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Journal of Chromatography A, 1027 (2004) 103–108
JOURNAL OF CHROMATOGRAPHY A
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Determination of alkyltrimethylammonium surfactants in hair conditioners and fabric softeners by gas chromatography–mass spectrometry with electron-impact and chemical ionization

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Abstract

The commercial hair conditioners and fabric softeners were analyzed for the content of alkyltrimethylammonium compounds (ATMACs) by gas chromatography–mass spectrometry (GC–MS) with electron impact (EI) and low-pressure positive-ion chemical ionization (PICI) modes. The method involves mixed diluted samples (adjust pH to 10.0) with potassium iodide to enhance the extraction of iodide–$ATMA^+$ ion pairs by direct liquid–liquid extraction. The iodide–$ATMA^+$ pairs were then demethylated to their corresponding nonionic alkyldimethylamines (ADMAs) by thermal decomposition in a GC injection-port. A high abundance of ADMAs was detected at the temperature above 300 °C in the GC injection-port. The enhanced selectivity of quasi-molecular ion chromatograms of C_{12}–C_{18}-ADMA, obtained using methanol PICI-MS enables ADMAs to be identified. The accuracy and precision of the method was validated and was successfully applied to determine contents of ATMAC in commercial hair conditioners and fabric softeners. The contents of total measured ATMAC ranged from 0.4 to 6.9% for hair conditioners, and from 3.3 to 4.6% for fabric softeners.

Keywords: Cosmetics; Surfactants; Alkyltrimethylammonium compounds

1. Introduction

Cationic surfactants are applied in many commercial hair conditioners and fabric softeners as softeners, antistatics and bactericides. Alkyltrimethylammonium compounds (ATMACs) are one of the most important softening agents as a mixture of linear alkyl homologues of dodecyl- (C_{12}), tetradecyl- (C_{14}), hexadecyl- (C_{16}) and octadecyl- (C_{18}) trimethylammonium chlorides or bromides. After use, ATMAC are normally discharged via wastewater treatment facilities to surface waters. Hence, they can disturb the ecosystem due to their toxicity to aquatic organisms [1–3]. However, information on the content of ATMAC in most commercial hair conditioners and fabric softeners in Taiwan is unavailable. None of them was labeled ATMAC in the products, and some products were only labeled as containing "cationic surfactants". Therefore, the concentration of ATMAC in hair conditioners and fabric softeners and the associated environmental risk are not assessable, and concentrations of ATMAC in municipal effluents and sewage could not be evaluated. The widespread use of ATMAC, and the increasing public concern over environmental issues have stimulated our interest to investigate the content and distribution of ATMAC in commercial hair conditioners and fabric softeners.

Numerous analytical methods for cationic surfactants have been developed. Typically, cationic surfactants are treated with anionic dyes, to form ion-pair complexes, which can be then extracted by solvents and followed by spectrophotometry [4–6]. However, these methods lack specificity to differential individual homologues, and suffer from many interfering compounds. HPLC is the most promising method for the analysis of these cationic surfactants. However, due to the lack of UV absorption by long-chain quaternary ammonium surfactants, electrical conductivity detection or indirect detection were usually employed with HPLC [7–13]. LC–MS with electrospray may represent a powerful method for determining of QACs [14–16], but the required equipment is expensive and not easily available. GC or GC–MS is not only more readily available in many

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doi:10.1016/j.chroma.2003.10.047

analytical laboratories, but also provides a higher chromatographic resolution with a capillary column. GC and GC–MS has been used for determination of long-chain cationic surfactants by converting them to the corresponding tertiary amines by thermal decomposition in the injection-port, or by the Hofmann elimination to decompose them [17–23]. Currently, demethylation of alkyltrimethyl ammonium bromides in Bayer process liquors with potassium iodide in injection-port has been reported [24]. However, quantitative determination of content of C_{12}–C_{18}-ATMACs by GC–MS in commercial product samples has yet to be achieved.

