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EVALUATION OF GAS CHROMATOGRAPHIC INJECTION TECHNIQUES FOR PBDE

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Introduction

During the last years there has been an increasing concern for polybrominated diphenyl ethers (PBDEs) as environmental pollutants. These compounds are used as additive flame retardants in a wide range of materials[1] and have been found in sediments, sewage sludge and marine biota as well as in human blood and mothers milk[2]. The use of the fully brominated BDE-209 has been increasing while the use of the less brominated congeners is decreasing. Even though the BDE-209 is one of the most commonly used PBDE commercially only a few number of determinations have been reported, for instance in human blood[3] and in air[4, 5].

Gas chromatography is today the method of choice for the separation of PBDE due to high resolution and low detection limits using either the electron capture detector (ECD) or mass spectrometry (MS). Splitless is the most commonly used injection technique for GC separation of PBDE[6]. However, both the septum equipped temperature programmable injector (SPI) and the programmable temperature vaporising (PTV), injector as well as on-column has been successfully used[6]. Large volume injections (LVI) using either the PTV in solvent elimination mode or the loop type interface have also been used[4, 7, 8].

The injection of PBDE into the GC system is a critical and important part of the chromatographic analysis. Thus, a careful selection and optimization the injection techniques have to be performed in order to reduce the discrimination of theses compounds. In this paper we present an evaluation and optimisation of the most commonly used injection techniques for PBDE.

Materials and Methods

Similar columns (15m, 0.25 i.d., 0.10 μm f.t. J & W, DB-5MS) was used in all systems. The splitless, on-column, direct and the PTV injection technique was evaluated using an Agilent 6890 connected to a 5973 mass selective detector (Agilent Technologies, Palo Alto, SA, USA). A standard solution was prepared by dissolving the individual BDE congeners (Dept. Environmental Chemistry, Stockholm University) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) (kind gift from Amelie Kierkegaard, ITM, Stockholm University) in toluene and diluting to the desired concentration in hexane. Air samples were collected indoor in an electronics dismantling facility in accordance to previously published work[4].

Results and Discussion

On-column: Since the sample is introduced directly onto the column at temperatures below the boiling point of the solvent, the risk for thermal degradation and discrimination during the injection is very low. For clean matrices such as air samples, this injector provides a very good yield and a low RSD compared to other injection techniques, table 1. A comparison between the on-column injector and the splitless injector for an air sample is presented in figure 1.

Direct injection: An isothermal direct injection was evaluated using a direct injection insert in the splitless injector. The column is inserted tightly into the liner like in a pressfit connector, and the sample is injected close to the column inlet. In this way a kind of hot at-column injection is performed. As can be seen in figure 2, this injection mode provided a high yield for the investigated BDE-

congeners but with a higher RSD compared to the on-column injection. The direct injection is a promising technique, combining the robustness of the splitless injector with the low discrimination of the on-column injector, but needs to be further optimised.

Splitless injection: The vaporizing injectors such as the commonly used splitless injector is suitable for complex matrices, *e.g.* sediment, blood and biota samples. However, the technique may discriminate the high molecular weight congeners, partially by degradation, resulting in high LOD and low precision. A factorial design experiment was performed to optimize the splitless injection of PBDE with respect to the yield of BDE-209. The factors evaluated were injection temperature (256-325 °C), splitless time (1-3.5 min) and injection pulse (0.11-3.6 bar). The significant factors, injector temperature and splitless time, is plotted as a function of peak area for BDE-209 in figure 3. As illustrated, the temperature should be kept as high as possible and the splitless time should be as long as possible. No increased degradation with temperature was observed within the investigated interval. Surprisingly, according to the results from the factorial design, the injection pulse did not significantly affect the yield for any of the investigated BDE-congeners. However, it should be noted that this results may differ between different instrument set-ups *e.g.* when using the PTV injector. The optimized splitless injection was compared to the mean settings for the splitless injection used for the GC analysis of BDE-209 in an interlaboratory study[6]: inj temp 275 °C, splitless time 2 min and no pressure pulse. Figure 2 shows that the optimized method was clearly better than the mean settings. When analyzing an air sample, both the mean and the optimized settings gave unsatisfactory results with RSDs in the range of 7-19 %. The optimized splitless did, however give a 2-3 times higher S/N value for BDE-209 in the sample.

