
Analysis of Cationic Surfactants in Cosmetics By Reverse phase Ion-Pair Chromatography with Suppressed Conductivity Detector and UV Detector

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Keywords

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Abstract

Determination of several cationic surfactants in cosmetics has been investigated. Reverse phase ion pair chromatography was used to identify and quantitate cationic surfactants. Cationic surfactants analyzed in this experiment were cetylpyridium chloride (CPC), cetyltrimethyl ammonium chloride (CTAC), stearyltrimethylammonium chloride (STAC), bezalkonium chloride (BKC), benzyldimethylcetyl ammonium chloride (BDCAC), and bihenyltrimethyl ammonium chloride (BTAC). The separation was achieved on a reverse phase (C18) column with 10mM HCl-acetonitrile eluent. In this condition, the most of cationic surfactants with exception of CPC and CTAC were easily separated from each other. In contrast to CTAC, CPC absorbs UV light ($\lambda_{max} = 263nm$). Thus, based on this fact, we were able to characterize and quantitate CPC and CTAC respectively with suppressed conductivity detector (SCD) and UV detector connected in series. The calibration curves obtained by plotting the peak areas of the cationic surfactants were linear at levels ranging from 0.005 to 0.1% (correlation coefficient, $r = 0.9988$ (0.9998)). The detection limits were 1 to 5ppm (25ng (125ng) in sample solution. The average recoveries of cationic surfactants added to hair treatment cream and hair rinse in three to five experiments were 96.7 (105.2% and relative standard deviations were 1.1-3.8%. The case that there were CPC and CTAC in same solution was also tested. CPC and CTAC which couldn't be separated on reverse phase column were quantitated with suppressed conductivity detector and UV detector connected in series. Recovery of CPC and CTAC were 101.6 and 89.2% respectively. The proposed method was applied to the determination of cationic surfactants in commercial hair treatment cream.

Introduction

Surfactants are used as emulsifiers and solubilizers in cosmetics. They are generally classified into nonionic, anionic, cationic and amphoteric according to their ionogenic properties. Because cationic surfactants of these surfactants are useful as fabric softeners, corrosion inhibitors, and antimicrobial agents, they are commonly used in a wide variety of health care, domestic products and cosmetic preparations. However they are not used in general-purpose detergents, for they do not provide effective cleaning at neutral pH.

Several publications[1] have described the analysis of cationic surfactants by high-temperature gas chromatography (GC), injection port pyrolysis GC[2], nuclear magnetic resonance (NMR), thin-layer chromatography (TLC) coupled with flame ionization detection and high-performance liquid chromatography. But, the HPLC method of the various techniques available seems to be the most promising because the analysis is performed directly on the cationic surfactant without derivatization or modification, simultaneously providing information on the chain length distribution of the fatty moieties and the nature of the quaternary substitution. Thus, most of published papers are HPLC method.

Because the charge of cationic surfactants makes it difficult to separate them with reverse phase HPLC method ion-pairing agents such as HCl and HClO₄ are added to mobile phase for neutralizing their charge. This method that is widely used to separate cationic surfactants is reverse phase ion-pair chromatography (RP-IPC)[3].

The available HPLC detection methods[3-9] refer to refractive index (RI), evaporative light scattering (ELS) conductivity, photometry and inverse photometry (IP). In this mode of detection, photometry is commonly used to detect cationic surfactant (for example, cetylpyridium chloride, benzalkonium chloride) but it cannot detect ones that do not have a UV-absorbing chromophore (for example, alkyltrimethylammonium chloride). Thus such cationic surfactants are detected with RI, ELS and IP. However RI and IP are not sensitive, and ELS is not compatible with mobile phase containing salts such as ion-pairing agents. Conductivity detector, like refractive index detector, can detect cationic surfactants that don't absorb UV light, and it is as sensitive as UV detector. Suppressed and nonsuppressed ion-chromatographic techniques of conductivity detector are available for the analysis. Because background conductivity of suppressed technique is low and baseline is stable, suppressed conductivity is more sensitive than nonsuppressed technique.

Cosmetic products are enough complex that twenty and fifty raw materials are mixed. Therefore, several pretreatment have been developed to remove matrix for analyzing cationic surfactants such as clean-up with minicolumn, liquid-liquid extraction, etc.[4,10,11,12].