As part of a larger effort to characterize the impact of ATMACs in the environment, a simple and rapid method for routinely determining the contents of ATMAC homologues in various hair conditioners and fabric softeners was developed. The method involves sample dilution, liquid–liquid extraction and GC–MS analysis of their corresponding alkyldimethylamines (ADMAs) using various MS techniques. In addition to the EI studies, the methanol as CI reagent gas was also applied to facilitate molecular weight determination of these corresponding ADMAs in hair conditioners and fabric softeners [25]. This work undertakes a preliminary study of the ATMAC content in hair conditioners and fabric softeners sold in Taiwan, to support the surface water pollution prevention and control programs.

2. Experimental

2.1. Chemicals and reagents

Dodecyltrimethyl ammonium bromide (99% purity) was from Sigma (St. Louis, MO, USA). Hexadecyl- and octadecyltrimethyl ammonium bromides (all above 98% purity) were obtained from ChemServices. Tetradecyl trimethyl ammonium bromide and undecyldimethylamine (C_{11}-ADMA, as an internal standard) were purchased from Aldrich (Milwaukee, WI, USA). All other high purity chemicals and solvents were purchased from Aldrich, Tedia (Fairfield, OH, USA) and Merck (Darmstadt, Germany), and were used without further purification. Standard mixture containing 100 μg/ml of each ATMAC compound in methanol was prepared. Reagent grade potassium iodide was purchased from Mallinckrodt. Deionized water was further purified with a Millipore water purification device (Bedford, MA, USA). The hair conditioners and fabric softeners as liquid forms were purchased from local supermarkets or nationwide wholesale markets.

2.2. Sample preparation

The hair conditioners and fabric softeners were diluted with water. In order to provide the effective demethylation results, an exchange of ATMAC from chloride or bromide salts to iodide salts was attempted by mixing with solid KI and then extracted as iodide ion-pairs by dichloromethane liquid–liquid extraction [24,25]. Solid KI (0.5 g) was added into 5 ml of diluted hair conditioners and fabric softeners, and the pH of the solution was adjusted to 10.0 by 1 M NaOH. The iodide–$ATMA^+$ ion-pair was then consecutively extracted by dichloromethane (1 ml each) liquid–liquid extraction three times in a vial. The organic extracts were dried by sodium sulfate and transferred to a 5-ml Reacti-Vial. The extract was evaporated to dryness under a stream of nitrogen. The residue was then redissolved in 100 μl of dichloromethane containing 20 μg/ml of C_{11}-ADMA, and made ready for thermal demethylation GC–MS analysis. To eliminate contamination, all glassware was cleaned and rinsed subsequently with hot tap water, deionized water, methanol and acetone before drying, and then heated overnight at 250 °C.

2.3. GC–MS Analysis

Analyses were carried out on a Varian 3400CX gas chromatograph directly connected to a Saturn 2000 ion-trap mass spectrometry (Walnut Creek, CA, USA) at unit resolution. A ChromatoProbe and a temperature-programmed injector were used to introduce a large-volume sample and on-line derivatization approach, as described elsewhere [25]. The injector temperature was held at 80 °C for 4 min for solvent vaporization, then the injector was heated to 300 °C immediately and held for another 20 min. A DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film, from J&W, USA) connected to 2 m of deactivated fused-silica per-column (as retention gap), was used. After 2 min of holding the injector temperature at 300 °C, the GC temperature program began as follows: 70 °C for 6 min, followed by a temperature ramp at 10 °C/min to 300 °C, and hold for 2 min.

