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Analysis of special surfactants by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry

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ABSTRACT

Multidimensional gas-chromatographic analyses of olesochemically based nonionic, anionic and several cationic surfactants in industrial cleaners are demonstrated. Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry allows the simultaneous determination of fatty alcohols, fatty alcohol sulphates and alkyl polyglucosides. In addition, the determination of fatty alcohol ethoxylates up to $C_{10}EO_8$ (highest degree of ethoxylation) and $C_{18}EO_5$ (longest C-chain at an ethoxylation degree of five) and the analysis of fatty alcohol alkoxylates that contain ethoxy (EO) and propoxy (PO) groups could be realized. Because of decomposition in the injector and a weak EI-fragmentation, cationic surfactants such as alkyl benzyl dimethyl ammonium chloride could also be identified by their characteristic fragments. Thermogravimetric analyses confirmed that the temperature in a normal GC injector is not high enough to cause thermal decomposition of esterquats. However, we could demonstrate that a modified silylation procedure forms decomposition products of esterquats in the GC injector which are detectable by GC × GC–(TOF)MS and allows the identification of such GC-atypical analytes.

1. Introduction

Surface-active agents play an important role in many areas of the daily life. Their characteristic features and functions are of great importance. In nature as well as in technology many processes take place in the interfaces between two immiscible phases. To improve contact between those phases, surfactants are employed [1,2].

Depending on the chemical structure and the charge of the hydrophilic head-group, surfactants are classified as anionic, cationic, nonionic and amphoteric. In general, hydrocarbon chains serve as hydrophobic groups, but there are also other lipophilic groups, such as polysiloxane units or perfluoroalkyl chains [1,3,4]. In industrial products, surfactants are used, e.g. in cleaning and washing agents, dispersal agents, emulsifiers and wetting and foaming agents [1].

Many methods have been described for the determination of individual surfactants or single surfactant classes, including classical wet chemical methods, ion chromatography (IC) [5,6], thin-layer chromatography (TLC) [7,8], capillary electrophoresis (CE) [9–14] and several high-performance liquid chromatography (HPLC) and gas-chromatography (GC) applications. HPLC and GC techniques combined with various detection methods are especially suitable for the analysis of these substances. By means of these methods, nonionic surfactants, e.g. fatty alcohol ethoxylates (FAEO) and alkyl polyglucosides (AG), can be derivatised at free OH-groups with UV or fluorescence markers and analysed by HPLC-UV or HPLC-FLD [12,15–17]. In addition, refractive index (RI)-detectors and evaporative light-scattering detectors (ELSD) can be used without any derivatisation for the detection of such surfactants in liquid chromatography [18,19]. However, the use of an RI detector requires an isocratic procedure, which limits the separation capacity. The ELSD has an extremely limited linear range. Usually a square calibration has to be carried out for quantification, which is influenced by external factors. As an alternative, the coupling of a mass spectrometer with separation methods allows the detection of underivatised surfactants. Recently, chemical ionisation at atmospheric pressure (APCI) and electrospray ionisation (ESI) have been especially preferred [20,21]. Ion chromatography is also suitable for separating charged surfactants and is used in practice for the quantification of anionic and cationic compounds. A further method for the analysis of oligomeric or polymeric surfactants that are difficult to evaporate is matrix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS) [7,9,22–26]. Another new method is the derivatisation of low-molecular-weight ethoxylated surfactants with an ionization label and analysis by atmospheric-pressure laser ionization (APLI) [27]. For analysis by gas chromatography, silylation of surfactants is often necessary [28]. One of the advantages of

