

DETERMINATION OF SURFACTANTS USED IN AGROCHEMICALS

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Abstract

Examples for determination of surfactants used in agrochemicals will be presented by using different instrumental analytical methods. Liquid chromatography coupled to mass spectrometry (LC-MS) is more convenient for characterization of these mixtures compared to gas chromatographic (GC) methods. However, due to better separation of GC it allows more detailed information about the composition of the mixtures analysed, but usually prior to GC derivatisation is required. Two chemical modifications for GC-MS measurements were investigated in detail: conversion of sulfonates to trifluoroacyl esters as well as silylation of hydroxy compounds.

Introduction

Surfactants are often used in formulated pesticides to improve water solubility or as spray adjuvants to improve spreading and penetration abilities of pesticide active ingredients in tank mixture. These formulation additives are had widely been regarded as inert components, but have been proven in many cases to exert detrimental side-effects or modify the toxicity of the active ingredient(s). Thus, authorisation and use of these agricultural additives should be regulated more strictly.

Environmental assessment, i.e. identification of toxic hazards, as well as determination of maximum residue levels require reliable analytical methods. Analysis is often challenging as surfactants are usually complex mixtures, their composition is not exactly known or not well defined, and reliable information and certified reference materials are not available. In addition, they represent a wide range of chemicals in a broad range of polarity, which should be monitored in the environment as pollutants. Surfactants are determined mainly by liquid chromatography coupled to mass spectrometry (LC-MS) [1], as gas chromatography (GC) can be applied only to smaller groups and often rely on derivatisation. An advantage of the GC method is that due to better separation it allows more detailed information about the composition of the mixtures analysed.

To facilitate our ecotoxicology studies of the components in formulated pesticides containing neonicotinoid insecticides (clothianidin, CLO; acetamiprid, ACE) and herbicide glyphosate (GLY) as active ingredients, methods for analytical determination of these ingredients and their surfactant additives were assessed. We have developed an LC-MS method for characterisation of sulfonic acid surfactants in CLO-based insecticide formulation, found to be 46.5 times more toxic than CLO itself on the great water flea *Daphnia magna* Straus [2]. Similarly, linear alkylbenzene sulfonate (LAS) surfactants in an ACE-based insecticide were analysed, and their decomposition in surface water was determined. Thus, the dissipation of LASs was determined alone and in the presence of ACE by using an HPLC-UV instrumental method.

In the present work we focussed on investigation of derivatisation reactions of different sulfonates, as well as silylation of a trisiloxane surfactant and similar surfactants.

Measurements were carried out by using GC coupled to MS (GC-MS), and the results were compared to those obtained by GC with electron capture detection mode or by HPLC-UV.

Experimental

Liquid chromatographic analyses using UV detection mode were performed on a Younglin YL9100 HPLC system equipped with a YL9150 autosampler. LASs were separated on an Acclaim Surfactant Plus column (150 mm × 4.6 mm i.d., 5 μm) at 30°C, and UV detector signals were recorded at λ=225 nm. Quantitative analysis was performed by external calibration. The eluent flow rate was 0.6 mL/min with isocratic elution for 8 minutes (25:75 = A:B eluents, A = 100 mM ammonium acetate in water, B= acetonitrile. Limit of detection (LOD), determined with standard solutions, was at 1.0 μg/mL for dodecylbenzene sulfonate. Analysis of sulfonates in CLO-based formulation was carried out by LC-MS according to the method described in [2].

For GC measurements conversion of LASs and alkylsulfonates (e.g. Nonit, dioctyl sulfosuccinate salt) were investigated. Derivatisation reactions with potassium iodide and trifluoroacetic acid were studied in detail (See Figure 1.). Procedures were carried out according to the method published by Cohen et al. [3].

For chemical modification of Silvet Star, a silylcarbamate derivatising reagent was used [4] (See Figure 2.). This silylating agent was also applied to other surfactants (Triton X, Genamin and Sapogenat).

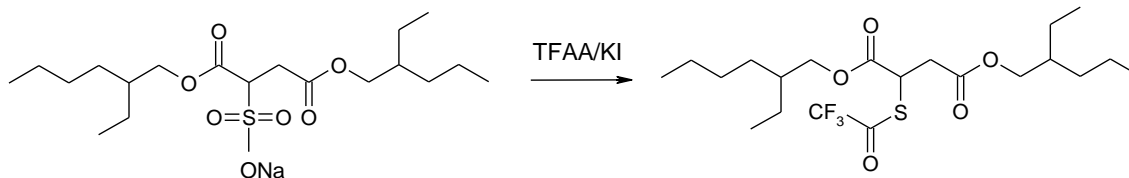


Figure 1. Derivatisation of sulfonates (e.g. Nonit)

