Comparative Studies of PTV On-column Injection for Improved Sensitivity in High Resolution GC/MS Analysis of Thermolabile High Boiling Brominated Flame Retardants

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Introduction

Brominated biphenyl ethers (BDE's) are among the most important and most widely used flame retardants in a range of different industrial products. They are found worldwide in practically all types of matrices moving them into the focus of legislation.
Among the BDE congeners decabromodiphenylether (BDE-209) is the most important commercial BDE flame retardant. Due to it's intrinsic properties – very high boiling point combined with low thermal stability - BDE-209 is difficult to analyze.
In this study chromatographic parameters including different injection techniques have been compared and optimized in order to achieve minimal thermal breakdown resulting in optimum achievable sensitivity. PTV on column injection is presented as a versatile alternative to a standard on column injector.

Methods

All measurements were carried out on a DFS high resolution GC/MS system (Thermo Fisher Scientific, Bremen, Germany) coupled to a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, Milan, Italy), equipped with a split/splitless (SSL) and a programmed temperature injector (PTV). Samples were automatically injected using a TriPlus XT autosampler (Thermo Fisher Scientific, Milan, Italy). 1µl of each sample was injected on a 15 m x 0.25 mm x 0.1 µm TR-5MS column, installed inside the GC either attached to the SSL or PTV injector. For PTV on-column injections the column was coupled to a widebore 0.53 mm pre-column via a standard press-fit connector. A special PTV on-column liner was used working as a needle guide.

Results

The studies were carried out on two individual brominated flame retardants, which can act as models for high boiling thermally sensitive analytical compounds: Decabromodiphenylether (BDE-209) and Decabromodiphenylethane (DBDPE).

It could be demonstrated that the degree of thermal decomposition strongly depends on the chromatographic parameters e.g. column dimensions, GC oven program. For BDE-209 the effect of thermal decomposition increases with fast oven ramps. In addition the effect of column length on the analytical response has been studied. Short columns result in less degradation and significantly increased signal heights.
In conclusion, the lower the temperature at which the compound is eluted off the column the higher is the response. A compromise between acceptable sensitivity for high boiling thermolabile congeners and

sufficient separation power for the analysis of the lower brominated BDE's is a 15 m TR-5MS column. The detection of 1 pg on column of BDE-209 is achievable using standard SSL or PTV injectors. Even under optimized conditions still thermal decomposition on the column and in the injector takes place. For this reason investigations on the identification of degradation products of BDE-209 were carried out, in order to validate, if lower brominated BDE's are produced, which might influence the correct quantification of BDE's of the same type.

Finally an analysis method was developed using the versatile PTV injector for on-column injections in order to decrease thermal degradation during the injection phase. As an alternative to a conventional on column injector this techniques results in a sensitivity increase by a factor of 5 to 10 compared to SSL or standard PTV injection.

Novel Aspect:

Different injection techniques for thermolabile brominated flame retardants in GC/HRMS analysis of were optimized, compared and evaluated.