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GC techniques is the possibility that much information about the distribution of alkyl chain lengths and isomers can be obtained. As a disadvantage, high-molecular-weight surfactants have extremely low vapour pressures or undergo thermolysis in the GC injector and elude analysis by classical gas chromatography. As a result, the determination of FAEO is limited to oligomers with a low degree of ethoxylation, for which reason high-temperature gas chromatography (HT-GC) is often used to analyse FAEO of higher degree [29–31]. The methods mentioned above can be used efficiently to analyse several surfactant classes but – in daily practice – characterising more complex mixtures still requires time- and cost-intensive sample preparation. Furthermore, for fast and reliable analysis of such complex samples, multidimensional separation techniques with a high separation efficiency become more and more important. Multidimensional approaches have been published in the field of liquid chromatography and gas chromatography (e.g. comprehensive two-dimensional LC × LC or LC × GC–(TOF)MS), but they have not established themselves in routine laboratory practice [32–35]. However, comprehensive two-dimensional gas-chromatography systems are nowadays commercially available from several instrument manufacturers and have successfully solved many separation problems in recent years [36,37]. In contrast to conventional two-dimensional gas chromatography [38,39], comprehensive two-dimensional gas chromatography (GC × GC) – which was first established in 1991 by Liu and Phillips [40] – captures all sample constituents and not only a limited number of factions of the first dimension. In addition, the orthogonality of GC × GC applications is often high, because of different separation mechanisms (vapour pressure of the analytes and interaction with the stationary phase) in two dimensions, which result in high peak capacities [41]. GC × GC–EI-(TOF)MS was already successfully applied to the analysis of complex mixtures based on oleochemistry compounds (shampoo, shower gel) [42].

In this work, we present a GC × GC application for the analysis of technical cleaning agents containing special surfactants like copolymers for foam control, biocides, wetting agents and hydrophobising products with good economy of time and costs.

2. Material and methods

2.1. Reagents

All technical detergent products and cleaning formulations were obtained from Cognis GmbH (Düsseldorf, Germany). Ethyl acetate was purchased from Fisher Scientific UK Ltd. (Loughborough, United Kingdom). Tetrahydrofuran (THF), isooctane, sulphuric acid (≥95%, p.a.) and pyridine (≥99.5%, p.a.) were obtained from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). *N*,*O*-bis-trimethylsilyltrifluoroacetamide (BSTFA) and *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) were purchased from Machery-Nagel GmbH & Co. KG (Düren, Germany). Tetramethylammonium hydroxide pentahydrate (≥97%; TMAH) was from Sigma–Aldrich (Steinheim, Germany). All chemicals were used without further purification.

2.2. Instrumental analysis

2.2.1. GC × GC–(TOF)MS

Comprehensive two-dimensional gas chromatography was carried out on a 6890N gas chromatograph made by Agilent Technologies Inc. (Santa Clara, California, USA). The GC was attached to a time-of-flight mass spectrometer (TOF-MS, Pegasus III) from LECO® Corporation (St. Joseph, Michigan, USA). The classical electron-impact mode at 70 eV served as the ionization method. Chromatograms and MS data were stored and processed by ChromaTOF™ software (version 3.22) from LECO® Corporation (St. Joseph, Michigan, USA). The GC carrier gas was helium, and a four-jet modulator working with liquid nitrogen (cold-jets) and gaseous nitrogen (hot-jets) was used as the cryo-interface. For the first dimension a nonpolar column (FactorFour VF-5ms; 30 m × 0.25 mm × 0.25 μm from Varian, Darmstadt, Germany) and for the second dimension a moderately polar column (BPX50; 1 m × 0.1 mm × 0.1 μm from SGE, Darmstadt, Germany) were used. All analyses were performed with constant flow at 1.4 mL/min and a modulation time of 3 s. The temperature for the first dimension was programmed, starting at 70 °C. After 1 min, the temperature was first increased at a rate of 40°/min to 150 °C, then at 5°/min to 300 °C. The final temperature was held for 10 min. The temperature for the second dimension was programmed, starting at 90 °C. After 1 min, the temperature was first increased at the rate of 40°/min to 170 °C, then at 5°/min to 320 °C. The final temperature was held for 12 min. The injector temperature and the transfer line temperature were held constant at 320 and 300 °C, respectively. One microliter of the sample was injected with a split of 1:10 for technical formulations and 1:100 for technical standards. With a solvent delay of 300 s, data was acquired at a detector voltage of 1.6 kV and a mass spectra collecting rate of 200 Hz.

2.2.2. Thermogravimetric analysis (TGA)

The decrease in the weight of several samples caused by thermal decomposition was investigated by thermogravimetric analysis. It was performed on a TGA-Q5000 made by TA Instruments (Eschborn, Germany) coupled to a Nicolet™ 380 FTIR spectrometer from Thermo Fisher Scientific (Dreieich, Germany) as detector. The heating rate in the thermolysis run was adjusted to 10°/min in a nitrogen flow of 2.1 L/h, in the temperature range of 35–600 °C with samples of about 20 mg.

2.3. Sample preparation

2.3.1. Silylation

For silylation 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 isooctane.

