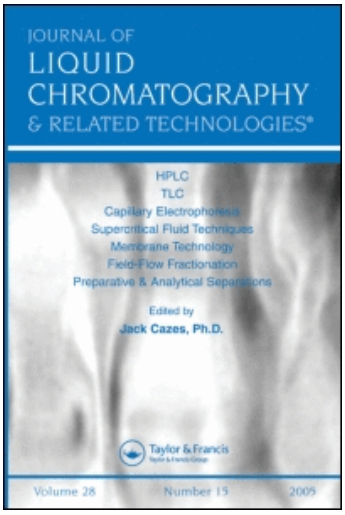

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ANALYSIS OF QUATERNARY AMMONIUM COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH EVAPORATIVE LIGHT SCATTERING DETECTION

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ABSTRACT

A high performance liquid chromatographic (HPLC) procedure employing an Evaporative Light Scattering Detector (ELSD) for the analysis of quaternary ammonium compounds in ethnic hair care formulations is reported.

INTRODUCTION

Quaternary ammonium compounds (quats) comprise a great number of materials used primarily as surfactants and antimicrobials. They are used in applications ranging from laundry softeners to phase-transfer catalysts and hair conditioners. Chemically, these compounds are substituted ammonium salts, where the nitrogen atom is covalently bound to four alkyl or aryl groups. The result is a nitrogen atom with a net positive charge that maintains its character regardless of the surrounding pH.

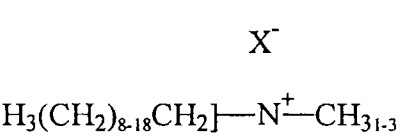


Figure 1. Simplified Structure of Typical, Commercially Available Quaternary Ammonium Mixture

The associated anionic component of a quat can be a bromide, chloride or methosulfate ion. Quats are usually marketed with a solvent which can be water, isopropyl alcohol, propylene glycol or sold as a flake to make handling easier.

Analysis of quaternary ammonium compounds is difficult by reverse phase HPLC due to the nature of their composition. The alkyl portion of these compounds is typically a homologous series of C8 through C20 varying in percent composition based upon the source used in production. This means that commercial quaternary ammonium compounds are comprised of many similar molecules with a distribution based upon the aliphatic chain length (see Figure 1). This type of molecular distribution actually enhaces the effectiveness of surfactants. Being a surfactant, the quaternary ammonium molecule has both hydrophobic and hydrophilic moieties. Furthermore, direct determination of these quaternary surfactants in their various sample matrices is complicated.

Many HPLC methods for the determination of quaternary alkylammonium compounds have been reported. These methods generally fall into the categories of environmental recovery and quality control. Wee and Kennedy reported a normal phase method for the determination of cationic surfactants without separation of the homologous series in environmental samples.[1] This method has been continuously improved by others.[2-4] Many HPLC methods exist for the determination of alkylammonium compounds in which the homologous series is resolved.[5-7]

Additionally, other HPLC methods have been reported for the determination of alkylammonium compounds in pharmaceuticals in which the homologous series may or may not be resolved.[8-11] A suitable method for the quality control of quaternary ammonium compounds in cosmetic formulations was reported by Matsuzaki and others.[12]

The requirement of the reported analysis was that the homologous series of the quaternary ammonium compounds not be resolved. The goal was to elute the series as a single peak separated from all other components in the sample matrix. The charge of the quaternary amine appeared the most logical approach to obtain the goal. It followed that the selectivity of ion-exchange chromatography would elute the homologous series as a single peak.

The selectivity of organic compounds in cation-exchange chromatography is complex. Extraneous to true ion exchange, hydrophobic interactions between the polymer backbone of the ion exchanger and the fatty portion of the ion, as well as solvation, play a major role in selectivity of organic ions.

