

# Analysis of propoxylated fatty alcohols, benzalkonium chlorides and triethanolamine-based esterquat surfactants

## in technical products for detergents by means of GCxGC-EI-(TOF)MS



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### Overview

Three different types of special surfactants in technical products for detergents were analysed. The technique is based on a derivatisation procedure with ensuing chromatographic separation by comprehensive two-dimensional gas chromatography (GCxGC) coupled with a time-of-flight mass spectrometer.

### Introduction

Surface-active agents play an important role in many areas of daily life. Their characteristic features and functions are of great significance. Surfactants are used in cleaning and washing agents, fabric softeners, dispersal agents, emulsifiers and in wetting and foaming agents [1, 2].

For application in the so called I&I-sector (industrial & institutional) detergents are produced and sold which contain substances for "special effects". These may be surface-refining or disinfectant substances which can be mixed into the basic detergent [3, 4].

As a result of the multitude of useable surfactant components of various chemical compositions, modern technical detergents are very complex mixtures. This puts extremely high requirements on the corresponding analyses of the technical products.

Here we present an analysis of three different types of special surfactants in technical products for detergents which is based on comprehensive two-dimensional gas chromatography (GCxGC) coupled with a time-of-flight mass spectrometer [5, 6].

### Methods

Sample preparation:  
50 mg of the technical product was silylated with 2 mL of a BSTFA / MSTFA mixture (5:1; v/v). The derivatisation was carried out for 1 h at 80 °C. Some of the samples were diluted with tetrahydrofuran or isoocctane.

GCxGC-EI-(TOF)MS system:  
LECO Pegasus III; GC Agilent 6890 N; LECO Thermal Modulation System; LECO ChromaTOF™ v. 3.22

1st GC capillary - Varian FactorFour VF-5ms  
(30 m x 0.25 mm x 0.25 μm)  
2nd GC capillary - SGE BPX50  
(1 m x 0.1 mm x 0.1 μm)

BSTFA (N,O-bis-trimethylsilyl-trifluoroacetamide)  
MSTFA (N-methyl-N-trimethylsilyl-trifluoroacetamide)