2.3.2. Hydrolysis and silylation

For hydrolysis and silylation, 75 mg of the technical product was dissolved in 5 mL 1 M H_2SO_4 and heated for 90 min in a water bath at 100 °C. After cooling to room temperature, the sample was extracted with 8 mL ethyl acetate. The isolated organic phase was then silylated with 2 mL of a BSTFA/MSTFA mixture (5:1; v/v) for 1 h at 80 °C without further drying.

2.3.3. TMAH treatment and silylation

55 mg of the technical esterquat product and 50 mg tetramethyammonium hydroxide (TMAH) were mixed and dissolved in 5 mL tetrahydrofuran. After 2 h at 50 °C the mixture was silylated with 2 mL of a BSTFA/MSTFA mixture (5:1; v/v) for 1 h at 80 °C.

3. Results and discussion

As described above, modern cleaning agents consist of a large number of active compounds from various types of surfactants. Fig. 1 shows structures of the classes of surfactants analysed in this work.

3.1. Analysis of anionic and nonionic surfactants

Besides a high concentration of water and pH regulators, the analysed cleaner A (a ready-to-use all-purpose cleaner) contains two anionic and three nonionic types of surfactants as active ingredients (see Table 1). Technical fatty alcohol sulphates (FAS) and

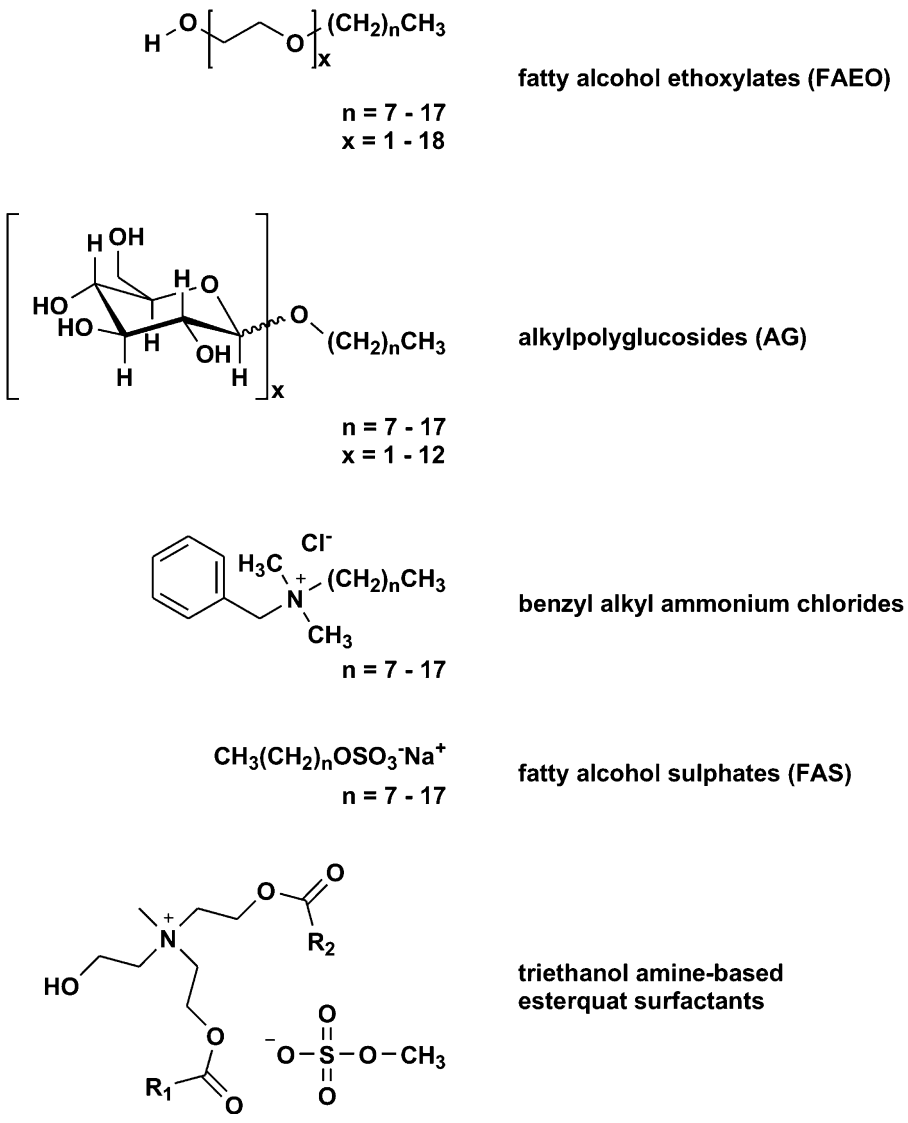

Fig. 1. Chemical structures of surfactants commonly used in cleaning agents and structure of the analysed triethanol amine-based esterquat surfactant *N*-methyl-*N*,*N*-bis[2-(C_n-acyloxy)ethyl]-*N*-(2-hydroxyethyl)ammonium-methyl sulphate; R_1 and R_2 are alkyl chains (n = 14:0, 16:0, 16:1, 18:0, 18:1 or 18:2).

fatty acids (at the existing pH as free carboxylates) serve as anionic components. The nonionic part is represented by alkyl polyglucosides (AG), fatty alcohol ethoxylates (FAEO) and a mixture of fatty alcohol alkoxylates (FAAO), which contains ethoxy (EO) and propoxy (PO) groups.

The GC × GC chromatograms of the silylated cleaner A are shown in Figs. 2. The latter one (Fig. 2b) shows an enlarged part of the chromatogram from Fig. 2a, but with additional mass traces.