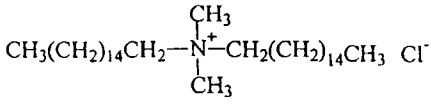
Dumont, Fritz and Schmidt reported the use of non-aqueous solvents in cation-exchange for the selective separation of protonated primary, secondary and tertiary amines.[13] By using strictly non-aqueous mobile phases, the hydrophobic interactions and solvation effects were minimized. These workers concluded that the size and shape of the cation may affect ion-exchange selectivity. Alternatively, Spagnolo and others, reported an ion-exchange HPLC method using non-aqueous buffers.[14]

Similarly, the described methods have been modified to demonstrate selectivity for several different types of quaternary alkylammonium chlorides in a typical hair relaxer formulation. The new method disclosed here is a selective, precise and accurate method for the determination of alkylammonium chlorides in a typical hair relaxer formulation.

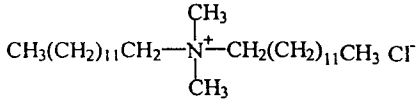
EXPERIMENTAL

Chemicals and Reagents

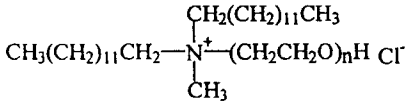
HPLC grade acetonitrile, HPLC grade methanol, and reagent grade ammonium formate all were purchased from Fisher Scientific. N-Hexadecyl-N,N-dimethyl-1-hexadecanaminium chloride (Varisoft 432 PPG, 68.02%), N-Tridecyl-N,N-dimethyl-1-tridecanaminium chloride (Varisoft 2TD, 74.5%), Polyethylene glycol (5) ditridecylmonium chloride (Varisoft 5TD, 56.62%), and N,N-Dimethyl-N-octadecylbenzenemethanaminium chloride (Varisoft SDC-85, 86.7%) were obtained from Witco Corp. The structures of the alkylammonium chlorides are given in Figure 2.



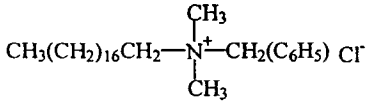
Varisoft 432 PPG



Varisoft 2TD



Varisoft 5TD



Varisoft SDC-85

Figure 2. Aklyammonium Chlorides Under Investigation.

In this study, a typical base phase of a two-part hair relaxer formulation was examined. The materials used in this formulation were as follows: Deionized water, polyoxypropylene (12) polyoxyethylene (65) lanolin oil, petroleum jelly, liquid paraffin, polyoxyethylene (20) cetyl/stearyl ether, 1-hexadecanol, 1-octadecanol, and calcium hydroxide. To this blend was added 3% actives of each experimental quat (see Figure 2.). Hair relaxers are formulated to a pH range of 11-13 to effectively modify the secondary protein structure of hair.

Apparatus

The chromatographic system consisted of a Thermo Separation Products (TSP) P4000 pump, TSP AS3000 autosampler, TSP 4400 interface, TSP inline

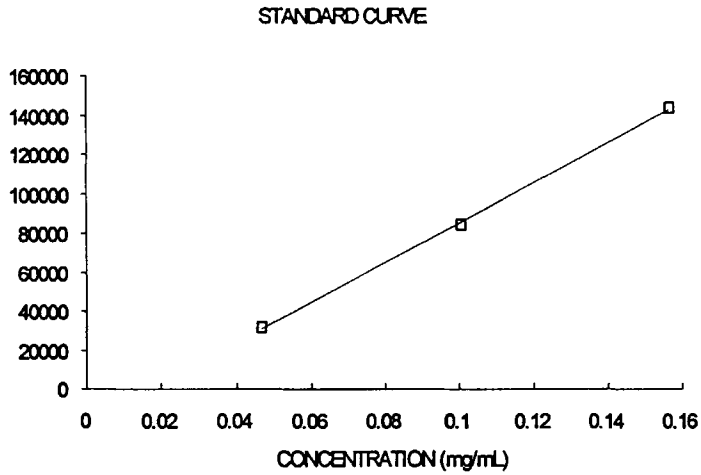


Figure 3. Typical Standard Curve with Linear Regression Shown.

membrane degasser, Varex MKIIIA ELSD set at 85°C and 2.4 SLPM (standard liters per minute), and TSP PC1000 data acquisition system. A Metachem Spherisorb SCX (150 x 4.6 mm, 5 μM) was maintained at ambient temperature.