### Results

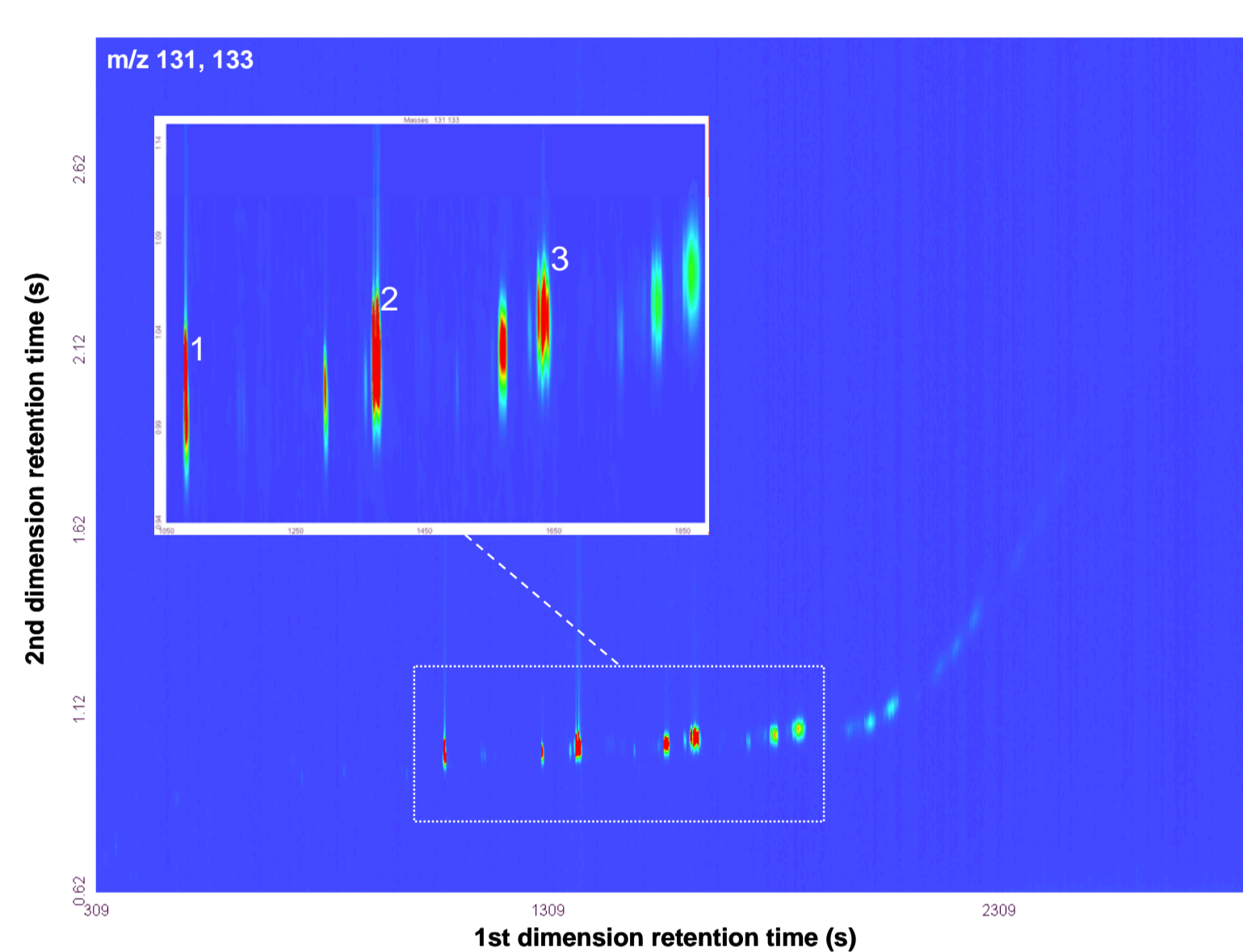


Figure 1  
Extracted GCxGC chromatogram of a propoxylated fatty alcohol (FA-2PO standard)

