Abstract

Haloacetic acids（HAAs）are one class of disinfection byproducts（DBPs）, which are formed when chlorinated disinfectants react with natural organic matter. In Taiwan, chlorination is the main disinfection step of in drinking water treatment. Haloacetic acids have been shown to possess hepatic, reproductive and developmental toxicity, as well as embryotoxicity, mutagenicity and carcinogenicity in laboratory animals. Because HAAs are non-volatile, ingestion is the major exposure route; people usually expose to HAAs through the consumtion of drinking water.

To determine low levels of HAAs is a challenge because of their hydrophilic and strong acidic characteristics. USEPA 552.3 is a standard method for determining HAAs. The method uses gas chromatography–electron capture detection（GC-ECD）for quantitation and can reach a low detection limit to analyze HAAs in aqueous samples, but needs time-consuming and labor-intensive processes of extraction and derivatization.

Due to the strong polarity of HAAs, liquid chromatography（LC）technique is more suitable than GC technique for analyzing non-volatile chemicals in aqueous samples. However, how to retain and separate HAAs with LC columns is the main problem.

Nine chlorinated and brominated haloacetic acids and one emerging disinfection byproduct-monoiodoacetic acid were analyzed without dervatization in this study. HAAs were separated on BetaMax Acid column and HILIC UPLC column, and detected by negative electrospray ionization-tandem mass spectrometry（ESI (-)－MS/MS）. The samples of drinking water were concentrated with vacuum for 40 or 400 times. The recovery of 40-fold preconcentration was 69.7－114%, and was 86.2－102% in that of 400-fold preconcentration. The preconcentration methods had good recoveries, but the matrix effects were high. The ion suppression of HAAs analyzed by BetaMax Acid column was between 12.6－88.6%, and was 53.4－89.2% with HILIC UPLC column.

The on-column detection limit （LOD）of HAAs by BetaMax Acid column ranged from 0.18 to 71.5 pg/μL, and was in the range of 0.08－2.73 pg/μL by HILIC UPLC column. The limits of quantification（LOQ）by BetaMax Acid column and HILIC UPLC column were 1.03－222 pg/μL and 0.31－9.78 pg/μL, respectively.

The LOD of HAAs is lower on HILIC UPLC column, but the sample of HAAs needed to be dissolved in 90% acetonitrile（ACN）before injection. There were no suitable methods to transfer the HAAs from water to ACN directly. So, BetaMax Acid column with 100% aqueous injection was more suitable for analyzing HAAs in drinking water.

BetaMax Acid column can be applied to determine major species of HAAs, such as dichloroacetic acid（DCAA）and trichloroacetic acid（TCAA）without concentration. BetaMax Acid column can also be applied to determine dibromoacetic acid（DBAA）, bromochloroacetic acid（BCAA） and bromodichloroacetic acid（BDCAA）, when the concentrations of these HAAs are higher than 1－3 pg/μL in drinking water. This study provided a method for determination of some HAAs without extraction, derivatization and concentration.

Key words：haloacetic acid, disinfection byproducts, LC/MS/MS