Mobile Phase

The mobile phase consisted of a methanol buffer containing 0.06M ammonium formate. The mobile phase was filtered through a .45 μm filter (Gelman Sciences, Supor-460, 47 mm) and degassed. The flow rate was 1.0 mL/min.

Preparation of Standards

Stock solutions were prepared by accurately weighing Varisoft 432 PPG, Varisoft 2TD, Varisoft 5TD and Varisoft SDC-85 standards into separate 50 mL volumetric flasks and diluting to volume with acetonitrile.

Standard solutions were prepared by pipeting 1, 2 and 3 mL of the stock solutions into separate 10 mL volumetric flasks and diluting to volume with acetonitrile. A standard curve was generated in the range from 200 to 600 *ppm* (Figure 3).

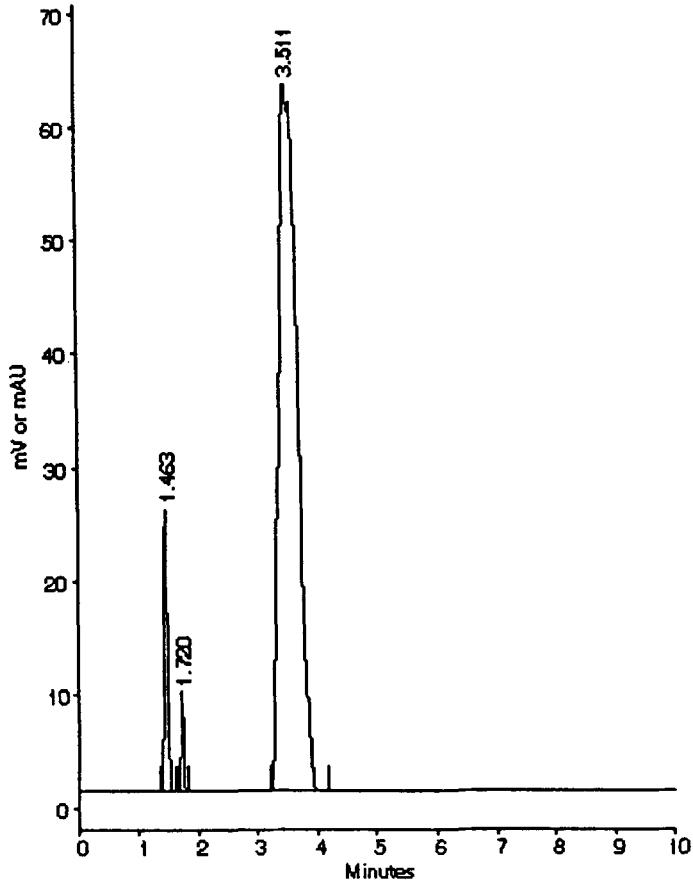


Figure 4. Varisoft 432 PPG Standard.

Preparation of Samples

The sample was placed in a 55°C oven for 15 minutes. The sample was removed, shaken vigorously and *ca.* 100 mg tranferred into a 10 mL volumetric flask in triplicate. These samples were diluted to volume with acetonitrile, sonicated (10 min), shaken (manually) and sonicated (10 min). The samples were left overnight to prevent leaching difficulties. The following day the samples were sonicated (10 min), shaken (manually) and filtered through a .45μM PTFE syringe filter (Alltech Cat. #2386). This sample preparation selectively "floated" the sample matrix in acetonitrile, thereby, extracting the quat.