PTV injection: The PTV injector can be operated in many different modes such as split, splitless and pulsed splitless, either at constant temperature or with temperature programming. Figure 4 shows the yield and RSD for some selected BDE-congeners for the different operational modes. The yield of especially the high molecular weight BDE-congeners was increased when a temperature programming is applied compared to constant temperature. The highest yield as well as the lowest RSD was obtained when both a temperature programming and a pressure pulse were applied.

Large volume injection PTV: The solvent vent mode offers the possibility of large volume injection on the GC system. Since PBDE comprise a group of high boiling compounds, trapping of the analytes during the solvent elimination time is usually not a problem. However, some losses of mono- and diBDE were observed. Some difficulties with the LVI-PTV injection are associated with the risk of flooding of the injector, to various extent. This is due to too high injection rates compared to the evaporation rate, resulting in a reduced yield, mostly for the high molecular weight congeners. To avoid flooding an injection temperature above the boiling point of the solvent and a high vent flow can, and should, be applied.

The composition of the sample and the sample matrix should determine which injector should be used for the analysis of PBDE. The on-column injection showed the highest yield of the investigated BDE-congeners and good RSD values. However, this injection technique is sensitive to contamination. For ‘dirty’ samples the PTV injector in temperature programmed pulsed splitless mode is the best choice, providing high precision and relatively low discrimination. The splitless injector is, even when optimised, not suitable for the high molecular weight congeners.

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Injection type	Standard absolute areas n=5	Standard relative areas n=5	Sample 1st run n=3	Sample 2nd run n=3
On-column	3.1 %	1.2 %	3.5 %	2.3 %
Splitless (opt)	2.3 %	2.0 %	7.6%	19%
Splitless (mean)	25 %	21 %	19 %	10 %
Direct injection	12 %	9.4 %	11%	-
PTV	1.3 %	0.7 %	-	-
LVI-PTV	2.4 %	1.3 %	4.3 %	-

Table 1: The RSD for different injection techniques for injection of a BDE-209 standard and an air sample.

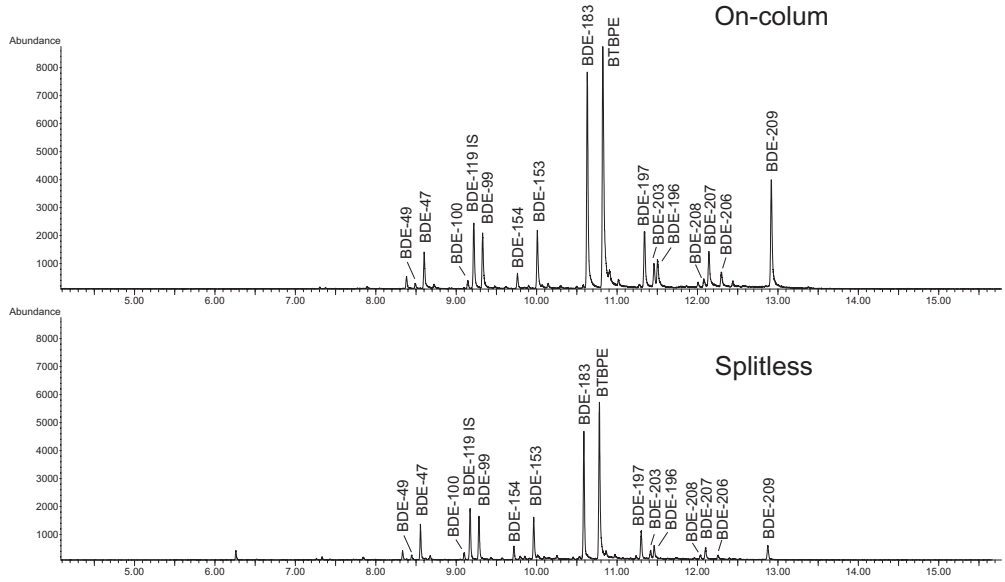

Figure 1: Chromatograms from an air sample using A) on-column and B) splitless injection.

