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

The complexity of detergent formulation requires a multi-method approach to fully characterize the composition of the 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 (in the case of AEOS), and the concentration of each surfactant type, the 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).

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 cations markafest and used in the titrations. At pH 2, titration results represent the sum of the sulfonated (S-O3) and sulfated (O-SO3) surfactants. Post-acid hydrolyzations 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 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 corresponding fatty acid methyl esters and analyzed by GC. The C-Chain distribution of 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.

5. C-Chain distribution of sulfonated surfactants: The anionic fraction of the detergent, separated by AN-SPE, is “cracked” using a mixture of H3PO2/HI 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. 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.

RESULTS Cont.

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.