LIQUID CHROMATOGRAPHY-ATMOSPHERIC PRESSURE PHOTOIONIZATION – TANDEM SPECTROMETRY (LC-APPI-MS/MS) FOR THE DETERMINATION OF POLYBROMINATED DIPHENYL ETHERS (PBDEs)

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Polybrominated diphenyl ethers (PBDEs) are a group of aromatic compounds having the formula C12H10-nBrnO (n: 1-10). They have been produced synthetically and used extensively as flame retardants, and are now detected in the environment. They have been found to act as endocrine disruptors and due to their adverse health effects, their production in Europe and the USA has been banned. The aim of this study was the development of a method for the simultaneous determination of six PBDEs: BDE 28, 47, 99, 100, 153 and 154, using liquid chromatography – atmospheric pressure photoionization – tandem mass spectrometry (LC-APPI-MS/MS) technique. The difficulty presented in the acquisition of mass spectra was the selection of the ionization mode. More specifically, five of the congeners (PDE 47, 99, 100, 153 and 154) could be ionized in negative mode and in all cases an intense peak that corresponds to [M-Br+O]- ions was observed. However, this was not possible for BDE 28. In this case, it was necessary to use positive ionization mode, where a peak that corresponds to [M]+ was noted. Therefore the use of both positive and negative ionization modes in the same method was the key to the simultaneous determination of the selected PBDEs. To the best of our knowledge, such method has not been reported before. The mass spectra, in full scan mode, of the selected congeners were recorded. Toluene was selected as the most appropriate dopant. Finally, single reaction monitoring (SRM) experiments were conducted in order to find the most intense fragments of each analyte and the optimization of MS parameters was carried out. An observation about MS parameters was that relatively low vaporizer and capillary temperatures should be used, and a low skimmer offset voltage should be applied. Liquid chromatography separation of the PBDEs was achieved using a Zorbax SB C18 Rapid Resolution HT (50×4.6mm, 1.8µm) column and a mixture of methanol – water as mobile phase following a gradient elution. Calibration curves were constructed for each analyte and instrumental limits of detection (LoDs) and quantification (LoQs) were estimated. Instrumental LoDs ranged from 41 to 119pg on column. The developed method showed a wide linearity range with sufficient correlation. In conclusion, the developed method can be applied for the determination of the selected PBDEs in trace amounts in environmental samples such as surface water.

KEYWORDS: polybrominated diphenyl ethers (PBDEs), atmospheric pressure photoionization (APPI), tandem mass spectrometry (MS/MS), dopant.

REFERENCES: