Characterization of technical mixtures with comprehensive two-dimensional gas-chromatography – mass spectrometry

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Introduction

In modern households today multifunctional detergents are ubiquitous. The detergents have to fulfil several functions like high cleaning efficiency, easy to use, preservation of surfaces and good cost/performance ratio. Thus high requirements on the functionality and versatility of the active ingredients are made. Hence modern detergents and also their ingredients become more and more complex.
The analysis of such technical mixtures possess an enormous challenge which consumes time, costs and resources. Frequently a combination of various analytical methods as well as extensive sample pre-separation procedures is necessary. The application of high-performance multidimensional techniques represents an innovation with economic potential [1].

Here we present the analysis of technical cleaning products with comprehensive two-dimensional gas chromatography – mass spectrometry (GCxGC-MS) and furthermore the advantages of chemical ionization for special ingredients.

The system used for these investigations was a GCxGC system coupled to a quadrupole mass spectrometer with electron (EI) and chemical ionisation (CI) (see methods). Data aquisition rates of 50 Hz at a mass range of 140 Da were used. With these settings relative standard deviations of integrated peaks have been determined closely comparable to a GCxGC-(TOF)MS system.

Results

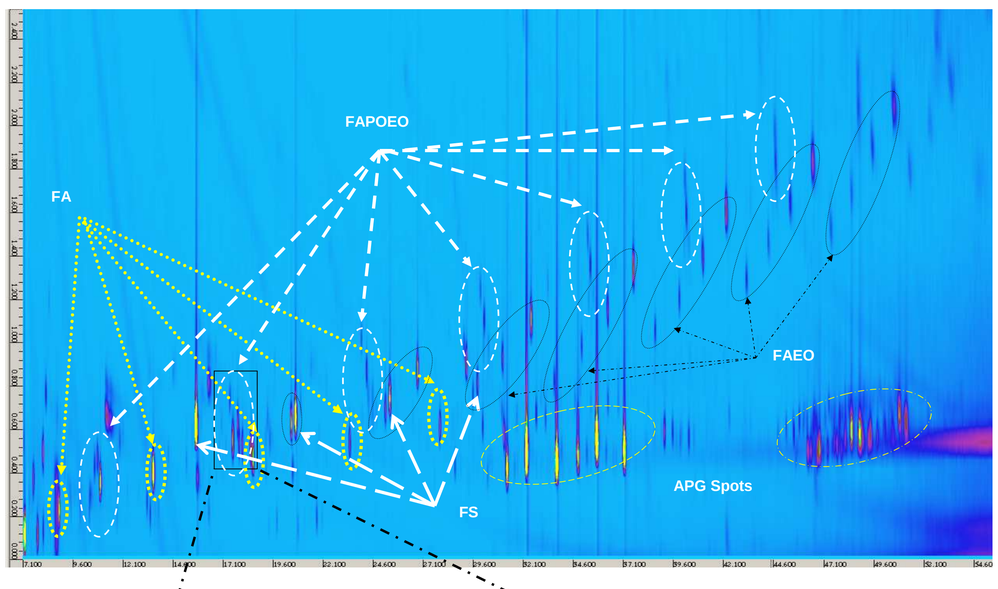


Figure 1: GCxGC chromatogram of an all purpose cleaning formulation
Abbreviations: FA = fatty alkohol; FS = fatty acid; FAEO = ethoxylated fatty alkohols; FAPOEO = fatty alkohol block copolymers (propoxylated and ethoxylated); APG = alkyl polyglucosides

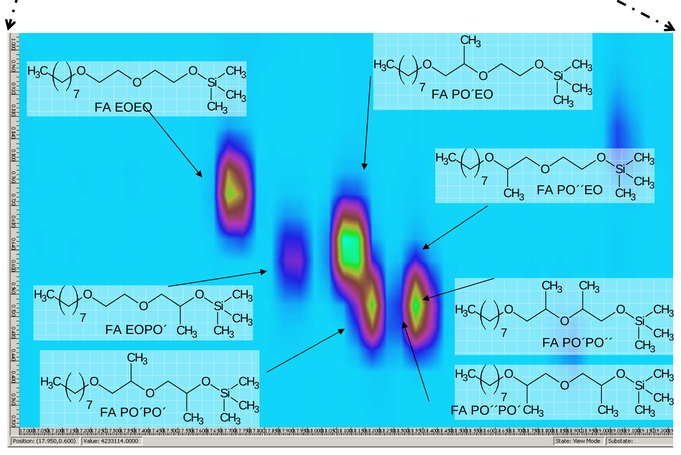
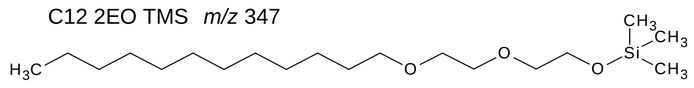
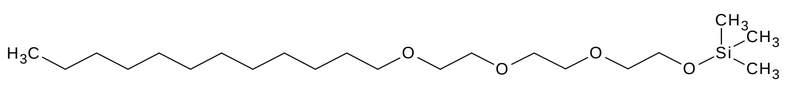


