ADVANCES IN AUTOMATION FOR THE MEASUREMENT OF SELECTED PBDEs IN HUMAN SERUM

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Introduction

The isolation and measurement of selected PBDEs in human serum is a challenging activity that requires high level of analytical skills. Although the number of target analytes is quite limited, compared to other POP situations, major challenges are related to general background contamination level of the laboratory environment, compared to the trace levels to be measured, especially in European specimen. Analytical procedure have thus to ensure proper control of blank levels to permit the use of small sample sizes. Key factors in that optic are first to ensure the use PBDE-free consumables and glassware, and also to reduce the contact between the laboratory environment and the sample extract at all stages of the procedure. Fulfilling those requirements is a necessary but not a sufficient condition. Sometimes, getting rid of background contamination is not feasible and one can only try to minimize the impact of the background contamination on actual measurements. The use of miniaturisation and automation and closed-vessel procedures can somehow help reducing contamination of specimen extracts from the environment[1]. Solid-phase extraction (SPE) and diatomaceous earth supported liquid-liquid extraction are amongst the most used approaches. This paper reports on the use of automated SPE and multi-column clean-up for the measurement of selected PBDEs in human serum. The results highlight the interest of automation.

Materials and Methods

Extraction was performed using C18 octadecyl (non-endcapped) 1g/6 mL (Argonaut, Mid Glamorgan, UK). The extraction was automated using the Power-Prep SPE system (Fluid Management Systems (FMS) Inc., Waltham, MA, USA) capable to extract 5 samples sequentially per module. All solvents and consumables were issued from routine dioxin procedures. The 10-12 mL issued from the SPE are directly loaded on the Power-Prep clean-up system (FMS). The clean-up procedure consisted in the use of multilayer silica (2 g acid, 1 g basic, and 0.75 g neutral) and basic alumina (4 g) Teflon disposable 'PBDE-free' columns[2]. The eluate (30 mL of hexane-dichloromethane 50:50) was concentrated to 500 µL in the PowerVap™ 6 system (FMS) using GC-vial connected evaporation tubes. Final solvent reduction took place overnight at room temperature after 5 µL of nonane was added as keeper. The final extract volume was 5 µL. Measurements were carried out on a MAT95 XL (ThermoFinniganMAT, Bremen, Germany). The GC column was a ZB-5 (15 m x 0.25 mm ID x 0.25 µm df) (Phenomenex, Utrecht, Netherlands). 2 µL of the final extract in nonane (5 µL) were injected into an SSL injector held at 275°C in splitless mode.

Results and Discussion

The automated SPE and clean-up take 1.5 h to complete. Recovery rates for the selected PBDEs (209 excluded) ranged between 50% and 90%. The closed-vessel approach allowed achieving better control on blank levels. This procedure allows measuring European human background levels in aliquots of 10 mL of serum (less than 10 pg/g fw for BDE-47, 2 pg/g fw for BDE-100 and BDE-99, and 5 pg/g fw for BDE-153). Blank levels for BDE-47 and BDE-99 are still of concern for us but this is related to a high environment signal. The use of carbon filter on the air flow of the evaporator is one of the extra actions that can be taken to limit this contamination. Further investigation of all different parts of the instrumentation is on-going to ensure that no 'hot-spots' exist in the procedure.

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[1] Sjödin et al., Anal. Chem. 76 (2004) 1921 and Sjödin et al., Anal. Chem. 76 (2004) 4508.
[2] Pirard et al., J. Chromatogr. A 1115 (2006) 125.