

NEW PERSPECTIVE ON THE DETERMINATION OF POLYBROMINATED DIPHENYL ETHERS AND OTHER FLAME RETARDANTS IN SEWAGE SLUDGE BY ULTRA HIGH PRESSURE LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY WITH ATMOSPHERIC PRESSURE CHEMICAL IONIZATION AND ATMOSPHERIC PRESSURE PHOTOIONIZATION

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Abstract

Analysis of eleven polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A bis 2,3-dibromopropylether (TBBPA-bis), tetrachlorobisphenol A (TCBPA), tetrabromobisphenol A (TBBPA) and hexabromocyclododecanes (HBCDs) was optimized by UPLC/MS-MS operating in negative ion mode. ESI, APPI and APCI sources were tested and for PBDEs APCI gave higher sensitivity than APPI while for TBBPA-bis APCI and APPI showed similar performance. ESI was the best option for TCBPA, TBBPA and HBCDs. On-column detection limits were between 20 and 59 fg for the compounds analyzed by NI-ESI, 0.10 and 0.72 pg for PBDEs and 6 pg for TBBPA-bis. The matrix effect of sewage sludge extract was also tested showing negligible ion suppression for APCI and an increase of the background level of all investigated pollutants leading to a worsening of the limits of quantification by a factor between 1.2 and 3.3. The UPLC/NI-APCI-MS-MS method for PBDEs, after pressurized liquid extraction (PLE), was validated by comparison with the concentration values from the NIST 1944 standard reference material. The advantages of the methods include low detection limits, PBDE congeners specificity using selected MRM transitions, and the absence of thermal degradation of higher PBDE congeners, especially BDE-209. The methods were applied for the determination of the above reported flame retardants in sewage sludge in order to get more information about the degradation on PBDEs (in particular BDE-209) during municipal wastewater treatments.