The MS system was tuned with perfluorotributylamine (PFTBA) by using the autotune program. The transfer line was set at 300 °C. Full scan EI data was acquired under the following conditions: mass range 50–500 *m/z*, scan time 1 s, solvent delay 11 min, manifold temperature 80 °C, emission current 10 μA (at 70 eV electron energy), automatic gain control (AGC) target 21,000. For low-pressure PICI mass spectrum analysis, methanol was used as CI reagent gases in the selected ejection chemical ionization mode (SECI), according to our previous report [25]. The CI full scan data was acquired under the following conditions: mass range 100–500 *m/z*, scan time 1 s, solvent delay 12 min, manifold temperature 80 °C and ion trap temperature 160 °C. Reagent ions were ionized for a variable duration set by automatic reaction control (ARC) of the instrument. The optimal conditions of ARC parameters was used as following: 0.1-ms ARC ionization time, 2.0-ms CI maximum ionization time, 40-μs CI maximum reaction time, 15-*m/z* CI ionization storage level, 15-*m/z* CI reaction storage level, 45-*m/z* CI background mass, and 10-V reagent ion eject amplitude [25]. The autotune program was used to set most instrument parameters with target 10 000 at a filament current of 10 μA. The pressures of reagent gases in the ion trap were

approximately 2×10^{-5} T (1 T = 133.322 Pa). The peak areas of the EI-extracted ion chromatograms (*m*/*z* 58) and CI-extracted ion chromatograms (their quasi-molecular ions $[M + H]^+$) of the corresponding ADMAs were applied for quantitation and identification, respectively.

3. Results and discussion

3.1. Method optimization

According to our previous experience with thermal demethylation, injecting the iodide–ATMA$^+$ ion-pairs could improve the chromatograms and produce the highest average peak areas and quantitative results [25]. The peak response was increased by more than one order of magnitude and peak tailing was reduced. Therefore, an exchange of ATMA$^+$ from bromide or chloride salts to iodide salts was employed as reported elsewhere [24,25]. The effect of injection temperature on the formation of ADMAs was also investigated. Among the temperature from 270 to 320 °C, the highest average peak areas of the corresponding ADMAs were detected when injection temperature exceeding 300 °C. Comparing the relative abundances of corresponding commercial ADMA standards at 300 °C, more than 80% of iodide–ATMA$^+$ ion-pairs had been converted to the corresponding ADMAs in the injection-port.

3.2. GC–MS analysis

Fig. 1a depicts the extracted ion chromatograms (*m*/*z* 58) of ADMAs, and their corresponding EI mass spectra (Fig. 1b) as detected in a hair conditioner sample-F. They are the same mass spectra as those of C_{12}–C_{18}-ADMAs reported in the database of the NIST/EPA Mass Spectra Library. Normally, the molecular ion $[M]^+$ was present in low abundance, consistent with the long-alkyl chain of the aliphatic amines. The base peak, showing an ion at *m*/*z* 58, corresponds to the carbon–carbon bond α-cleavage with respect to nitrogen, which is stabilized by an imminium ion ($[CH_2{=}N(CH_3)_2]^+$), as reported previously for aliphatic amines [25,26]. PICI-MS technique was applied to ascertain the corresponding ADMAs identification by their protonated molecular signals $[M + H]^+$. The use of methane, methanol and acetonitrile as CI reagent gases had been evaluated. Among them, methanol provided the most stable and large $[M + H]^+$ signals, especially for C_{16}- and C_{18}-ADMAs as reported previous [25]. Under low pressure CI condition, the methanol mainly contains ions of protonated methanol (*m*/*z* 33). Fig. 2a shows the quasi-molecular ion chromatograms of C_{11}–C_{18}-ADMA,

