The use of LC-MS/MS and GC-MS methods for the quantification and characterization of anionic surfactants in detergent formulations

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INTRODUCTION

Anionic surfactants are the most abundant surfactants used in both liquid and powder laundry detergents commercialized worldwide. Over the past decades, an increasing variety of anionic surfactants, such as linear alkylbenzenesulfonate (LAS), alkyl sulfates (AS) and ethoxy sulfates (AEOS), fatty acid methyl ester sulfonate (MES), secondary alkanesulfonate (SAS), alpha-olefin sulfonate (AOS), and others have been introduced to the market and used in large quantities for synthetic detergent formulation.
The mission of the Battelle detergent program is to provide industry and regulators with information on the chemical composition of home care products in order to monitor formulation changes in response to consumer demand, environmental regulation, and technologic developments.
The development of analytical methods to ensure the accurate identification, quantification, and speciation of anionic surfactants in detergent is crucial not only to the understanding of detergent market trends and cleaning properties, but also in modeling the environmental fate of this class of surfactants once the cleaning cycle is completed and detergents are discharged to wastewater treatment and ultimately to the environment. Modeling the environmental fate of surfactants requires data on the concentration of each surfactant type, the C-chain length distribution of the surfactant hydrophobic tail, whether the C-chain is linear or branched, the ethoxylation number (in the case of AEOS), and the isomeric distribution (in the case of LAS and SAS). This paper presents a systematic approach to the identification, characterization, and quantification of anionic surfactants in detergent formulation by using an array of LC-MS/MS and GC-MS analytical methods that require minimum sample preparation and allow the characterization of a large number of detergents.