Table 1
Surfactant mixture for the cleaner A.

Ingredients	Surfactant category
Fatty alcohol sulphates (FAS) primarily C_{12} + C_{14}	Anionic surfactants
Alkyl polyglucosides (AG) primarily C_8 + C_{10}	Nonionic sugar surfactants
Fatty alcohol ethoxylates C_{12}–C_{18} (FAEO) approximately 7 EO	Nonionic surfactants
Fatty alcohol alkoxylates C_8 (FAAO) EO/PO	Nonionic surfactants
Fatty acids C_8–C_{18} (FA)	Anionic surfactants
Alkaline ingredients and water	

Earlier work by Hübner et al. [42] and Asmussen [43] have shown that FAEO can be analysed by GC after silylation and the identification of free unethoxylated (EO_0) fatty alcohols with an increasing number of carbon atoms in the alkyl chain (C_8EO_0-$C_{18}EO_0$) is also possible from their mass spectra. With these methods, FAEO in this product can be determined by their specific fragments, e.g. by the corresponding mass traces (m/z 103 $[CH_2–O–Si(CH_3)_3]^+$and m/z 116 $[CH_2–CH–O–Si(CH_3)_3]^+$). In Fig. 2a, the series of FAEO with different chain lengths are marked by white dashed ovals. Free unethoxylated fatty alcohols (C_8EO_0-$18EO_0$) – starting materials for the production of FAEO and FAAO – can also be detected by this method (yellow dashed ovals). In addition, the fatty acids are detectable as fatty acid trimethylsilyl esters (C_{12}- to C_{16}-fatty acid-TMS, green ovals). To characterise this last group, the $[M]^{\bullet+}$-signals at m/z 257 for C_{12}-fatty acid-TMS, m/z 285 for C_{14}-fatty acid-TMS and m/z 313 for C_{16}-fatty acid-TMS are used. Furthermore, the typical spots for AG are in black dashed ovals. This class of nonionic surfactants can also be detected by the m/z-values shown in Fig. 2a and characterised by the main fragments m/z 204 $[(CH_3)_3SiOCH–CHOSi(CH_3)_3]^{\bullet+}$ for pyranosides and m/z 217 $[(CH_3)_3SiOCH{=}CH–CHOSi(CH_3)_3]^+$ for furanosides [28,42]. Fig. 2b shows that α- and β-anomers of each pyranoside form can also