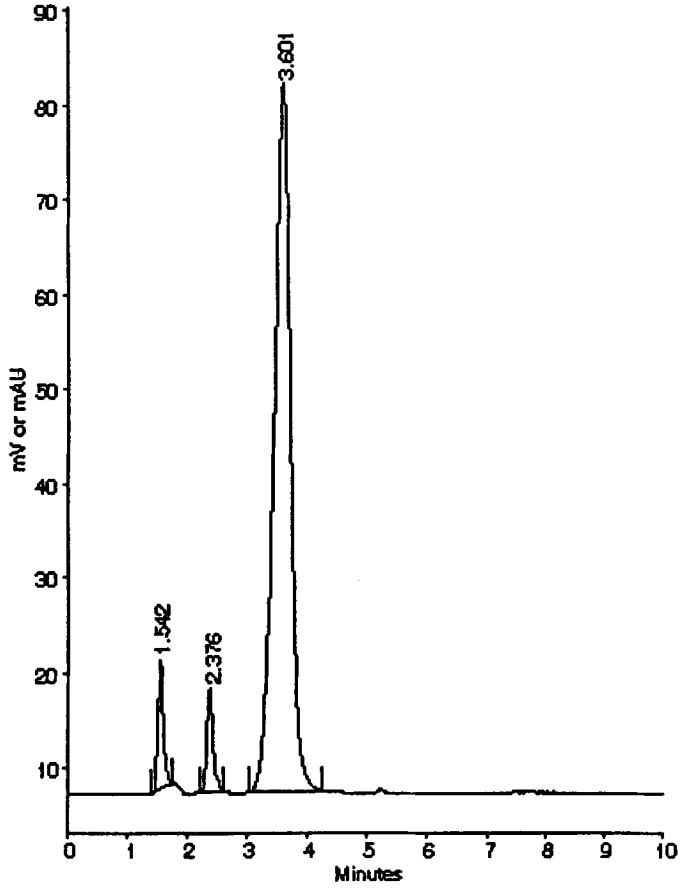


Figure 5. Varisoft 2TD Standard.

RESULTS AND DISCUSSION

Chromatography

Chromatograms resulting from a 20 mL injection of each standard preparation are given in Figures 4-7. The data acquisition time was 10 minutes for all injections.

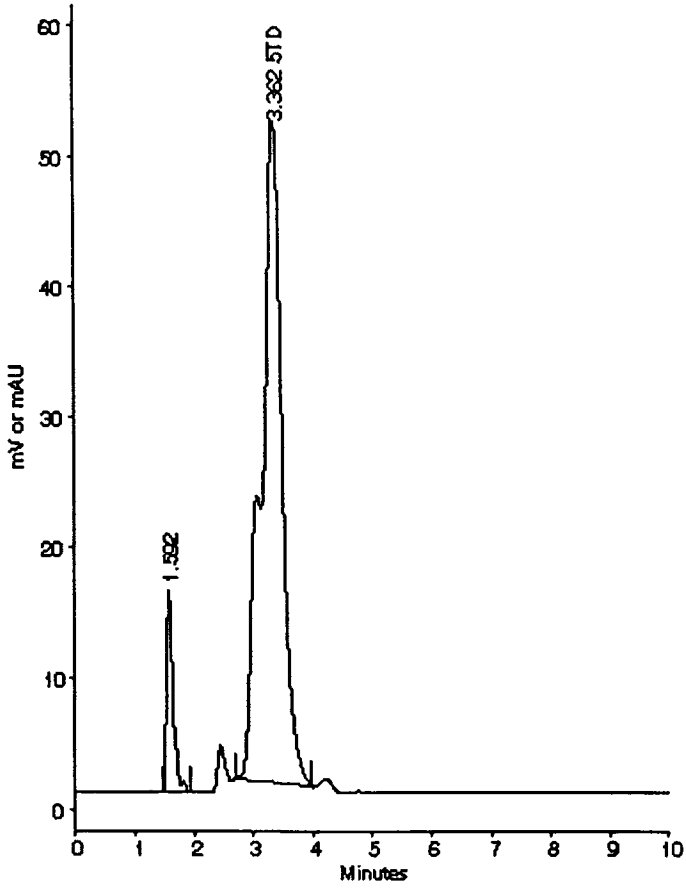


Figure 6. Varisoft 5TD Standard.

