CHAPTER 4

CONCLUSION

The proposed HPLC method and solid-phase extraction conditions were found to be applicable to the analysis of anionic and nonionic surfactants in various water samples. HPLC-UV conditions for the separation of LAS, simultaneous determination of LAS and Triton X-100 and analysis of SDS were optimized using a Zorbax Eclipse XDB C_8 column.

The optimum separation of LAS homologues containing 10-13 carbon atoms was obtained by appropriately adjusting the composition of mobile phase, type and the concentration of salt. The emphasis was placed on the use of common salts, i.e. sodium chloride, sodium acetate and ammonium acetate instead of using sodium perchlorate, in order to avoid capillary blockage when using mass spectrometric detection for confirmation results. The optimum HPLC condition was the mixture of 80% methanol in water containing 1 mM sodium chloride or 2 mM sodium acetate or 1.5 mM ammonium acetate at the flow rate of 1.0 ml min^{-1} and the detection wavelength of 224 nm. This method could be used to separate the four LAS compounds (resolution > 1.5) in approximately 5 min under isocratic condition at room temperature.

The HPLC method for the simultaneous determination of LAS compounds and Triton X-100 was obtained by improving the condition from the previous method. The mobile phase containing ammonium acetate was selected for this investigation due to its most suitability in mass spectrometric detection. The optimization was performed by increasing the concentrations of ammonium acetate from 1-5 mM in two mobile phase compositions, i.e. 75 and 80% methanol in water. The optimum condition for the separation of LAS and Triton X-100 was the mixture of 75% methanol in water containing 2 mM ammonium acetate at the flow rate of 1.0 ml min^{-1} and the detection wavelength of 224 nm.

The accuracy expressed in terms of percentage recovery of this method for C_{10} LAS, C_{11} LAS, C_{12} LAS, C_{13} LAS and Triton X-100 was found to be between 86 and 99, 84 and 106, 82 and 112, 93 and 123 and 91 and 101, respectively. The limit of detection for each LAS compound and Triton X-100 was calculated as three times the background standard deviation. The detection limits of C_{10} LAS, C_{11} LAS, C_{12} LAS, C_{13} LAS and Triton X-100 were 1.4, 7.9, 7.1, 8.4 and 28.5 ppb, respectively.

Prior to HPLC analysis of LAS and Triton X-100, water samples were subjected to purification and preconcentration on C_{18} cartridge using 3 ml of methanol as eluent. The concentration of C_{10} LAS, C_{11} LAS, C_{12} LAS and C_{13} LAS in wastewater samples were found to be between 5.0 and 310, 23.4 and 1173, 26.5 and 1145 and 21.1 and 424 ppb, respectively. For natural water samples, the concentrations of C_{10} LAS, C_{11} LAS, C_{12} LAS and C_{13} LAS were found to be between n.d. and 3.4, n.d. and 12.8, n.d. and 15.1 and n.d. and 16.7 ppb, respectively. Triton X-100 was not detected in all samples tested. The confirmation of LAS compounds was performed using the negative-ion electrospray-mass spectrometry (ES-MS). The mass spectra of water extracts show the ion at *m/z* 183 that is a common ion for LAS compounds. In addition, the high intensity of the pseudomolecular ions observed at *m/z* 297, 311, 325 and 339 corresponded to C_{10} LAS, C_{11} LAS, C_{12} LAS and C_{13} LAS, respectively.

The developed method for simultaneous determination of LAS and Triton X-100 offers superior performance characteristics, i.e. a simple method, significant improvement in resolution, short analysis time and using less amount of common salt under isocratic condition. With this regard, it is easy to use this method with a mass spectrometric detector without any blockage of MS capillary. In addition, the use of low amounts of salt also increases the column's life and it only requires very short re-equilibration time between each injection. Overall, features demonstrate that the method is suitable to be used for routine analysis for both the quantification and identification of individuals of C_{10} – C_{13} LAS surfactants.

In addition, the HPLC-UV method was developed for the analysis of SDS, non-absorption UV light. Lidocaine, an UV absorption compound, was chosen and added into mobile phase. The optimization was examined by adjusting composition of mobile phase, pH of mobile phase and concentration of lidocaine. The suitable condition for the analysis of SDS was the mixture of 40% methanol in water containing 5 ppm lidocaine at pH 3.4, the flow rate of 1.0 ml min^{-1} and the detection wavelength of 230 nm. This method offers simple method and short analysis time for the screening of SDS in water samples using HPLC-UV technique.

Suggestion for further work

In the case of SDS analysis, the results originating from real water samples showed a negative peak close to the SDS peak. This makes the quantification of SDS in water samples so difficult. Therefore, the development of sample pretreatments or HPLC conditions should be carried out in detail.

The Relevancy of the Research Work to Thailand

Surfactants are a group of chemicals that are widely used both industrially and domestically, hence they have become ubiquitous in the environment. Among these surfactants, linear alkylbenzene sulfonates (LAS) are the most commonly used anionic surfactants in large quantities. They have been used in household laundry and dishwashing detergents. This causes LAS compounds to be released into the environment, the LAS content of which is important in assessing ecological impact due to their toxicity on aquatic organisms. The toxicity of these surfactants depends on its carbon atoms. Therefore, it is essential to determine the amount of individual LAS compound in various water samples. Several methods based on HPLC have been developed for the analysis of LAS. However, most existing methods and procedures are still far from being considered suitable for the routine determination of individual chemical forms of LAS. In this study, HPLC method was developed for routine analysis of LAS mixture, particularly in respect to reducing analysis time, improving separation efficiency and improving suitability of the identification of LAS in water samples using mass spectrometric detection.