In this work, six cationic surfactants which are frequently mixed in cosmetics were determined by RP-IPC with suppressed conductivity detector (SCD) and UV detector. This method developed in our laboratory was simple and convenient because it did not need any special pretreatment in sample preparation steps. Recovery tests for evaluating the reproducibility and accuracy of this method were performed on hair treatment cream and hair rinse, and good results were acquired. And cationic surfactants of commercial hair treatment cream were analyzed with this proposed method.

Experimental

Reagent and surfactants.

The solvents were HPLC-grade from Fisher scientific (USA). Hydrochloric acid (reagent-grade) was purchased from Junsei Chemical Co. (Japan) and Tetrabutylammonium hydroxide (TBAOH) was purchased from Sigma Chemical Co. (USA). Six cationic surfactants were analyzed in this experiment. Their chemical structure and symbolic names used in this study are illustrated in Table 1. Cetylpyridinium chloride (CPC) was purchased from Wako Pure Chemical Co. (Japan) and benzyldimethylcetylammmonium chloride (BDMCAC) was purchased from Tokyo Chemical Co. (Japan). Benzalkonium chloride (BKC) was purchased from Aldrich Chemical Co. (USA). bihenyltrimethyl ammonium chloride (BTAC), ceryltrimethylammonium chloride (CTAC), and stearyltrimethylammonium chloride (STAC) were purchased from Keon Chang Chemical Co. (Korea).

HPLC analysis.

A Dionex Ion Chromatography equipped with IP20 isocratic pump, rheodyne injector (25 µl injection volume) and CD20 conductivity detector was used to separate cationic surfactants. Suppression was achieved with a Dionex Cationic Micromembrane Suppressor and 5mM TBAOH as regenerant at 6-8mL/min. A Spectroflow 757 UV detector (ABI Analytical Kratos Division, USA) was used in series with the suppressed conductivity detector to characterize and quantify CPC. A Spectra-Physics DataJet Integrator (Spectra-Physics, San Jose, OA) was used to obtain and process data. All separations were performed isocratically on a YMC-Pack ODS A analytical column (Octadecyl bonded silica, 5µm packing, 25cm long x 4.6mm i.d., YMC inc, Japan) and IonPack AG 12A guard column (Dionex, USA) to remove anions (containing anionic surfactant) in sample solutions which may be acted as ion-pairing agents. The mobile phase was 10mM HCl-acetonitrile (20:80) and flow rate was 1mL/min.

Sample preparation.[2]

Samples containing about 20mg of cationic surfactants, were suspended with 30mL ethanol by mild heating and vigorous shaking, sonicated for 10-20min, and diluted to 50mL. Before HPLC analysis the homogenized samples were filtered through a 0.45µm membrane filter.

Standard solution.

Raw materials (standards) were diluted in ethanol, sonicated for 10-20min and filtered through a 0.45 µm membrane filter before analysis. The concentrations of them are 0.005, 0.01, 0.02, 0.04, 0.06 and 0.1%.

Recovery test.

Hair treatment cream without cationic surfactant was made for recovery test. Because hair rinse without cationic surfactant was not stable, it was made with 2% of STAC for recovery test. 5g of these samples for recovery test were taken in 50mL volumetric flask and 2mL of 1% raw material solutions was added. And then the next procedures for analysis were the same as previous sample preparation.

Results and Discussion

HPLC analysis of cationic surfactants.

The separation of cationic surfactants was performed on reverse phase C18 column with acetonitrile/water mobile phase and hydrochloric acid was added as ion-pairing agent to improve peak shape and to reduce tailing. A Dionex Cationic Micromembrane Suppressor was used to reduce the background conductivity of the electrolyte in eluent before it enters the conductivity cell. Because only anions can go to another side of cationic micromembrane in suppresser, anions (in our case, Cl⁻) of eluent were exchanged with those of regenerant anions (typically OH⁻) and cations (H⁺) of eluent was neutralized with OH⁻ from regenerant. Therefore the background conductivity of eluent which has been passed through suppresser is low. Suppression with 5mM TBAOH as a regenerant was effective enough that the total conductivity of eluent was only 0.5-1.0 μ S and baseline was very stable. Fig. 1 is typical chromatogram of cationic surfactants detected with SCD. Most cationic surfactants with exception of CPC and CTAC were clearly separated. CPC absorbs the UV light ($\lambda_{max} = 263nm$) in contrast to CTAC. Thus, although CPC and CTAC could not separate with HPLC, they, based on UV absorbing properties of them, could be characterized by connecting UV detector in series with SCD (Fig. 2).