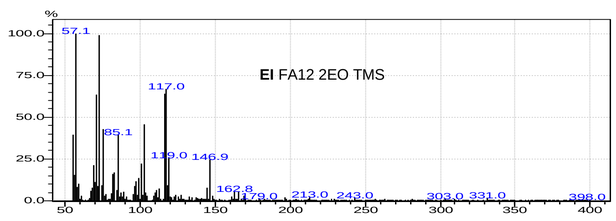
Figure 2: Extracted chromatogram of an fatty alcohol alcoxylate (propoxylate-ethoxylate block copolymer) in CI mode and the assigned structures of different monomer sequences at alkoxylation degree 2.
Abbreviations: PO´ = main isomer resulting from nucleophile ring opening reaction of propylenoxide; PO´´ = co-isomer resulting from nucleophile ring opening reaction of propylenoxide

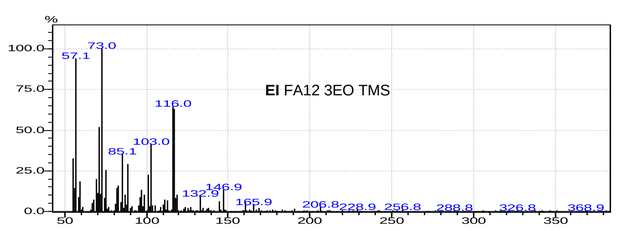
C12 2EO TMS *m/z* 347

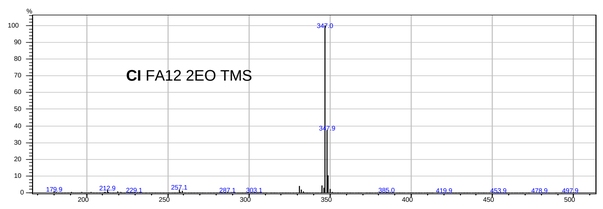


C12 3EO TMS *m/z* 391









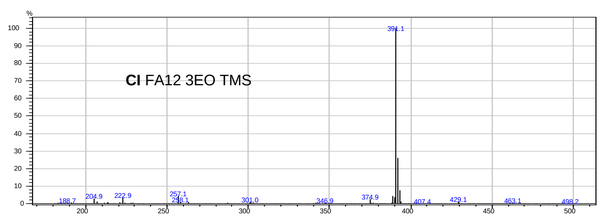


Figure 3: Comparison of EI and CI mass spectra of the C12 based fatty alcohol ethoxylate spots with ethoxylation degrees of 2 and 3

The combination of both ionisation techniques lead to an additional dimension in selectivity in comparison to a system with only one ionisation mode. Due to that a fully identification of all active ingredients of multifunctional cleaning products could be realised.
Figure 1 shows an overview chromatogram of a technical cleaning agent containing oleochemical based ingredients, figure 3 the comparison of the EI and CI mass spectra from a part of a nonionic ingredient (fatty alcohol ethoxylate) and figure 2 shows an extracted chromatogram in CI mode of an even more complex nonionic ingredient (fatty alcohol alkoxylate).

All active ingredients in such agents are no strictly defined single chemical compounds but mixtures of substances of the same type. Fatty acids, fatty alcohols and alkylpolyglucosides could be well identified only with EI, but an exact identification of fatty alcohol ethoxylates only by EI-MS is problematic because the mass spectra of the higher homolgous (ethoxylation degree > 2) are nearly the same. With combination of EI and CI the exact identification is simply realisable and furthermore a completely peak identification of alkoxylate copolymers is also possible.
Anionic surfactants like fatty alcohol sulfates could be determined after acid hydrolysis followed by GC analysis [2, 3].

