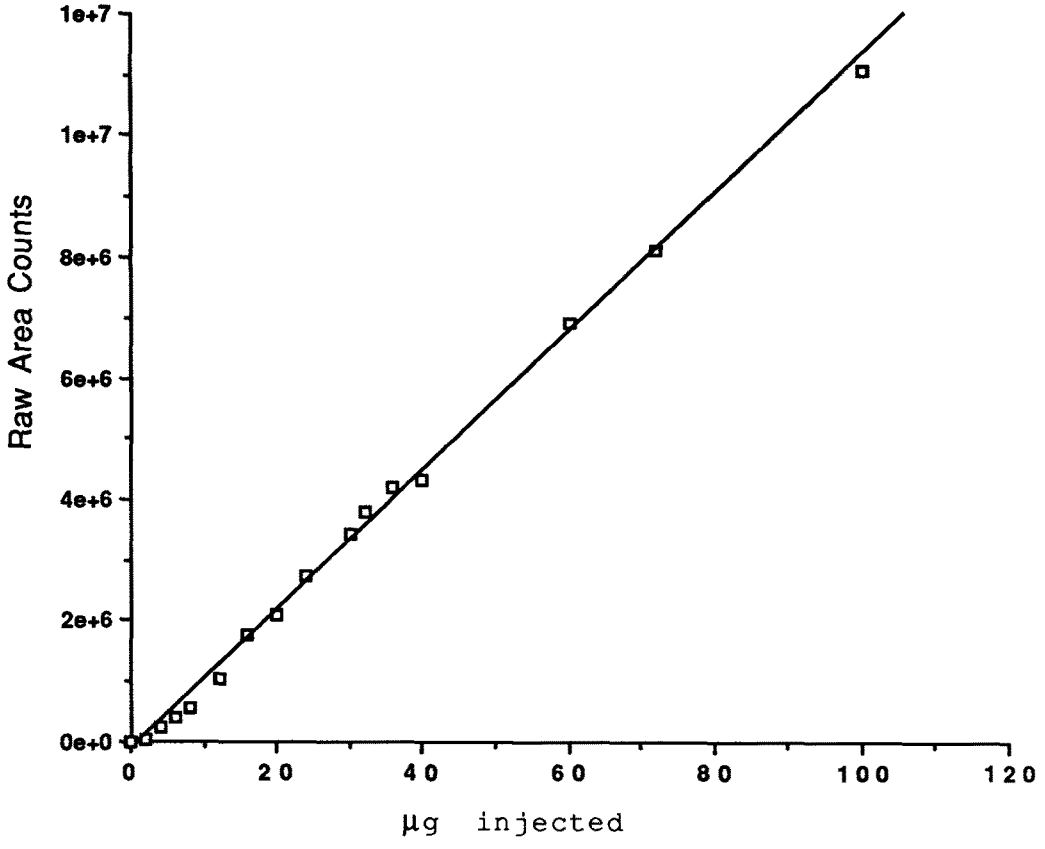

FIG. 3. Detector response for trialkyl quat.