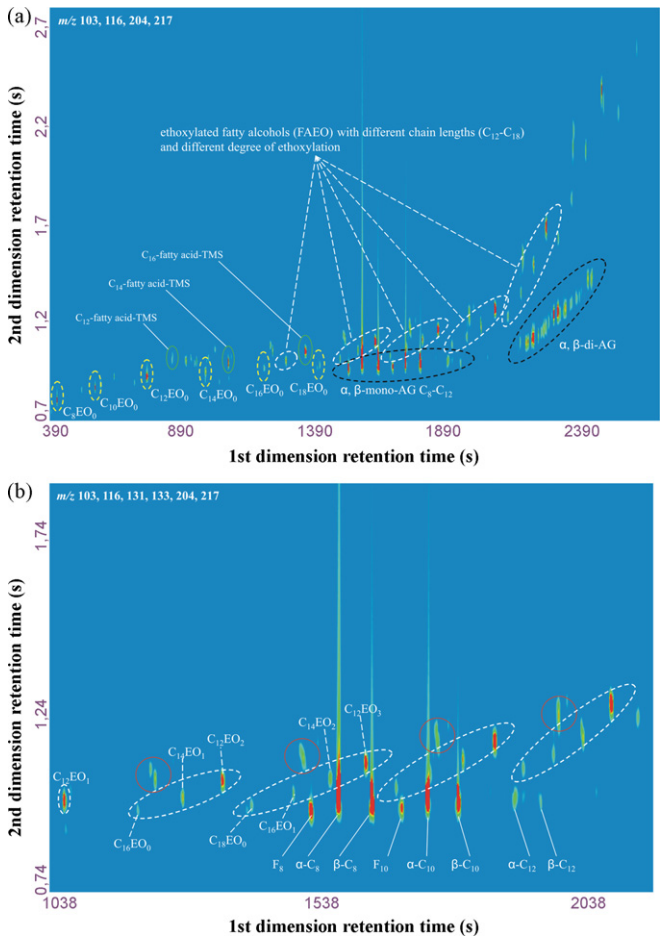

Fig. 2. (a) GC × GC chromatogram overview of the cleaner A containing two anionic and three nonionic classes of surfactants as active ingredients. Only the mass traces 103, 116, 204 and 217 are shown. (b) Expanded part of the GC × GC chromatogram of the cleaner A in a spot-view of the mass traces 103, 116, 131, 133, 204 and 217.

be separated (α-C_8 to α-C_{12} and β-C_8 to β-C_{12}), as well as the furanosides present (e.g. F_8 and F_{10}).

In the expanded GC × GC chromatogram (Fig. 2b), the series of ethoxylated fatty alcohols with different chain lengths are very readily distinguished (dashed white ovals). The first group (on the left) contains only the single ethoxylated dodecanol. In the second group, the free hexadecanol and the fatty alcohol ethoxylates $C_{14}EO_1$ and $C_{12}EO_2$ are detectable. By studying the other series, a strong pattern can be observed. Within a single group, the degree of ethoxylation increases from 0 to *x*. Furthermore, the successive peaks within a group show alkyl chains continuously reduced by loss of C_2H_4 groups. The retention times in the 1st dimension are increased because of the rising degree of ethoxylation (lower vapour pressure). At higher degrees of ethoxylation, the increased polarity of the substances also results in longer 2nd dimension retention times. With this regularity, the peaks in the fifth group (right dashed white oval) can be identified as fatty alcohol ethoxylates $C_{18}EO_2$, $C_{16}EO_3$, $C_{14}EO_4$ and $C_{12}EO_5$.

With the GC × GC method described here, it is possible to analyse the fatty alcohol ethoxylates in a single analysis up to $C_{10}EO_8$ (highest degree of ethoxylation) and $C_{18}EO_5$ (longest C-chain at an ethoxylation degree of five; data not shown). The analysis of fatty alcohol sulphates is also possible after hydrolysis with aqueous sulphuric acid and silylation. The resulting fatty alcohols can be detected by GC as fatty alcohol trimethylsilyl ethers (data not shown). It should be mentioned that, if alkyl polyglucosides are present in the same mixture, these may be hydrolysed unintentionally when aqueous hydrochloric acid is used. Systematic studies in our group have shown that 1 M aqueous sulphuric acid is a good compromise for hydrolysing the fatty alcohol sulphates without AG cleavage.

Table 2
Surfactant mixture for the cleaner B.

Ingredients	Surfactant category
Alkyl benzyl dimethyl ammonium chlorides primary $C_{12}+C_{14}$	Cationic surfactants
Fatty alcohol alkoxylates C_{10}–C_{16} EO/PO	Nonionic surfactants
Acidic ingredients and water	