Calibration curve for quantitation cationic surfactants.

The linearity of SCD and UV detector (in the case of CPC) was investigated for the cationic surfactants. The detector response curves, i.e., the amount injected on column vs. peak area, are linear over the range 0.005-0.1% (Table 2). And detector response for cationic surfactant was sensitive enough to detect about 1 to 5ppm (25-125ng) of them.

Recovery test.

Recovery tests were carried out to evaluate the reproducibility and accuracy of the proposed method. A hair treatment cream and a hair rinse were spiked with the amounts of cationic surfactants reported in Table 3 and subjected to the described analytical procedure. Recoveries of six cationic surfactants in cosmetic products were excellent as shown in Table 3. The pretreatment of this proposed method is simple and conventional, that is, there is no any special pretreatment such as clean-up with minicolumn (for example Sep-Pak cartridge). But, in spite of that, the analysis of cationic surfactants was not interfered by matrix of sample, as shown in Fig. 3 and Fig. 4.

The case that there were CPC and CTAC in the same solution, was also tested (Table 4). These cationic surfactants which were spiked in advance as if previous experiments were separated and detected with SCD and UV detector connected in series. And data analysis was performed with two steps. At first, the concentration of CPC was calculated with peak areas of a chromatogram obtained with UV detector. At second, the area equivalent to the conductivity of CPC concentration was subtracted from the total area of sample peak (CPC and CTAC) of a chromatogram obtained with SCD. Then, from this data CTAC was quantified. Results of this experiment were shown in Table 4. Recovery of CPC was excellent and that of CTAC was reasonable.

Analysis of commercial hair treatment cream.

This method set up previously was applied to the analysis of hairtreatment cream which was commercially sold in common store. Sample was subjected to the described analytical procedure (Fig.5). From the chromatogram of sample it was found that the cationic surfactant mixed in this sample was CTAC. And from the area of CTAC peak, the concentration of CTAC was calculated as 6.0%. Sample matrix did not also interfere analyzing CTAC with this proposed method, as shown in Fig.5.

Conclusion

We developed a method of simultaneously determining six cationic surfactants used commonly in cosmetic products by RPIPC. This method is simple and convenient. The accuracy of this proposed method was found to be very good from the results of recovery test. And this method was applied to analyze the commercial hair treatment cream.

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Table 1. Chemical structures of cationic surfactants studied

Peak NO.	Surfactant Name	Symbolic Name	Chemical Structure
1, 2	Benzalkonium Chloride	BKC	<p style="text-align: right;">Cl⁻ R: C₁₂ - C₁₄</p>
3	Cetyltrimethyl ammonium Chloride	CTAC	<p style="text-align: right;">Cl⁻</p>
4	Cetylpyridium Chloride	CPC	<p style="text-align: right;">Cl⁻</p>
5	Benzylcetyldimethyl ammonium Chloride	BCDAC	<p style="text-align: right;">Cl⁻</p>
6	Stearyltrimethyl ammonium Chloride	STAC	<p style="text-align: right;">Cl⁻</p>
7	Bihenyltrimethyl ammonium Chloride	BTAC	<p style="text-align: right;">Cl⁻</p>

Table 2. Calibration results for cationic surfactants

Sample	Correlation coefficient
BKC	0.9991
CPC	0.9998
CTAC	0.9993
BCDAC	0.9988
STAC	0.9988
BTAC	0.9998

Table 3. Recovery of cationic surfactants added to hair treatment cream and hair rinse

Cationic Surfactants	Amount added	Hair treatment cream		Hair rinse	
		Ave. recovery(%)	RSD(%)	Ave. recovery(%)	RSD(%)
BKC	2%	99.4	1.7	102.8	1.3
CPC	2%	100.5	2.5	102.2	0.5
CTAC	2%	100.9	2.0	100.7	3.0
BCDAC	2%	98.9	2.5	99.4	1.9
STAC	2%	99.0	2.0	105.2	1.1
BTAC	2%	96.7	3.8	97.8	2.1

Table 4. Recovery of CPC and CTAC added to a hair treatment cream in the same time.

