

MASTER'S THESIS

Analysis of polar nitroaromatics in groundwater by using solid-phase extraction and liquid chromatography-mass spectrometry

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Analysis of Polar Nitroaromatics in Groundwater
by using Solid-Phase Extraction and
Liquid Chromatography-Mass Spectrometry

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Abstract

Underground water contamination by the toxic substances associated with 2,4,6-trinitrotoluene(TNT) production had aroused public concern. The contaminations are more serious especially in the vicinity of former ammunition plants. Recently, nitrotoluenesulfonic acids, nitrobenzoic acids and nitrobenzyl alcohols were found to be the major transformation products during the process. Their solubilities are assumed to be higher than the TNT, which implies a greater mobility in water. The high polarity nature definitely complicated the analysis.

Liquid chromatography coupled with mass spectrometry was found to be effective in tackling the analysis. Reversed-phase LC/High-resolution mass spectrometric (HRMS) methods for the determination of six nitrotoluenesulfonic acid, five nitrobenzoic acid and three nitrobenzyl alcohol type compounds in underground water were developed. HRMS analysis using negative ion electrospray (ESI) or atmospheric pressure chemical (APCI) ionization provided good selectivity and sensitivity for the detection. For the determination of nitrotoluenesulfonic acids and nitrobenzoic acids, $^{15}\text{N}_2$ -labeled internal standard was incorporated for better quantitation and mass assignment. For nitrobenzyl alcohols determination, due to the lack of internal standards, fluctuation in signal sensitivity and results in larger relative standard deviation was observed. Structure elucidation and confirmation were accomplished by tandem mass spectrometry. Characteristic ions resulting from the loss of NO, and NO₂ from the [M-H]⁻ ions were detected.

Pre-concentration process using solid phase extraction (SPE) cartridge was promising. Co-polymer HLB SPE cartridge was used for the extraction of both toluenesulfonic and nitrobenzoic acids whereas traditional C₁₈ cartridge was used for

the extraction of benzyl alcohols. Recovery of better than 80 % was achieved when 10 mL of water sample was analyzed.

The combination of the SPE and LC-HRMS gave the method detection limits less than 80 ng/L, 2 µg/L and 2 µg/L for nitrotoluenesulfonic acids, nitrobenzoic acids and nitrobenzyl alcohols, respectively. The method had been applied for analyzing underground water samples collected from a site of a former ammunition plant. The contamination levels can be up to ppb levels.

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