The peak spots marked in red circles (Fig. 2b) show fatty alcohol alkoxylates as copolymers from ethoxylated (EO) and propoxylated (PO) fatty alcohols. The different degrees of alkoxylation can be separated readily – in the same way as FAEO – by GC × GC. The analyses of technical FAPO standards indicate that – in analogy to the specific EI-MS-fragments of the FAEO (*m*/*z* 103 and *m*/*z* 116) – the mass fragments *m*/*z* 133 (for the first degree of propoxylation) and *m*/*z* 131 ($[CH_2–CH(CH_3)–O–Si(CH_3)_3]^+$ for higher degrees of propoxylation) are formed during EI ionisation of the pure fatty alcohol propoxylates (data not shown). Therefore, the *m*/*z*-values 103, 113, 131 and 133 can be used to differentiate between pure fatty alcohol ethoxylates and propoxylates by their different EI fragmentation. Nevertheless, an exact identification of the EO/PO-copolymers contained in cleaner A and an identification of the different PO constitutional isomers is not possible by GC–(TOF)MS with electron impact ionisation due to the strong fragmentation.

3.2. Analysis of cationic surfactants

In 1974, Denig was already able to detect quaternary ammonium compounds successfully by pyrolysis gas chromatography [44]. He has shown that these compounds decompose at two different positions by Hofmann elimination, in which not only olefins but also benzyl dimethyl amines and alkyl dimethyl amines are formed.

We also analysed cleaner B, which contains quaternary ammonium compounds as disinfection ingredients (see Table 2).

Fig. 3a shows the analysis of cleaner B, where typical spots of alkoxylated fatty alcohols (EO/PO) can be observed. Additional spots can be identified in an expanded part of this chromatogram (Fig. 3b).

By single ion monitoring of the masses *m*/*z* 58 ($[CH_2N(CH_3)_2]^+$) and *m*/*z* 91 ($[C_7H_7]^+$), the decomposition products of the alkyl benzyl dimethyl ammonium chlorides can be identified. Because of the limited EI fragmentation of alkyl dimethyl amines, it is possible to identify *N*,*N*-dimethyl dodecyl amine and *N*,*N*-dimethyl tetradecyl amine by mass spectrometry. Fig. 4a shows the mass spectrum of *N*,*N*-dimethyl dodecyl amine with the molecular mass *m*/*z* 213. *N*-benzyl-*N*-methyl alkyl amines can also be separated and identified by the signal of the tropylium ion ($[C_7H_7]^+$, *m*/*z* 91). However, the signal of the fragment *m*/*z* 134 is also very intense (Fig. 4b). This *m*/*z*-value describes the very stable and – for benzyl methyl amines – typical cation $[CH_2N(CH_3)CH_2C_6H_5]^+$.

3.3. Analysis of triethanol amine-based esterquat surfactants

Ng et al. [45] described how quaternary ammonium cations are decomposed at typically used GC-injector temperatures between 200 and 350 °C. This was verified through our measurements with an injector temperature of 350 °C, and Fig. 5 shows the thermal decomposition pathways for these compounds. In further GC applications, the decomposition of quaternary ammonium compounds has been used for their analysis [46–49].

