
COMPREHENSIVE NON-TARGETED ANALYSIS OF CONTAMINATED GROUNDWATER OF A FORMER AMMUNITION DESTRUCTION SITE USING ¹H-NMR AND HPLC-SPE-NMR/TOF-MS

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The aim of the present study was to explore the capabilities of the combination of ¹H-NMR (proton nuclear magnetic resonance) mixture analysis and HPLC-SPE-NMR/TOF-MS hyphenation (high performance liquid chromatography coupled to solid phase extraction and nuclear magnetic resonance and time of flight mass spectrometry) for the characterization of groundwater samples contaminated by explosive residues. As an example, solid phase extracts of two ground water samples taken from a former ammunition destruction site in Switzerland were investigated. ¹H-NMR spectra of post column SPE enriched compounds, together with accurate mass measurements allowed the structural elucidation of unknowns. Contaminants identified by these techniques were quantified based on HPLC-UV (HPLC-ultra violet detection) and ¹H-NMR mixture analysis. Besides expected residues of explosives such as 2,4,6-trinitrotoluene (2,4,6-TNT), Hexogen (RDX) and Octogen (HMX), degradation products of TNT 1,3,5-trinitrobenzene (1,3,5-TNB), 2-amino-4,6-dinitrotouene (2-A-4,6-DNT), 3,5-dinitrophenol (3,5-DNP), 3,5-dinitroaniline (3,5-DNA), 2,6-dinitroanthranile were detected together with an unknown nitroaromatic degradation product. In addition to these explosive related contaminants, benzoic acid and Bisphenol A, a known endocrine disruptor compound, and some toxicologically relevant additives for propelling charges were found at concentrations at the µg/L-level: Centralite I (1,3-diethyl-1,3-diphenylurea), N-methyl-N-phenylurethane and N,N-diphenylurethane. The concentrations of the contaminants determined ranged between 0.1 and 48 µg/L assuming 100% recovery for the SPE step.