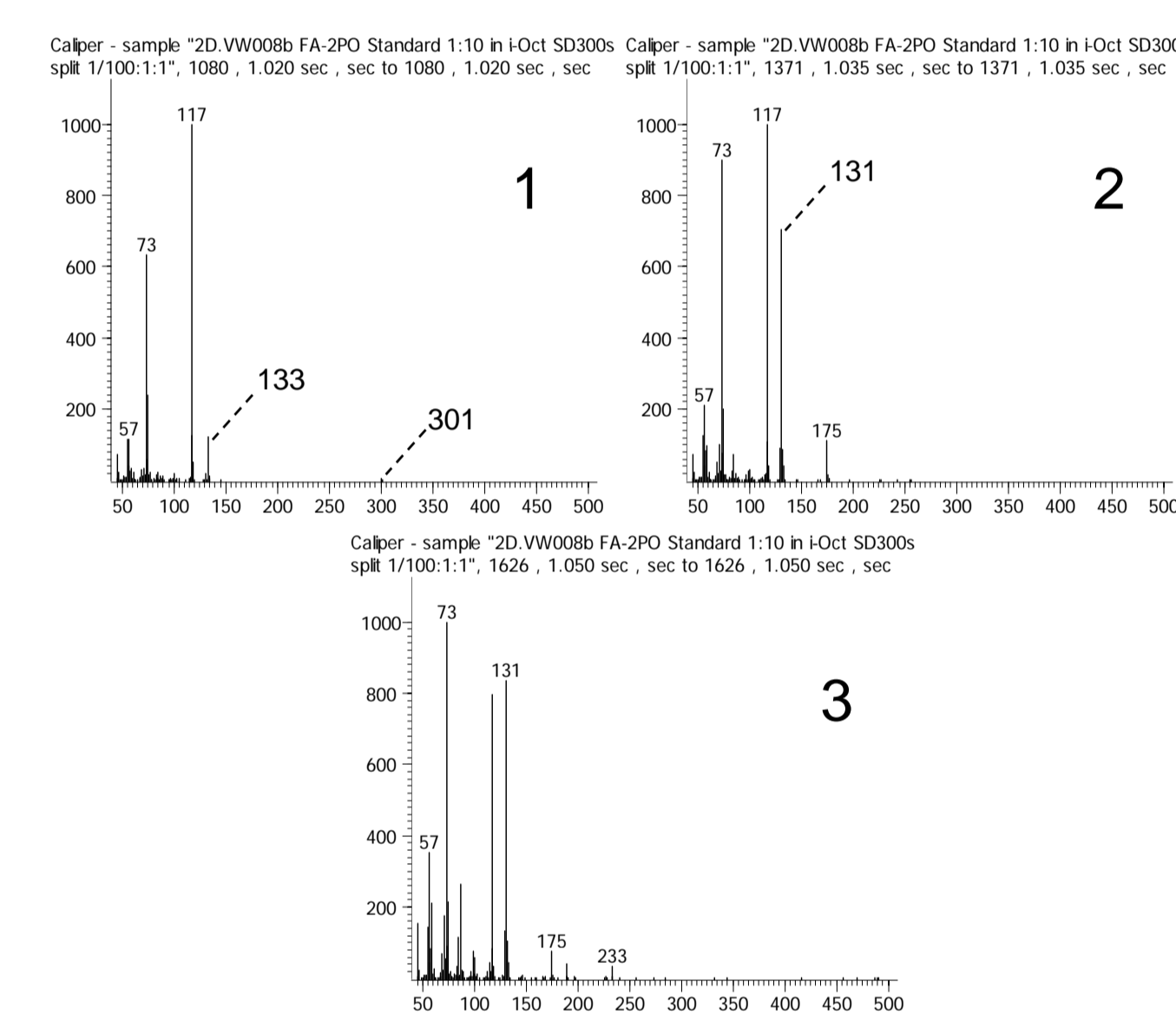


Figure 2  
EI-(TOF) mass spectra of the peaks 1-3 from the chromatogram in figure 1

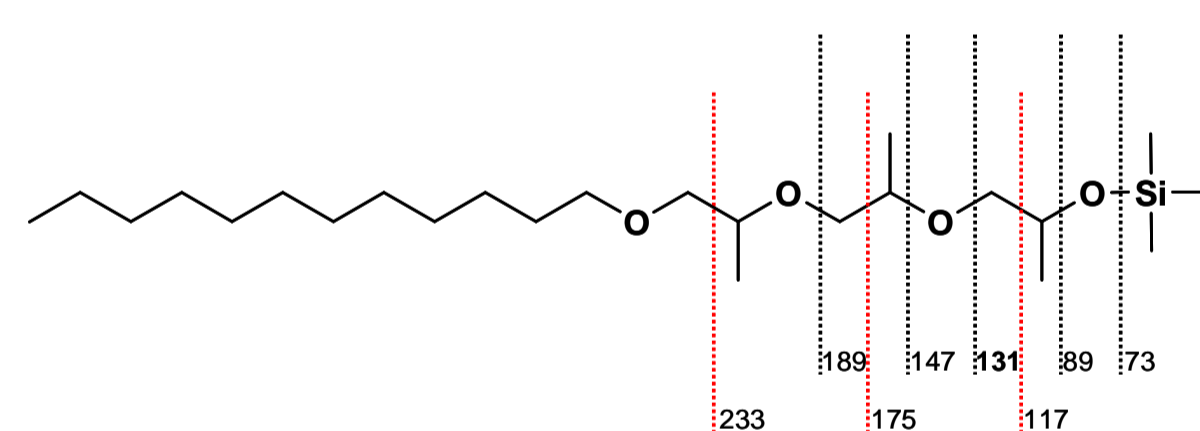


Figure 3  
Typical EI-fragmentation of a propoxylated fatty alcohol (FAPO)