Cationic surfactant	Amount added	Ave. Recovery(%)	RSD (%)
CPC	2%	101.6	1.1
CTAC	2%	89.2	2.1

Figure 1. RPIPC analysis of cationic surfactants mixture. Cationic surfactants were detected with SCD. Most of them with exception of CPC and CTAC were clearly separated. Peaks are listed in table 1.

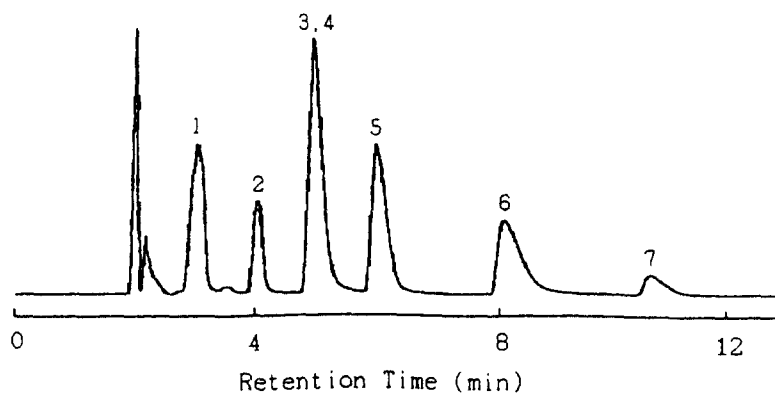


Figure 2. The characterization of CTAC and CPC by RPIPC with SCD and UV detector connected in series. Both were detected with SCD, but CTAC was not detected in contrast to CPC with UV detector.

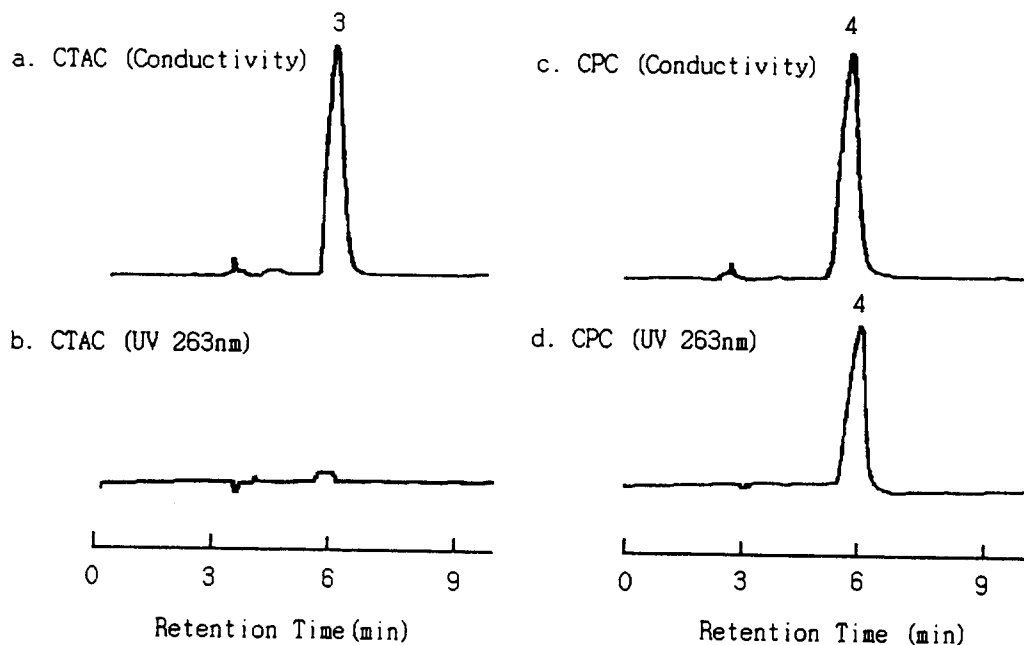


Figure 3. The chromatogram of cationic surfactants mixture in hair treatment cream. They were separated by RPIPC and detected with SCD. The matrix of hair treatment cream did not interfere analysis of cationic surfactants.