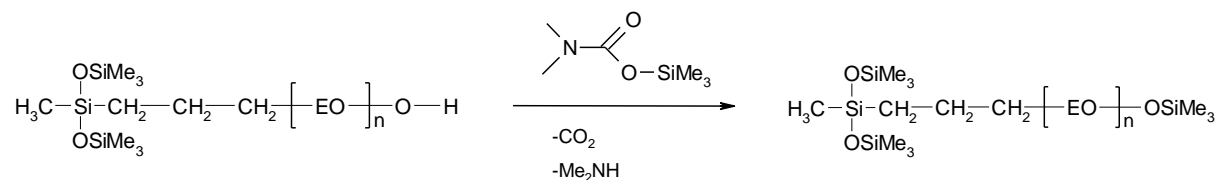


Figure 2. Silylation of Silvet Star

Typical procedures

A. Nonit 0,24 g, 0,42 g KI, 1 mL DMSO, 100 μL trifluoroacetic anhydride (TFAA), heated to 60°C for 60 min, stopped (quench) by Na₂S₂O₃ solution

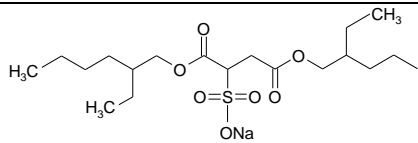
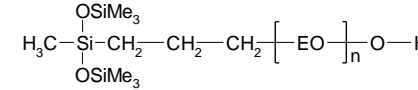
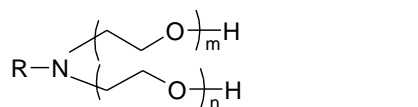
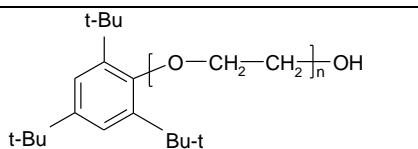
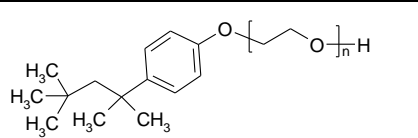
B. Silvet Star (Trisil) 20 μL, 100 μL *N,N*-dimethyl-*O*-trimethylsilyl carbamate (Me₂SiC), 1 mL hexane, room temperature, 30 min

Results and discussion

Several types of surfactants used for formulation of pesticides were studied (Table 1). In case of CLO-based formulation, components of a long-chain sulphonate mixture were detected by using liquid chromatography coupled with mass spectrometry [2]. Homologues were eluted separately from the Acclaim surfactant column, but only partial separation of isomers was achieved. In the extracted ion chromatograms appeared double, triple or even more peaks belonging to the different (groups of) isomers. Isomers containing a sulfonate group in an

internal position of the linear alkyl chain eluted earlier compared to the isomer where the sulfonate group was connected to the second carbon atom (external). As no standards were available for each homologue, we used a practical assumption that every homologue gives equal instrument responses. For quantitative determination of sulfonates, we used the linear calibration obtained for linear hexadecane-1-sulfonic acid that was not present in sample. Concentrations of homologues were calculated by their extracted ion intensities ($[M-H]^-$) related to that of linear hexadecane-1-sulfonic acid. The amounts of surfactants were underestimated, but probably more precise results are obtained if internal standard or standard addition methods are applied.

Table 1. Surfactant substances investigated in the present study

| Trade name | Chemical name | Chemical formula | Structure |
|-----------------|--|---|---|
| Nonit | Diocetyl sulfosuccinate sodium salt | $C_{20}H_{37}NaO_7S$ |  |
| Silvet Star | Trisiloxane (7.5 EO units on average) | $(C_2H_4O)_n$ $C_{10}H_{28}Si_3O_3$ |  |
| Genamin O 080 | Cetyl(C16)/oleyl(C18)-amine ethoxylate (8 EO unit on average) | $(C_2H_4O)_m$ $(C_2H_4O)_n-N-C_{16}H_{35}$ |  |
| Sapogenat T 080 | tributylphenyl ethoxylate (8 EO units on average) | $(C_2H_4O)_n C_{18}H_{30}OH$ |  |
| Triton X100 | polyoxyethylene-octyl-phenyl ether, (9-10 EO units on average) | $C_{14}H_{22}O-(C_2H_4O)_n$ |  |

Linear alkylbenzene sulfonates (LASs) were determined in an ACE-based insecticide, and the decomposition of these substances was characterised in distilled water and surface water. Dissipation of LASs was determined alone and in the presence of ACE by using an HPLC-UV method. DT_{50} values were found to be 67 ± 9 hrs and 21.7 ± 4.5 days for LAS alone and in formulation in surface water, respectively. No significant differences were determined between the corresponding DT_{50} values in distilled water.

Reactions of sulfonates with potassium iodide and trifluoroacetic acid progressed into completeness in 1 hr (Figure 3.), but the stability of these derivatives is poor. As responses recorded by ECD are high, LODs are low for these trifluoroacyl derivatives. Decomposition was observed after one day of incubation, thus, long-term storage of the derivative is not possible. Therefore, application of other reagents (e.g., in port derivatisation with tetrabutylammonium hydrogensulfate) resulting in more stable derivatives should be more suitable.