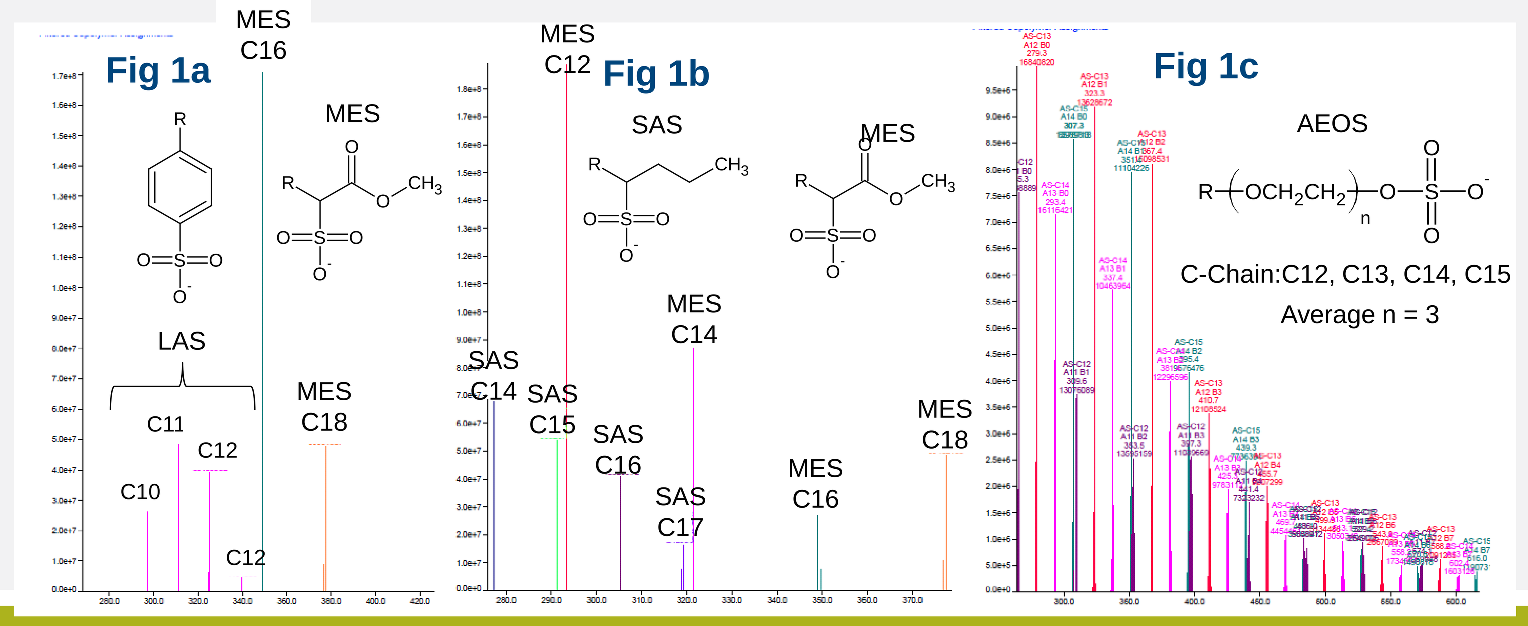
TECHNICAL APPROACH

The complexity of detergent formulation requires a multi-method approach to fully characterize the composition of their anionic system. Following a rigorous sub-sampling, several steps are undertaken in order to provide full characterization of the anionic system:

1. **Rapid identification of the anionic surfactant system** is accomplished by LC-MS infusion of a water/methanol solution of the detergent (Fig 1). This method allows also the estimation of the oligomeric distribution of AEOS and their average ethoxylation number (mole of O-CH2-CH2/ mole of surfactants) (Fig 1b).
2. **Anionic surfactant titrations:** Anionic surfactant concentrations in the detergent formulation are determined by potentiometric (Fig.2) or 2-phase titration of an aqueous/methanol solution of the detergent using a standard solution of cationic surfactants as the titrant. At pH 2, titration results represent the sum of the sulfonated (-SO3) and sulfated (-O-SO3) surfactants. Post-acid hydrolization titrations provide the concentration of the sulfonated surfactants only. Titration performed at pH 11 provides the sum of fatty acids, sulfonated, and sulfated surfactants.
3. **Separation of fatty acids and anionic surfactants from detergent formulation:** A methanolic solution of the detergent is eluted through an Anion Exchanger – Solid Phase Extraction column (AN-SPE). Sulfated and sulfonated surfactants and fatty acids are adsorbed by the anionic exchange resin, while cationic and non-ionic materials are eluted with the methanol solution. Fatty acids are eluted from the AN-SPE with a methanolic solution of acetic acid. Sulfated and sulfonated surfactants are eluted with a methanolic solution of HCl.
4. **Quantification and C-Chain distribution of fatty acids:** Fatty acids isolated from the detergent formulation by AN-SPE are derivatized to their corresponding fatty acid methyl esters and analyzed by GC/MS.
5. **C-Chain distribution of sulfated surfactants:** The anionic fraction of the detergent, separated by AN-SPE, is “cracked” using a mixture of HI/H3PO2 solution at 130ºC for 30 minutes. The resulting alkyl-iodides (R-I) formed during the cracking procedure are extracted in tetrachloroethylene and analyzed by GC-MS (Fig.3).
6. **Quantification and C-Chain distribution of LAS:** A water/methanol solution of the detergent is analyzed by High Performance Liquid Chromatography on a reversed phase column with an ion-pairing agent; LAS is detected using a PDA detector. This method allows the rapid and accurate quantification of LAS, determination of the LAS C-Chain distribution, and estimation of the 2-phenyl isomer content (Fig. 4a). High resolution analysis of the isomeric distribution for each C-Chain is obtained by post desulfonation GC-MS analysis (Fig. 4b).
7. **High throughput LC-MS/MS quantification of anionic surfactant mixture:** An LC-MS/MS method was developed for the quantification of the SAS-MES mixture in detergent formulations. A high throughput LC- MS/MS method is now under development for the quantification of complex mixtures of sulfated, sulfonated, and phosponated surfactants.

RESULTS

Figure 1: LC-MS identification of anionic surfactant mixtures used in laundry detergents. **Fig. 1a)** MES-LAS mixture; **Fig. 1b)** MES-SAS mixture; **Fig. 1c)** oligomeric distribution of alcohol ethoxysulfates and their average ethoxylation number .



RESULTS Cont.