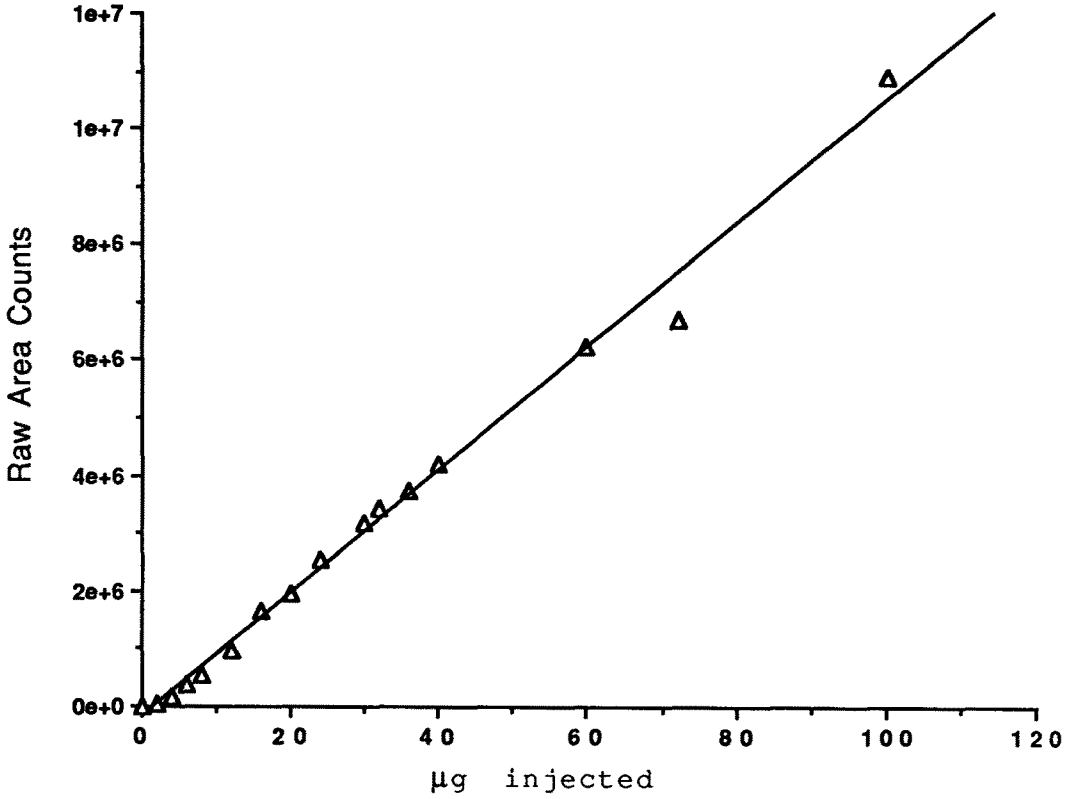

FIG. 4. Detector response for monoalkyl quat.

TABLE 3

HPLC-ELS Analysis of Dimethyl-Di- (Hydrogenated) Tallow Quat

Compound	Mean (n=6)	RSD[a]
Trialkyl quat	4.5%	0.8%
Monoalkyl quat	4.1%	1.2%

[a]Relative standard deviation.

procedure is possible; but it is not recommended with this type of sample because the ratio of dialkyl quat to internal standard is not optimum. For purposes of quality control it is sufficient to subtract the trialkyl and monoalkyl concentrations from the total cationic active matter obtained by two-phase titration with the mixed-indicator technique.

The capacity factor of several series of quaternary ammonium salts was investigated and these data are presented in Table 2. Within a homologous series, the retention time decreases as the molecular weight increases. The substitution of methyl groups by groups with a long alkyl chain greatly influences the retention time, from 23.5 min for the tetramethylammonium ion to 6.0 min for the trialkylmethylammonium ion. This can be explained by the greater nonpolar character, present in the trialkyl quats, allowing less interaction on a molar basis with the polar polyphenol groups of the column, resulting in lower k′ values for the quats of higher molecular weight. Furthermore, ion pairing with the trifluoroacetate ion is impeded due to shielding of the quaternary ammonium ion (retention times are shorter when trifluoroacetic acid is omitted from the mobile phase).

Quantitative analysis of quaternary ammonium salts. The linearity of the ELS detector was investigated for the trialkyl and monoalkyl quats. The detector response curves, *i.e.*, the amount injected on column *vs.* peak area, are linear over the range of 0–100 µg for both trialkyl quat and monoalkyl quat, as shown in Figures 3 and 4. All calibrations and analyses of these components were effected within this range of linear response. An internal standard procedure with dimethylbenzylhexadecylammonium chloride (CBDMC) as reference standard was adopted. Calibration standards were prepared by weighing appropriate amounts (20–100 mg) of both trialkyl and monoalkyl quats into 40-mL screw-cap tubes and adding 25 mL of internal standard solution, which was comprised of 50 mg of the reference standard in 25 mL of 5mM trifluoroacetic acid in hexane/methanol/THF (80:10:10). The sample solutions were prepared by dissolving one gram of quat in 25 mL of I.S. solution, and the injection volume was fixed at 20 µL. The results from the analysis of a commercial dimethyl-di- (hydrogenated) tallow ammonium chloride are collected in Table 3.

The HPLC results are in good agreement with the values obtained by quantitative carbon-13 NMR. The method has been successfully extended to household and cosmetic products. The combination of normal-phase HPLC with ELS detection provides a simple, rapid and efficient separation of a wide range of quaternary ammonium surfactants. The procedure has proved to be extremely valuable for both quality control of raw materials and analysis of commercial products.

REFERENCES

1. David, F., and P. Sandra, *HRC & CC 11*:897 (1986).
2. Fairchild, E.H., *J. Am. Oil Chem. Soc. 59*:305 (1982).
3. Neuman, J.M., *Iatron Technical Literature*, Hampshire, April 25, 1977, p. 10.
4. Nakamura, K., and Y. Morikawa, *J. Am. Oil Chem. Soc. 59*:64 (1982).
5. Spagnolo, F., M.T. Hatcher and B.K. Faulseit, *J. Chrom. Sci. 25*:399 (1987).
6. Wee, V.T., and J.M. Kennedy, *Anal. Chem. 54*:1631 (1982).
7. Helboe, P., *J. Chromatog. 261*:117 (1983).
8. Macrae, R., and J. Dick, *Ibid. 210*:138 (1981).
9. Stolyhwo, A., H. Colin and G. Guiochon, *Anal. Chem. 57*:1342 (1985).
10. Bear, G.R., *J. Chromatog 459*:91 (1988).
11. Van Damme, F., and M. Verzele, *Ibid. 351*:506 (1986).
12. Barry, J., M. Finklestein and S. Ross, *J. Org. Chem. 49*:1699 (1984).

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