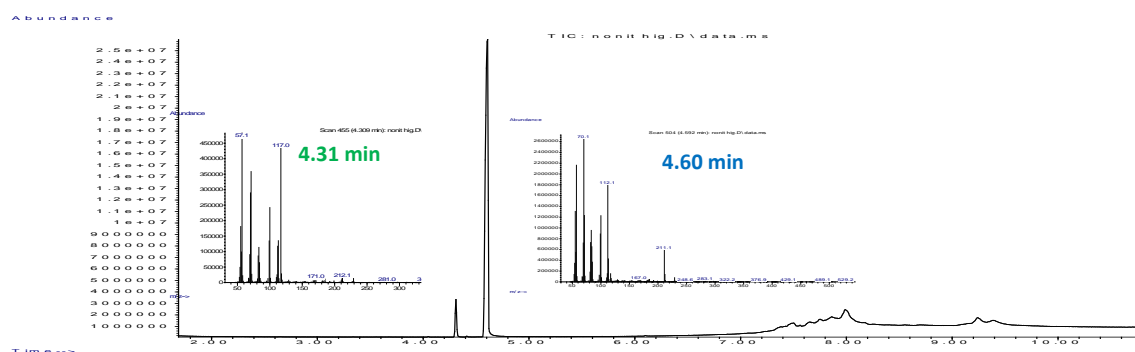


Figure 3. GC-MS chromatogram and mass spectra of Nonit derivative

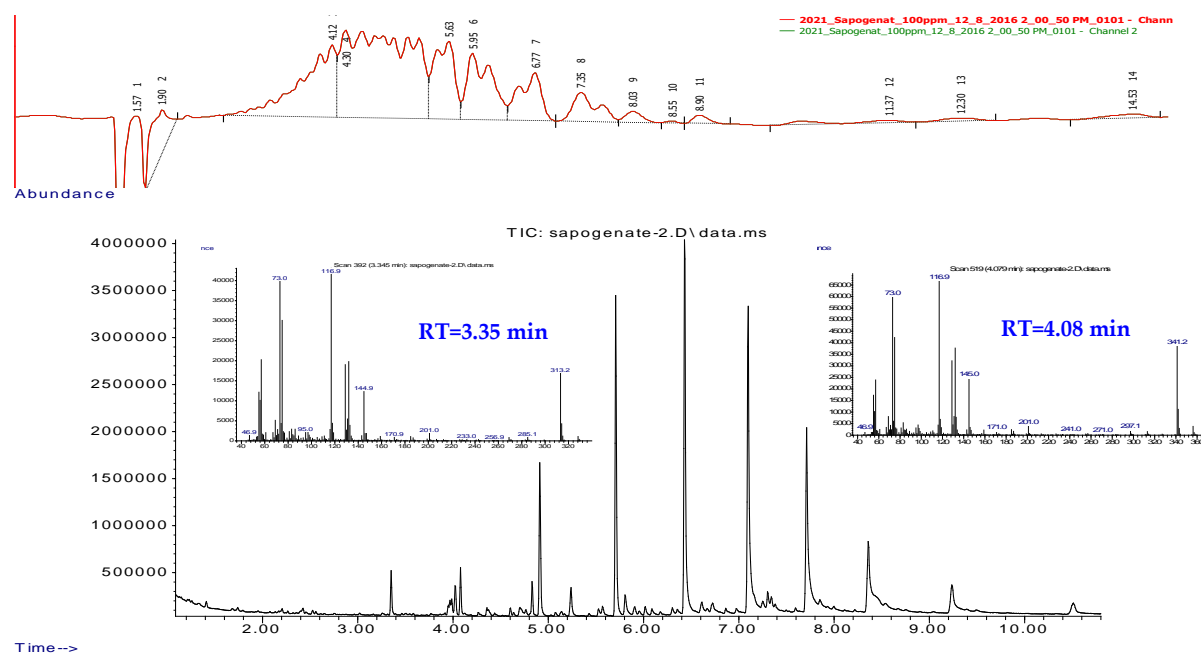


Figure 4. HPLC-UV chromatogram of Sapogenat (upper) and GC-MS chromatogram of silylated Sapogenat and mass spectra of two derivatives (lower)

Silvet Star (Trisil, heptamethyl-trisiloxane modified with polyalkene oxide) together with related surfactants (Triton X, Genamin and Sapogenat) were silylated by using silylcarbmates that were used earlier [4]. GC-MS chromatogram provides more detailed information compared to HPLC-UV chromatogram (See Figure 4.). Based on their mass spectra and chromatographic properties, oligomers of Silvet Star and other investigated surfactants were identified, and their distribution pattern was determined. Stability of the silyl derivatives was ensured by using the appropriate reagent excess or can be further improved by formation of corresponding tert-butyl-dimethylsilyl esters.

Conclusion

Usually liquid chromatography with UV detection or coupled to mass spectrometry (LC-MS) is more convenient for characterization of surfactant mixtures than gas chromatography. However, composition of the mixtures can be characterized in details by using derivatization

and GC separation. Conversion of sulfonates to trifluoroacyl esters and silylation of hydroxy functional group are suitable procedures for chemical modification of surfactants prior to GC measurements.

Acknowledgements

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