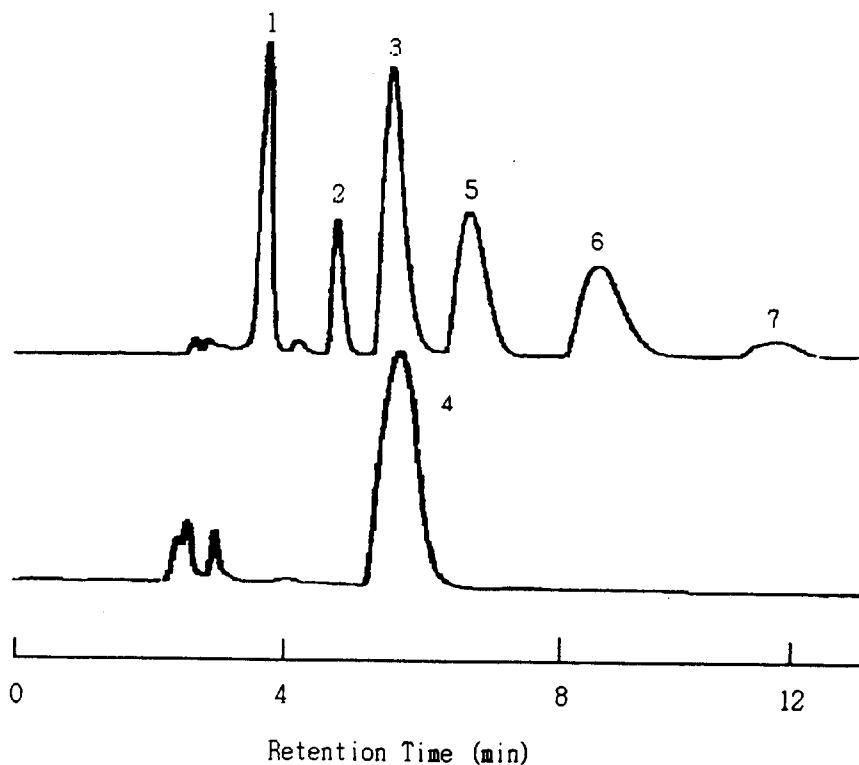


Figure 4. The chromatogram of cationic surfactants mixture in hair rinse. They were separated by RPIPC and detected with SCD. The matrix of hair rinse did not interfere analysis of cationic surfactants.

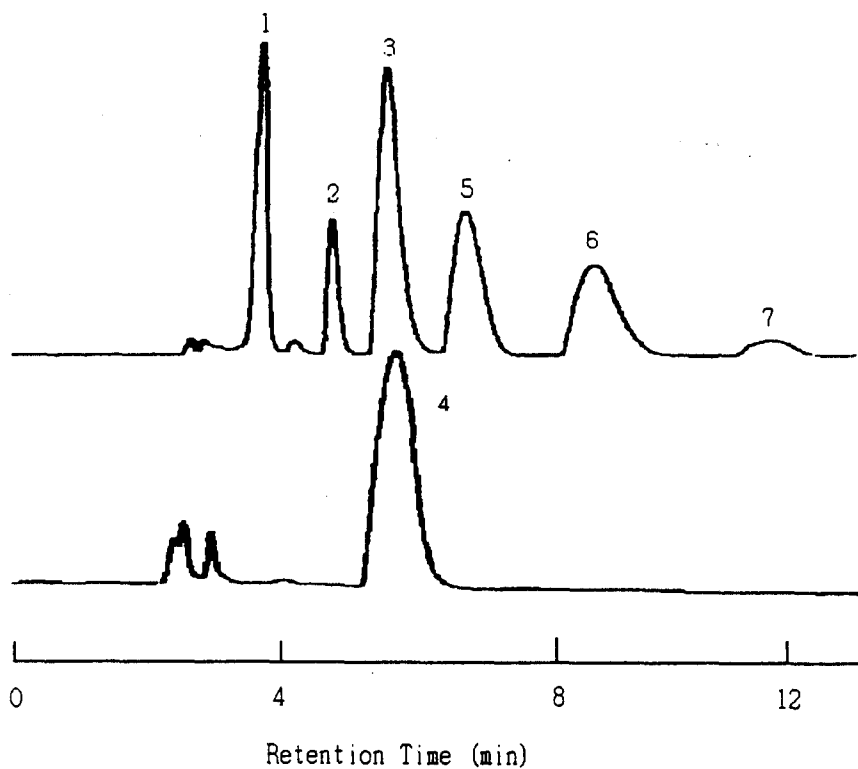


Figure 5. The chromatogram of commercial hair treatment cream. From this, it was found that the cationic surfactant mixed in commercial hair treatment cream was CTAC.