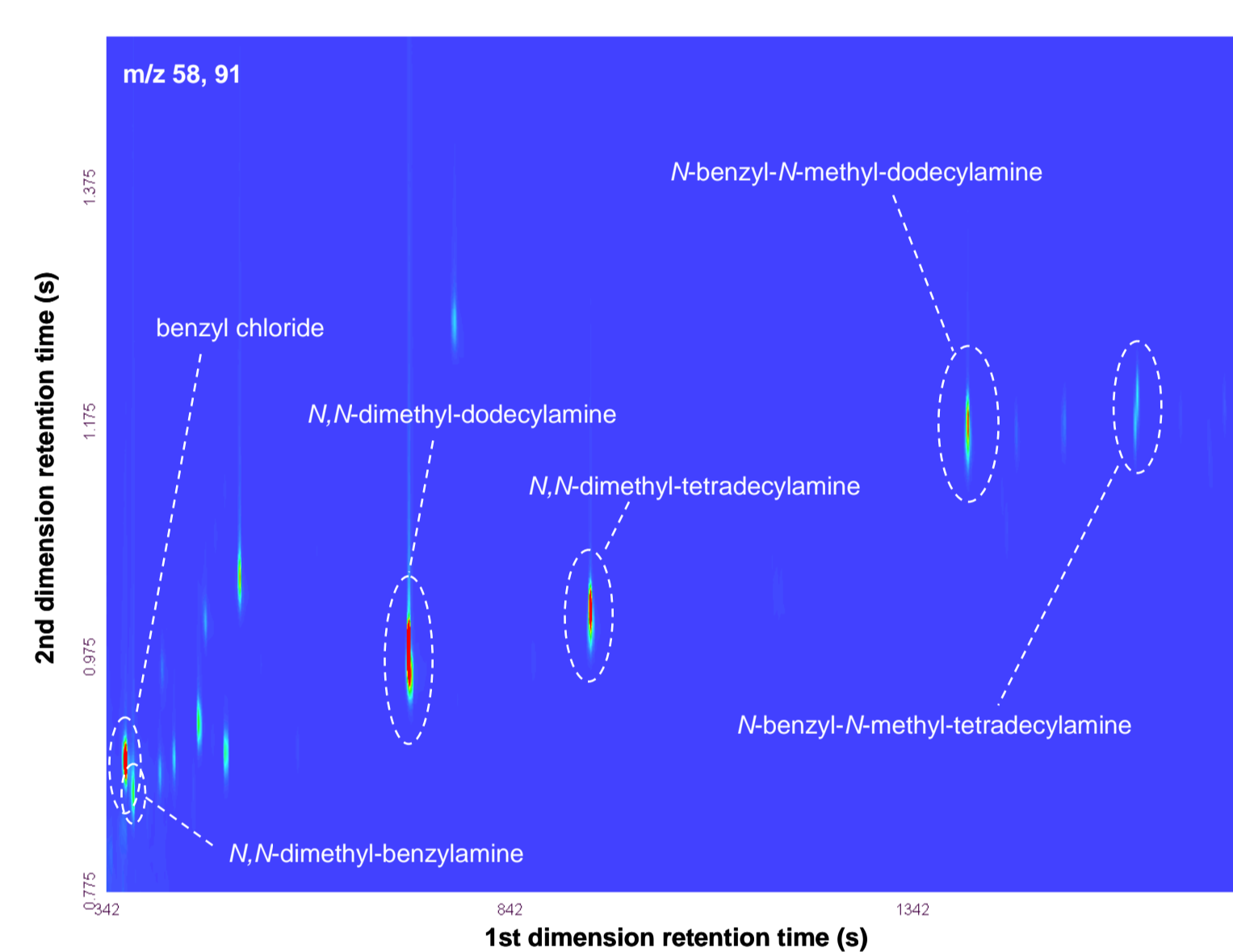


Figure 4  
Extracted GCxGC chromatogram of a cleaner-formulation containing N-benzyl-N,N-dimethyl-dodecylammonium chloride and N-benzyl-N,N-dimethyl-tetradecylammonium chloride