Figure 2: Example of quantification of total anionic surfactants in detergent formulation by potentiometric titration

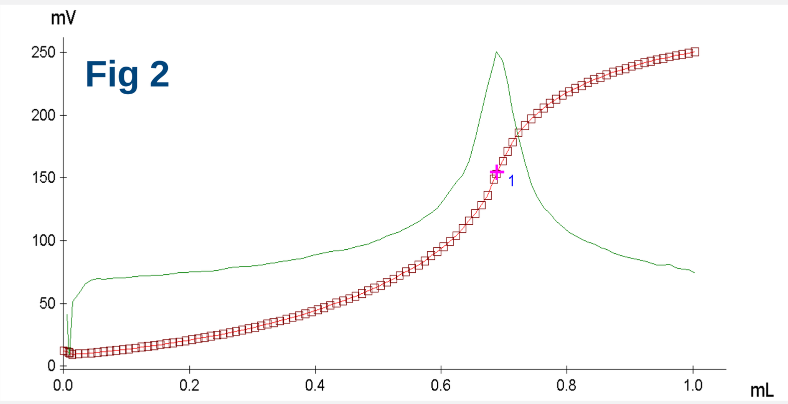


Figure 3: C-Chain distribution of AEOS used in a US laundry detergent

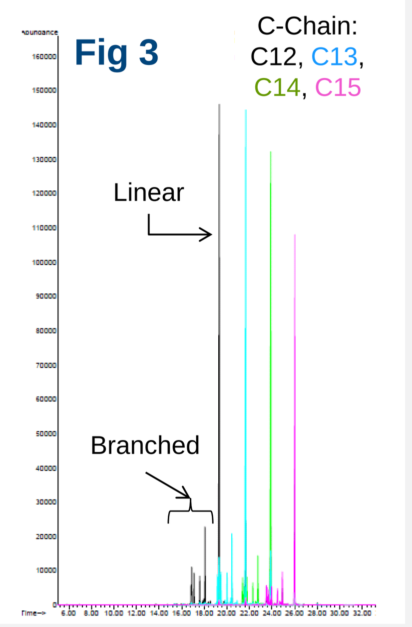


Figure 4: Determination of LAS in detergent formulation.
Fig 4a) HPLC-UV determination of LAS C-Chain distribution and 2-phenyl isomer content.
Fig 4b) High resolution of isomeric distribution for each C-Chain. Results by post desulfonation GC-MS analysis.

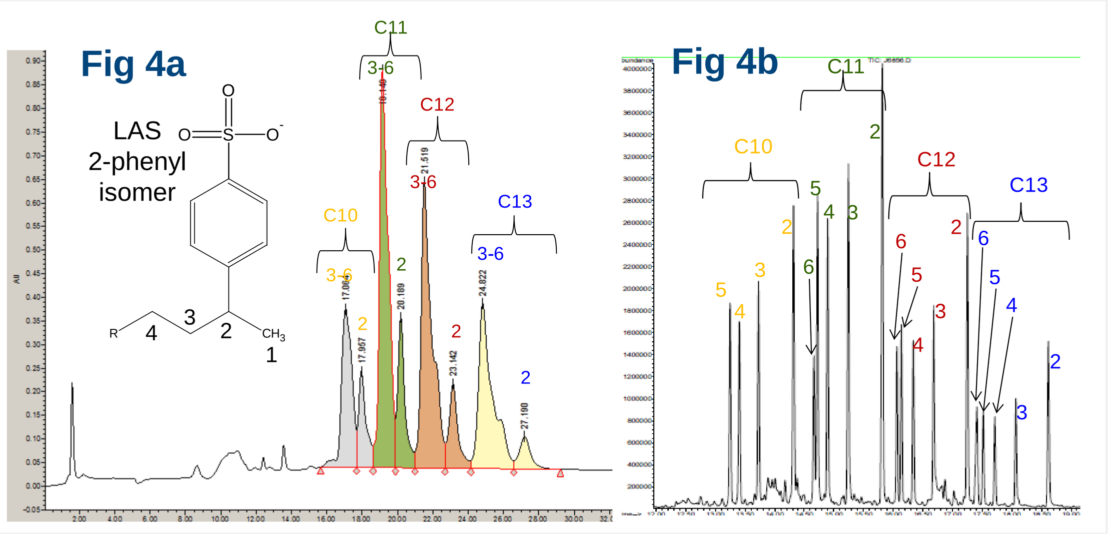
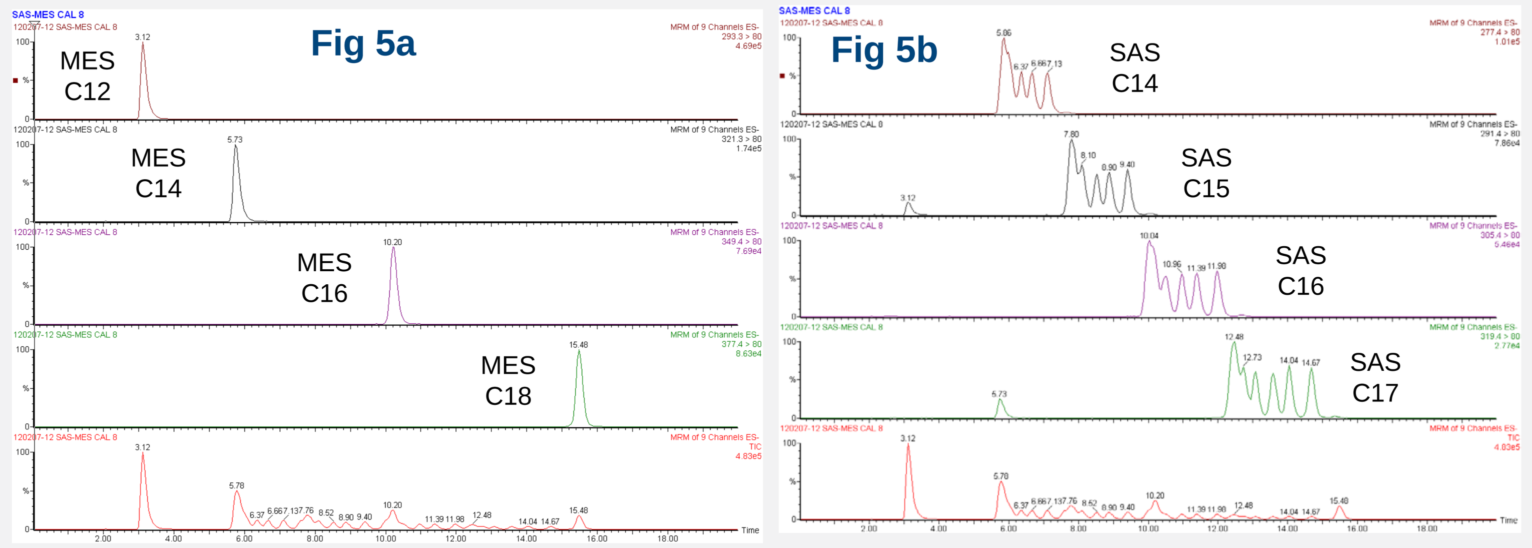