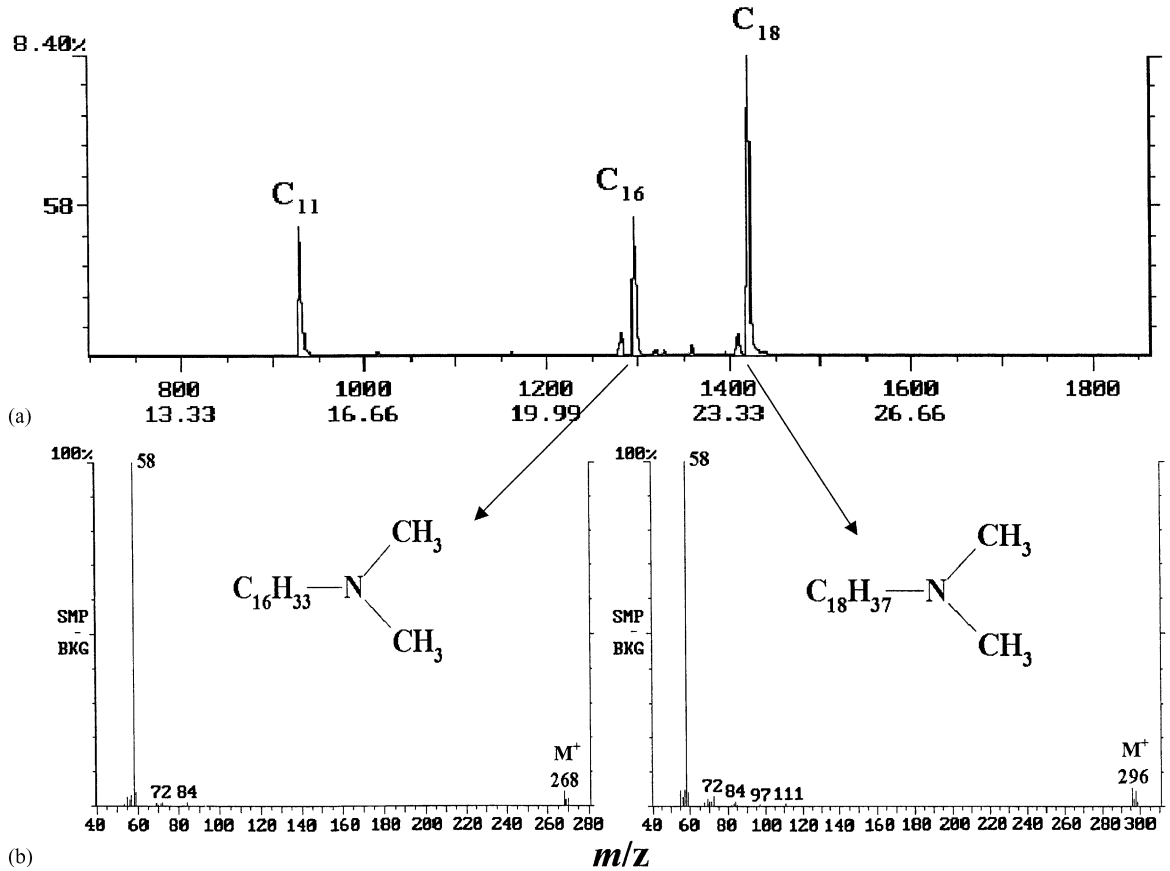

Fig. 1. (a) EI-extracted ion chromatograms (*m*/*z* 58) of ADMAs, and (b) their corresponding EI mass spectra as detected in a hair conditioner sample-F.

