Analytical protocol for the determination of polybrominated diphenyl ethers (PBDE) in sediments by GC-MS

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Introduction

Indiscriminate application of polybrominated diphenyl ethers (PBDE) in several products used by the people, associated to neglected factors such as toxicity, transportation and disposal of these flame retardants have been widely reported by literature once such compounds have been identified in environmental compartments[1]. In this work chromatographic conditions were optimized in order to determine 14 PBDE congeners using gas chromatography coupled to mass spectrometry (GC-MS), employing factorial design and taking into account a protocol recommended by the U.S. EPA[2]. Method adaptations were proposed for the extraction and clean-up steps in order to spend smaller amounts of organic solvents[3]. Thus, the aim of this work was to develop an analytical protocol aiming the determination of PBDE using environmentally friendly techniques, considering the precepts of Green Analytical Chemistry.

Results and Discussion

The development of the chromatographic method was carried out by the injection of standard solutions containing 14 congeners in the concentration of 15 ng mL^{-1} into the GC-MS (Focus-Polaris Q, Thermo). Monitored response was the geometric mean of chromatographic peaks areas. Initially a 2^3 factorial design was developed to evaluate the factors that could contribute to compounds degradation and discrimination. Factors assessed were: injector temperature [250ºC, level (-); 300℃ level (+)], splitless time [1 min, level (-); 3 min, level (+)] and transfer line temperature [250ºC, level (-); 300℃ level (+)] with triplicate in central point giving a total of 11 experiments. Optimized condition was based on the experiment in which all factors indicated level (+). Analysis of effects indicated that at 95% confidence level only injector and transfer line temperatures were significant. Optimization was repeated fixing the splitless time for 3 min for all subsequent tests. Variables such as time pressure and surge pressure were evaluated [0.25 min level (-), 1 min level (+)], [50 kPa, level (-); 150 kPa level (+)], respectively. These factors were evaluated in order to improve method sensitivity as well as selectivity. A 2^4 factorial design consisting of 19 random experiments was carried out with triplicate in central point. It was observed that only the pressure pulse was significant at 95% confidence level. However, analysis of chromatograms resolution showed that best conditions for PBDE determination were those ones whose level (+) were applied to all assessed factors. In order to optimize the clean-up procedure we used a 20 cm height pipette with a 0.6 cm internal diameter filled with 1.0 g of silica and 1.0 g of activated alumina. A PBDE solution (100 µL, 2 mg L^{-1}) was eluted with 9 mL of dichloromethane and hexane (3:1 v/v). Eluate was collected every 0.5 mL and dried under a nitrogen gas flow until 100 µL and then injected into the GC-MS. Tests showed a standard deviation in the range of 2% to 9% for the analytes areas, as shown in Figure 1, and recovery between 96% and 125%.
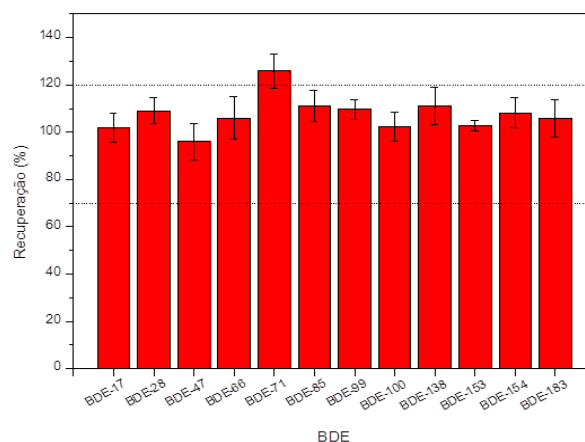

Figure 1: PBDE congeners recovery relative to clean-up step

Optimization of the extraction step was performed using a 500 W ultrasonic probe and through a 2^3 factorial design. The effects evaluated were the extracting solvents [n-hexane level (-), dichloromethane level (0) and acetone level (+)]; solvent volume [4.0 ml level (-) and 8 mL level (+)] and sonication time [3 min level (-) and 7 min level (+)]. To this end, 1.0 g of Na_2SO_4 was spiked with 15 ng mL^{-1} PBDE standard solution and kept at time-out for 48 h. The sonication was conducted in three consecutive stages and the final volume was reduced to 100 µL for the clean-up and injection into the GC-MS. Acetone was observed to be the most efficient extracting solvent in a volume of 4.0 mL and sonication during 3 min. Recovery values ranged from 76% to 87%, with a standard deviation from 10% to 14%. The method presented a linear range from 0.5 ng mL^{-1} to 10 ng mL^{-1}; correlation coefficients between 0.9900 and 0.9995; detection limits from 0.21 ng mL^{-1} to 1.36 mg mL^{-1} and quantification limits varying from 0.63 ng mL^{-1} to 4.12 ng mL^{-1}.

Conclusion

The factorial design applied to chromatographic conditions optimization allowed identifying 12 congeners in a small number of experiments, minimizing the effects of degradation and discrimination in addition to obtaining satisfactory sensitivity and efficiency. Similarly, optimization of clean-up and extraction steps allowed efficient analytes separation. Through the merit figures it is possible to conclude that the proposed method can be considered as a reliable alternative to the existing one with the advantage of significantly reducing the use of solvents aiming analyst and environmental safety, in addition to saving energy as recommend by the Green Chemistry.

Acknowledgements

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