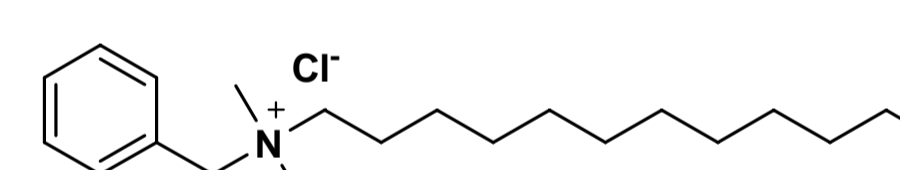


Figure 5  
Structure of N-benzyl-N,N-dimethyl-dodecylammonium chloride

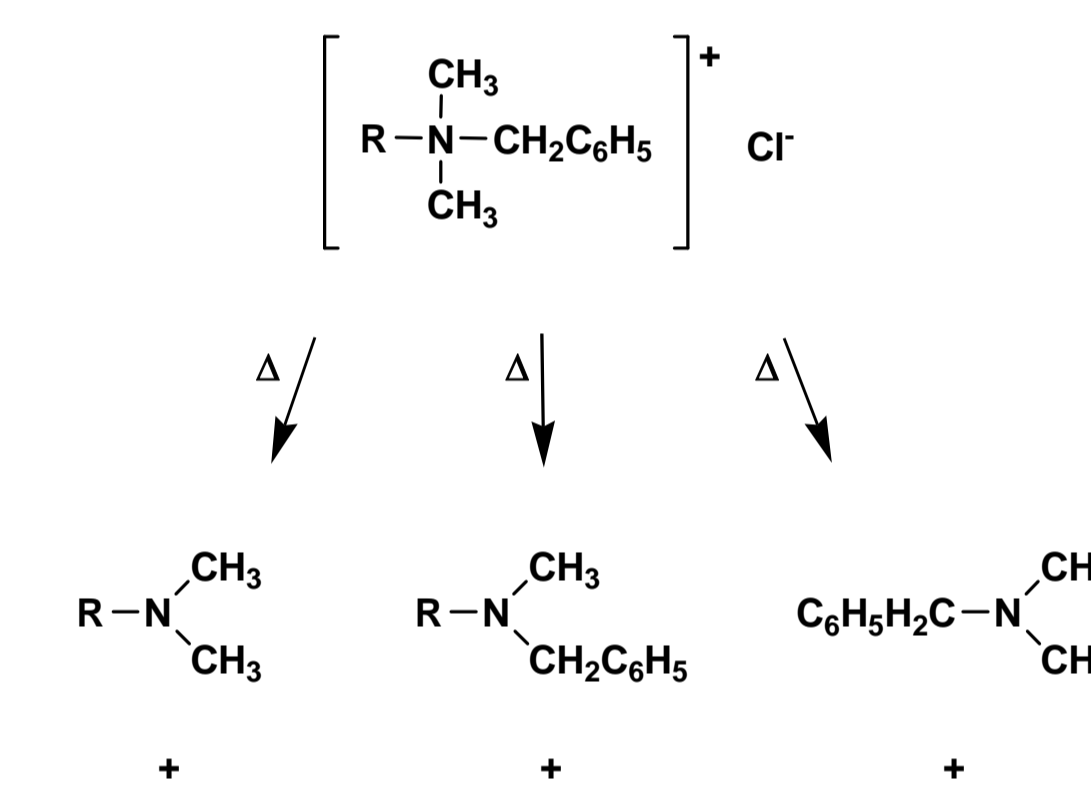


Figure 6  
Thermal fragmentation pathways of benzalkonium chlorides [7]

Most of the surfactants analysed are not strictly defined chemical compounds, but mixtures of substances of the same type.