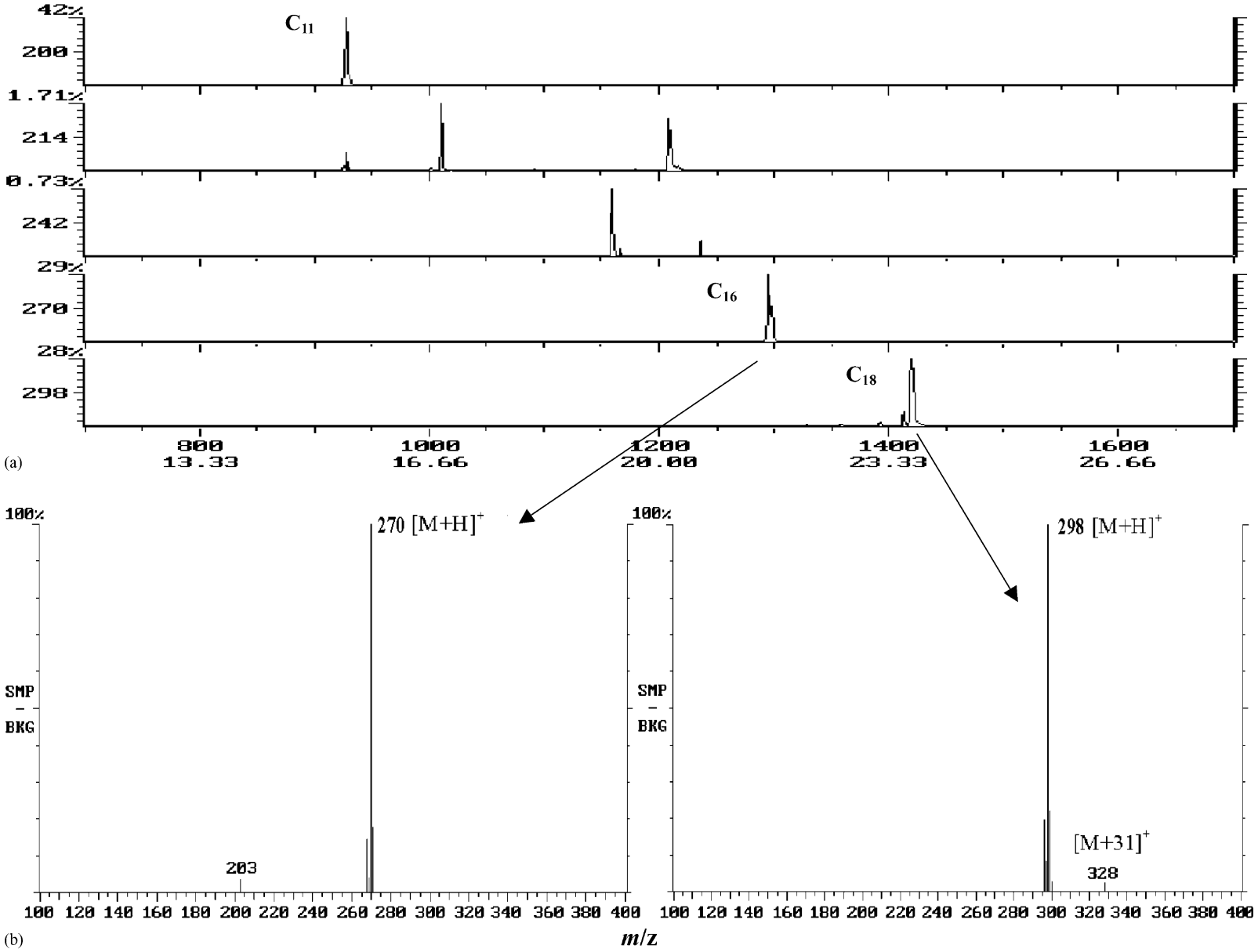

Fig. 2. (a) Quasi-molecular ion chromatograms of C_{11}–C_{18}-ADMA, and (b) their corresponding methanol PICI mass spectra as detected in a hair conditioner sample-F.

and their corresponding methanol PICI mass spectra as detected in a hair conditioner sample-F (Fig. 2b). Only protonated molecular signals ($[M+H]^+$) as base peaks associated with small $[M + 31]^+$ adduct ions were observed. These high abundance signals facilitate determining the molecular ions of corresponding ADMA homologues in complex samples.