System Suitability

Because an ELSD gives a linear response over a narrow range, a three point calibration curve was prepared for each quat each day. A correlation coefficient of 0.999 was the minimum requirement. To ascertain system precision, seven replicate injections of a sample preparation containing Varisoft SDC-85 were assayed and gave an RSD of 0.4%.

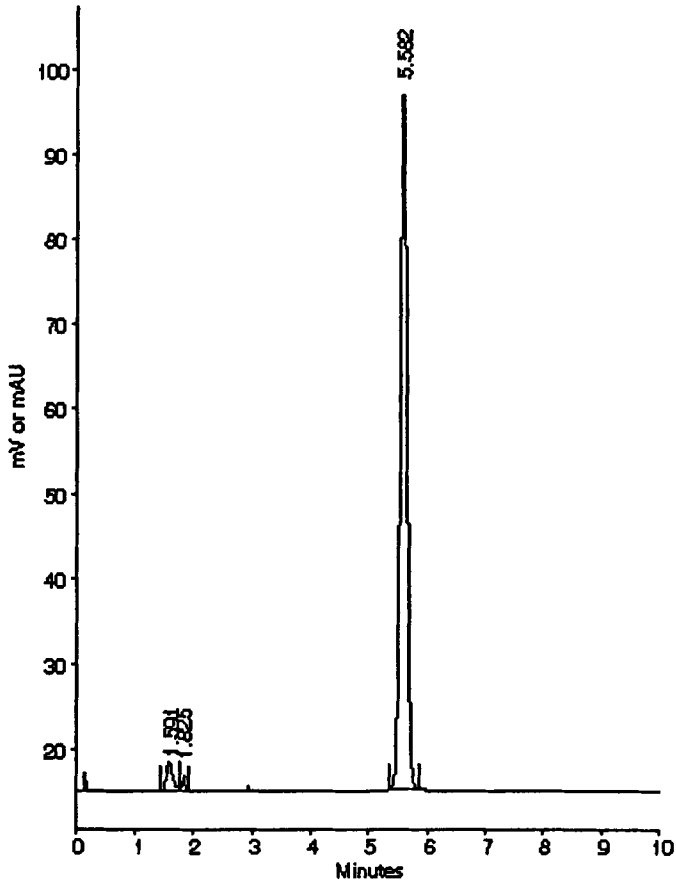


Figure 7. Varisoft SDC-85 Standard.

Sample Preparation

Originally, the sample formulation was dissolved in mobile phase, filtered and injected. Due to the polyoxypropylene/polyoxyethylene fatty alcohols, the chromatograms were quite complicated. Interference from coeluted peaks gave inconsistent results. The sample preparation employed was a novel, simple means of selectively extracting quaternary ammonium compounds from fatty alcohols, oils and waxes.

Precision of Recovery

The precision of recovery for the quaternary ammonium compounds was determined by assaying 10 separate sample preparations containing known concentrations of Varisoft 432 PPG (quat). The RSD of this experiment was 3.8%. The method accuracy was determined by comparing results obtained from the disclosed HPLC method to those obtained from gravimetric titration using silver nitrate. These results were in statistical agreement.

Stress Study

Hair relaxer formulation prepared with Varisoft SDC-85 was stressed with heat (105°C, the pH of the formulation was 13) for 5 days. Five replicate samples were prepared following the sample preparation procedure with the exception that these samples were not left overnight. A degradation of over 60% was noted in all replicates. No interfering peaks at the retention times of the quat were observed.

CONCLUSION

The described ion-exchange HPLC method for the quantitative determination of quaternary alkylammonium compounds in hair relaxer formulations is accurate, precise and reproducible. Additionally, the method is stability-indicating for alkylammonium quats at high pH.

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