Like the homologous fatty alcohol ethoxylates (FAEO), propoxylated fatty alcohols are also used as non-ionic surfactants in which the hydrocarbon chains have 8-18 carbon atoms and there is a distribution in the number of propylene oxide units.

Ethoxylated fatty alcohols (FAEO) can be identified by their characteristic fragments in the mass spectra after silylation and separation by means of GC [8 - 10]. In addition to these FAEO, fatty alcohol propoxylates (FAPO) are also identifiable by the EI-fragmentation masses. Figure 1 shows a GCxGC chromatogram (mass traces 131 and 133) of an FA-2PO standard. The EI mass spectra of peaks 1-3 and the characteristic fragmentation of the propoxylated fatty alcohols are shown in figures 2 and 3.

Cationic surfactants are applied in many commercial hair conditioners, antistatics and bactericides [4]. Figure 4 shows part of a GCxGC chromatogram of a cleaning formulation containing benzalkonium chlorides (figure 5) as disinfectants. By means of the different products of thermal decomposition (figure 6) during the GC injection, the cationic surfactants used in this technical formulation are determined.

Owing to the faster biodegradability and their surface-refining effect, triethanolamine-based esterquat surfactants (figure 7) are preferred as fabric softeners and antistatics [3]. These compounds can be detected by their decomposition products formed by alkaline hydrolysis with the silylation reagent. Figure 8 shows a GCxGC chromatogram of such a silylated esterquat. The resulting silylated fatty acids and the hydroxyamines are detectable.