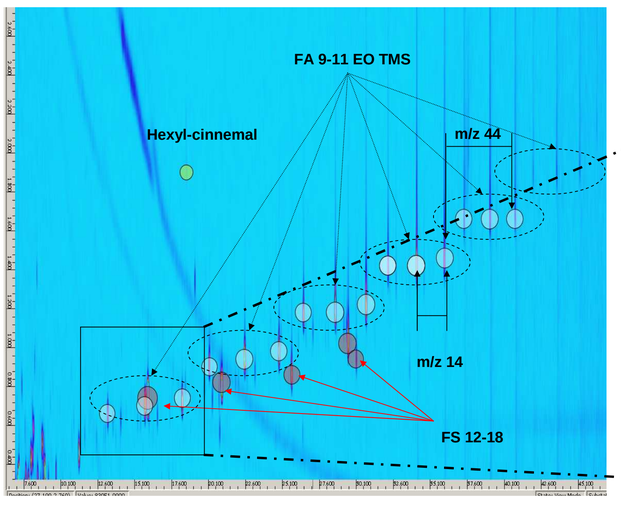


Figure 4: GCxGC chromatogram of a commercial available cleaner
m/z 44 = one ethoxy unit = CH_2CH_2O; m/z 14 = one alkyl-chain unit = CH_2

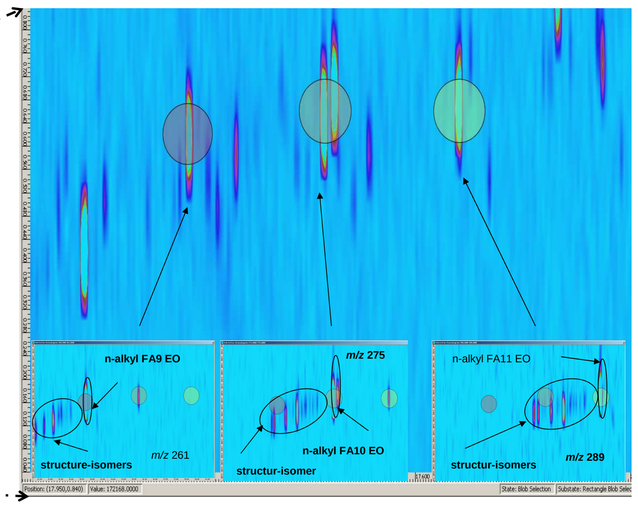


Figure 5: Extracted chromatogram of the petrochemical based ethoxylated C9-C11 fatty alcohol. CI. SIC, m/z 261 (left), m/z 275 (middle), m/z 289 (right)

Figure 4 shows an overview chromatogram of a commercial available cleaner. This cleaner contains oleochemical as well as petrochemical based ingredients, figure 5 shows an extract of this chromatogram describing the identification of the petrochemical based nonionic surfactant.

The peak groups marked in black ovals consists of the three alkyl homologous (C9-C11) of one ethoxylation degree respectively. Every homologous possesses the n-alkyl and the iso-alkyl distribution.

Conclusions and Outlook

The hyphenated separation technique used allows the comprehensive identification of active ingredients in complex technical mixtures like cleaning agents. The combination of electron and chemical ionisation shows a high benefits regarding a clear classification and characterisation of even very complex surfactants.

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 isooctane.

GCxGC-qMS system:
Shimadzu GCMS QP 2010 Plus; Shimadzu GC 2010 Gas Chromatograph; ZX1 LN2 cooled loop Modulater (Zoex); GCMS Solution 2.50 SU3; GC Image 1.9; CI gas isobutane
1st GC capillary - Phenomenex ZebronTM ZB-5HT Inferno (30 m x 0.25 mm I.D. x 0.25 µm)
2nd GC capillary - SGE BPX50 (1 m x 0.15 mm x 0.15 µm)

BSTFA (N,O-bis-trimethylsilyltrifluoroacetamide)
MSTFA (N-methyl-N-trimethylsilyltrifluoroacetamide)

References

1. Dallüge J, Beens J, Brinkman U A T (2003)
J Chromatogr. A 1000: 69 - 108
2. Hübner J, Taheri R, Melchior D, Kling H-W, Gäb S, Schmitz O J (2007)
Anal. Bioanal. Chem. 388: 1755 - 1762
3. Wulf V (2007)
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