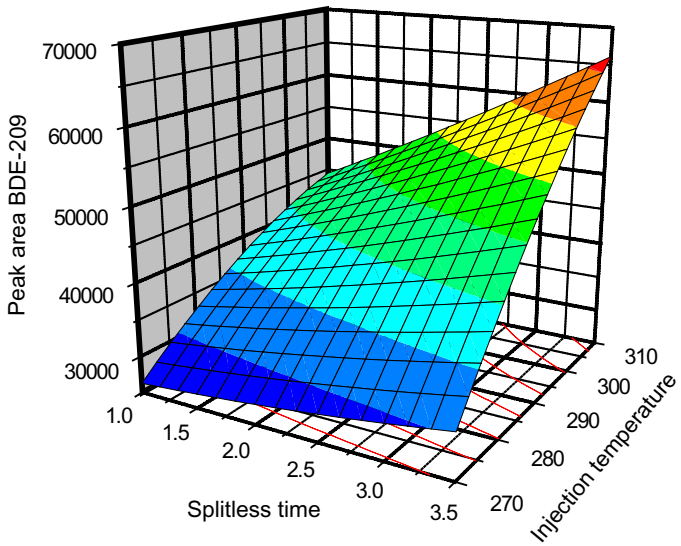

Figure 2: Surface response plot of the peak area of BDE-209 for the significant factors; splitless time and injection temperature.

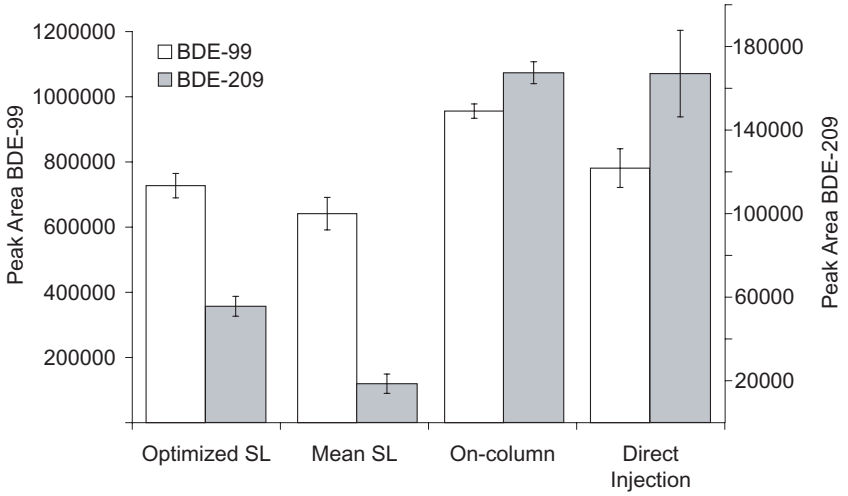

Figure 3: The yield of BDE-99 and BDE-209 obtained using different injection techniques.

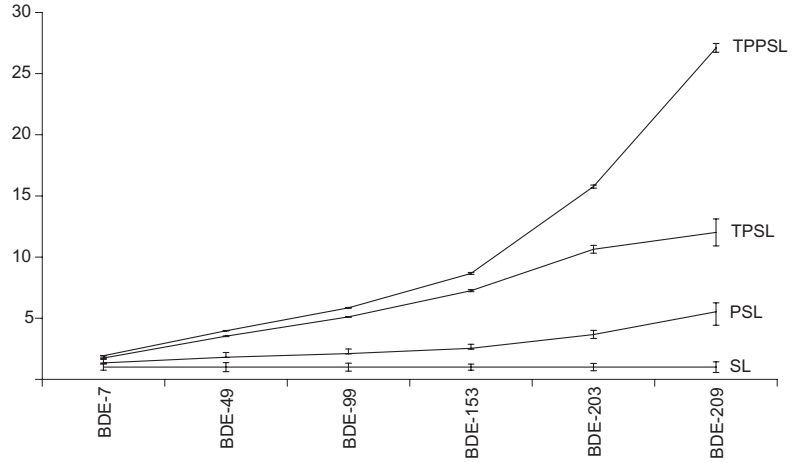

Figure 4: The yield of selected BDE-congeners for different modes of the PTV injection. SL= constant temperature splitless, PSL=constant temperature pulsed splitless, TPSL=temperature programmed splitless and TPPSL=temperature programmed pulse splitless.

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