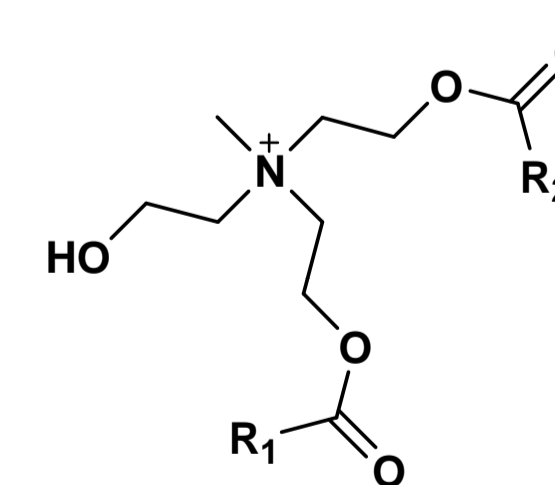


Figure 7  
Structure of a triethanolamine-based esterquat

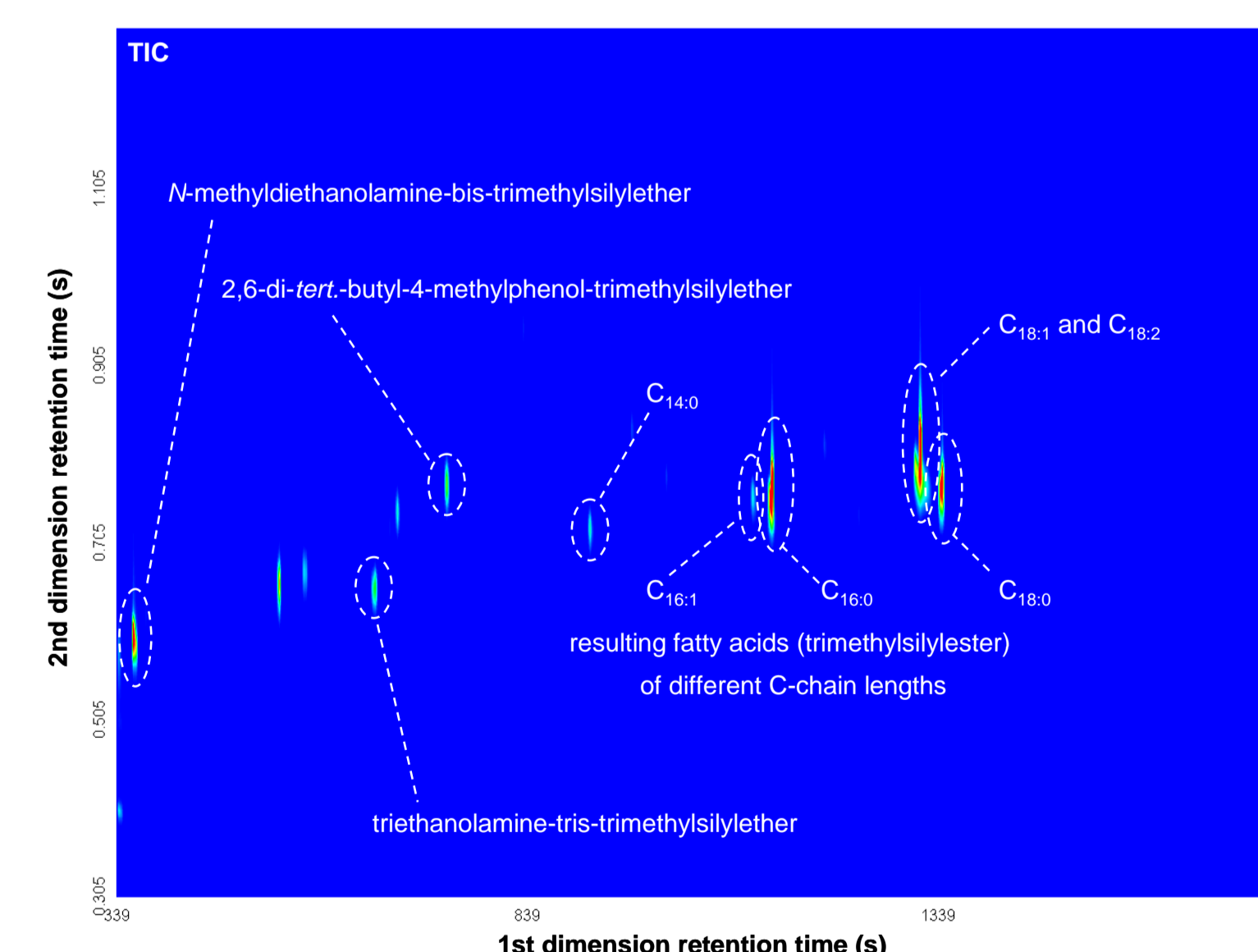


Figure 8  
Extracted GCxGC chromatogram of the triethanolamine-based esterquat compound shown in figure 7

### Conclusions And Outlook

The analysis of propoxylated fatty alcohols, benzalkonium chlorides and esterquat surfactants in technical products for detergents by comprehensive two-dimensional gas-chromatographic (GCxGC) analysis coupled with EI-(TOF)MS is demonstrated. Propoxylated fatty alcohols (FAPO) can be differentiated from the ethoxylated homologous series (FAEO) by the characteristic masses of their fragment ions in the EI-(TOF) mass spectrum. Quarternary ammonium compounds like benzalkonium chlorides can be determined by pyrolysis in the GC injector and analysis of the resulting decomposition products. Triethanolamine-based esterquat surfactants can be analyzed e.g. by alkaline hydrolysis of the ester function and silylation resulting in the silylated triethanolamine derivatives and the corresponding silylated fatty acids.

The hyphenated separation technique used allows the detection of the surfactants described in complex samples among other components and demonstrates that even compounds which are not typical for GC analysis can be determined by their decomposition products. However, because decomposition leads to an increase in the number of analyte components, the use of hyphenated techniques is necessary.

### Literature

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