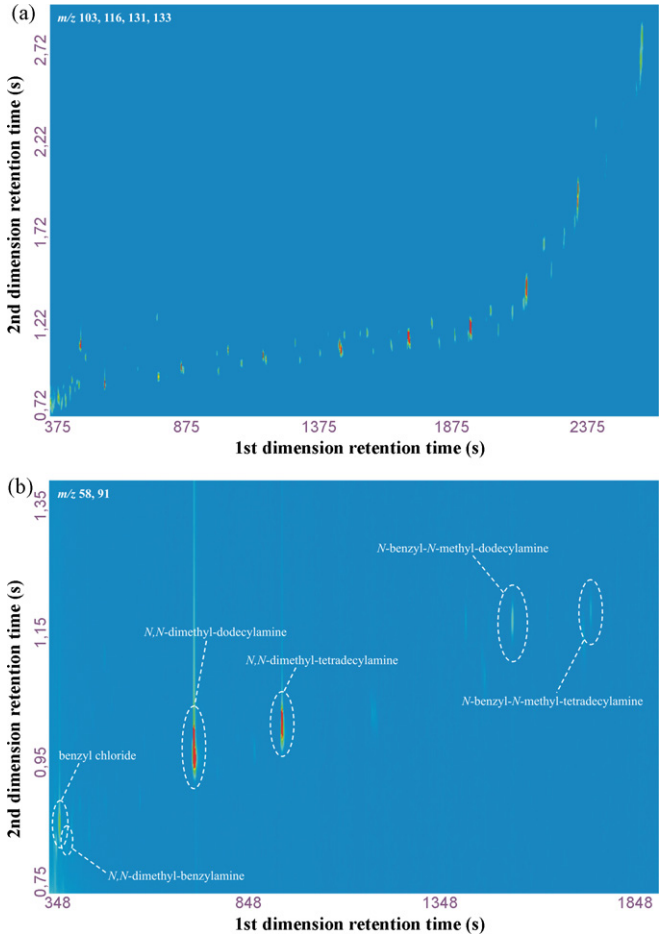

Fig. 3. (a) GC × GC chromatogram overview of the cleaner B. The typical mass traces for fatty alcohol alkoxylates are shown. (b) Extracted GC × GC chromatogram of the cleaner B. The mass traces 58 and 91 are shown.

As has already been shown for the analysis of quaternary ammonium compounds, we have tried to find a similar method for the characterisation of triethanol amine-based esterquat surfactants (see Fig. 1).

Esterquats are used as wetting agents, hydrophobising products and essentially as fabric softeners [50]. Products of these surfactant classes are mainly used in diluted solutions, usually without the addition of other surfactants.

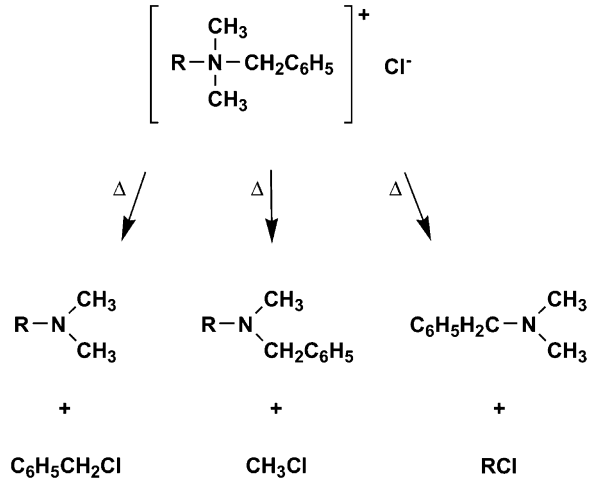

Fig. 5. Typical thermal decomposition of benzyl alkyl ammonium chlorides (in the GC injector) according to [45].

First experiments showed that the typical temperature of a GC injector was not high enough to decompose the esterquats in order to separate the decomposition products by GC. Therefore, samples of various benzyl alkyl ammonium chlorides and triethanolamine-based esterquat surfactants were analysed by thermogravimetric analysis to evaluate the thermal behavior of esterquats. These measurements were performed by a thermogravimetry instrument equipped with a Fourier transform infrared (FTIR) detector.

The thermogravimetric analysis of C_{12}-/C_{14}-alkyl dimethyl benzyl ammonium chloride was carried out in the presence of nitrogen. The dissociation of these compounds starts at about 175 °C and is almost complete at 220 °C. The maximum of the TG curves is located at 194 °C. The IR bands display some CH vibrations (2900–2800 cm^{-1} for the stretching vibrations and 1450 cm^{-1} for the deformation vibration), phenyl-H stretching vibrations (3100–3000 cm^{-1}) and a C-Cl-vibration (700 cm^{-1}). This is consistent with the expected reaction products of the tertiary amines and halogenated alkanes.

Compared with C_{12}-/C_{14}-alkyl dimethyl benzyl ammonium chloride the TGA of the technical esterquat *N*-methyl-*N*,*N*-bis[2-(C_n-acyloxy)ethyl]-*N*-(2-hydroxyethyl)ammonium-methyl sulphate – the structure is shown in Fig. 1 – shows different characteristics. The dissociation begins at 250 °C and is not complete until 400 °C. There are different peak maxima in the TGA of the esterquat, indicating different degradation mechanisms. Most of these maxima show the typical CH-stretching vibrations