Figure 5: Quantification of SAS-MES mixture in detergent formulations. High resolution C-Chain distribution of each surfactant is obtained (MES **Fig 5a**, SAS **Fig 5b)**. The SAS isomeric distribution for each C-Chain is identified (**Fig. 5b)**



CONCLUSION

The Battelle World Detergent Program uses an array of LC-MS/MS and GC-MS analytical methods that allow for the rapid and efficient identification, characterization, and quantification of anionic surfactants in detergent formulations. These data can be used to track global trends in the detergent composition and in modeling the input of chemicals from home care products into wastewater treatment plants and the environment.

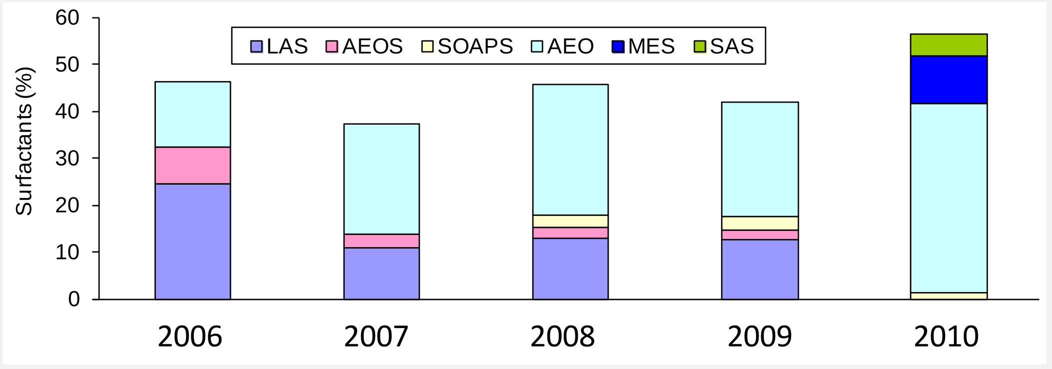


Figure 6: Evolution composition of a US laundry detergents. LAS was substituted with a mixture of SAS and MES in 2010