3.3. Method validation and applications

The analytical characteristics of the method, such as linear response range, reproducibility and quantitation limit, were investigated to evaluate the efficiency of the method and the possibility of the method application to real samples. The linearity of ATMAC homologues was calculated from the five-level calibration curve (or average response factor) over the range 0.5–10 μg/ml, each divided by the fixed concentration of the internal standard. The precision of the calibration curve, as indicated by the relative standard deviation (R.S.D.) of response factors, was 10, 5, 5 and 3% for C_{12}-, C_{14}-, C_{16}- and C_{18}-ADMAs, respectively. The correlation coefficients (r^2) exceeded 0.997 for all four homologues. The precision of the method, as indicated by the R.S.D. of the recovery, was assessed using five independent extractions of $ATMA^+$ in chloride forms exchange to iodide forms in deionized water. The recoveries were above 80% and R.S.D. ranging from 6 to 12%, as shown in Table 1, indicating good repeatability of the method developed in this work. Table 1 also lists the recovery of the matrix spiked sample and the contents of ATMAC detected in the samples of hair conditioners and fabric softeners. High rates of recovery, above 84% with R.S.D. ranged from 4 to 13%, were obtained for four homologues from the matrix spiked samples. The results indicate that the method is suited to analyzing ATMAC in hair conditioner samples. Six hair conditioners and three fabric softeners were employed as test samples after appropriate dilutions. The variation in the homologous distribution from different manufacturers was observed with the total ATMAC content ranging from 0.4 to 6.9% for hair conditioners, and 3.3–4.6% for fabric softeners (although the homologous distributions were not given by the manufacturers). Figs. 1 and 2 show the EI extracted ion chromatogram (*m*/*z* 58) and the PICI quasi-molecular ion chromatograms of ADMAs, as well as their corresponding mass spectra detected in the hair conditioner sample-F. During the analysis of the samples we found that, even through the calibration curves were measured down to the 0.5 μg/ml level, the real detection and quantitation limits appeared to be lower, as ATMAC of the order 0.2 μg/ml could still be determined.

Table 1
Analytical reproducibility and contents of ATMAC found in hair conditioners and fabric softeners

Sample	ATMAC (%)			
	C_{12}	C_{14}	C_{16}	C_{18}
Deionized water				
Spike recovery (%) ($n = 5$)	80[a] (12)[b]	92 (6)	88 (10)	89(7)
Hair conditioner-A				
Background content (%)	0.28	0.22	0.86	1.31
Spiked recovery (%) ($n = 3$)	93[a] (9)[b]	84 (13)	88 (4)	86 (11)
Hair conditioner-B	n.d.	n.d.	0.89	n.d
Hair conditioner-C	0.08	0.11.	0.19	0.06
Hair conditioner-D	n.d.	n.d.	2.72	n.d.
Hair conditioner-E	0.09	0.09	0.41	n.d.
Hair conditioner-F	n.d.	n.d.	0.89	5.98
Fabric softener-A	n.d.	0.13	1.38	3.09
Fabric softener-B	n.d.	n.d.	1.04	2.58
Fabric softener-C	n.d.	n.d.	1.04	2.24

[a] The spike recovery.
[b] The relative standard deviations (R.S.D., %) are given in parentheses; n.d.: not detected at method quantitation limit 0.02%.

4. Conclusion

The analytical procedure developed herein demonstrates that the liquid–liquid extraction and GC–MS methods that involve a thermal demethylation reaction are reliable, sensitive and offer convenient analytical techniques for determination of ATMAC in commercial product samples. The iodide salts enhanced the extraction and the thermal demethylation of $ATMA^+$ in GC injection-port. Using methanol as the reagent gas for PICI-MS provides high-intensities of protonated molecular signals, enabling confirmatory molecular ion data to be recorded by EI-MS. Preliminary results in this study demonstrated that ATMAC are widely used in various hair conditioners and fabric softeners in Taiwan. The survey is currently being studied across Taiwan in order to understand the homologous distribution of these cationic surfactants in the household products.

Acknowledgements

This research was supported by a grant from the National Science Council of Taiwan under contract No. NSC 91-2113-M-008-020.

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