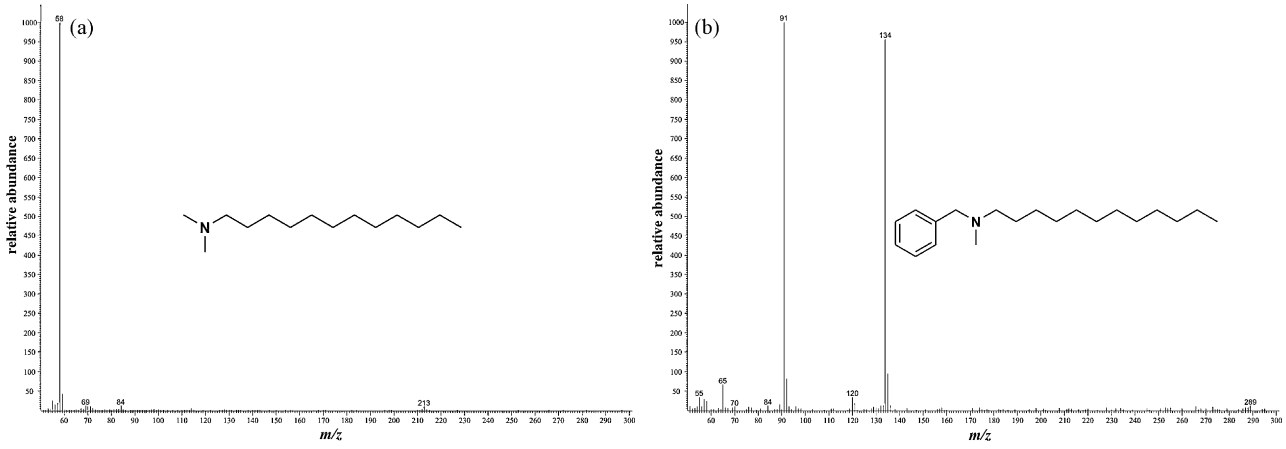

Fig. 4. Recorded EI-(TOF) mass spectra of *N*,*N*-dimethyl dodecylamine (a) and *N*-benzyl-*N*-methyl dodecylamine (b).

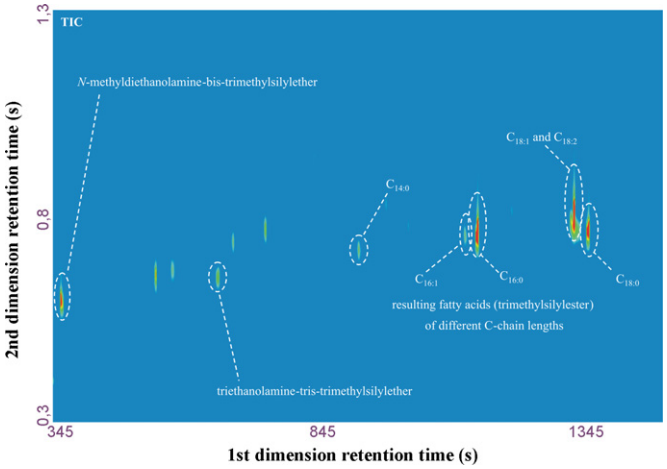

Fig. 6. GC × GC chromatogram of the esterquat surfactant treated with tetra methyl ammonium hydroxide, silylated and diluted in THF. The expanded part of the total ion chromatogram is shown.

at 2850–3000 cm^{-1}. At a temperature of about 270 °C, sulphates can be identified by the characteristic RO-SO_2-OR′-vibration at 1400–1300 cm^{-1}. The presence of sulphur can be explained by the esterquats' counterion methyl sulphate. In the range of 340–590 °C, mainly oxygenated hydrocarbons can be observed. An increase in the CO_2-vibration signal shows the complete decomposition of the esterquat.

It was demonstrated that the thermolysis in the GC injector cannot be used for all quaternary ammonium compounds. Thermogravimetric investigations of esterquats showed that the esterquat surfactant (Fig. 1) is not quantitatively thermolysed in a GC injector with temperatures below 400 °C. Therefore, with conventional GC systems (without pyrolysis injector) information about esterquat products cannot be obtained.

Although thermal decomposition of esterquats in the GC injector is problematical, we have developed an appropriate sample preparation method, which forms decomposition products detectable by GC × GC. Fig. 6 shows a chromatogram of an esterquat after a thermally assisted hydrolysis and silylation procedure. The resulting products which can be detected are silylated fatty acids and ethanolamines from a combination of alkaline hydrolysis and silylation.

The alkaline character of the silylation reagent used leads to a hydrolysis of the product. The addition of tetra methyl ammonium hydroxide (TMAH) to the sample leads to an increase of the hydrolysis efficiency.

The chromatographic separation and the identification of the decomposition products allow a screening of technical substances and provide insight into the structures of esterquats used in formulations.

4. Conclusion

The methods described allow the determination of various surfactants in complex samples and demonstrate 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, such as GC × GC, is necessary.

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