The Application of Large Volume Injection Techniques for increased Productivity and Sensitivity in Routine POPs Analysis with GC-HRMS and TripleQuad GC-MS

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Introduction

The three most important injectors for gas chromatography are the split/splitless (SSL), the programmed temperature (PTV) and the on column injector (OC). Simplicity, robustness and low price makes the SSL the by far most commonly used injector in routine GC-MS POPs analysis. While being the perfect injector for thermolabile compounds the OC is commonly considered to have a limited usability for dirty samples. The PTV finally is the most versatile and flexible injector. All three injectors feature specific large volume injection (LVI) properties, which are more or less suitable for a specific application.[1] Whereas in conventional analysis methods for POPs typical injection volumes are in the range of 1 or 2 ul, LVI techniques allow to inject 10 to over 100 ul depending on the selected technique and type of application.

The objective of this study is to demonstrate the specific suitability of PTV large volume injection techniques for POPs analysis on the example of dioxins/furans. The PTV basically offers 3 different modes for injecting mid to large volumes of sample extract: PTV delayed splitless (PTV SL), PTV large volume (PTV LVI) and PTV large volume backflush (PTV LVI BKF). Additionally a series of experiments for injecting samples with a standard splitless injector (SSL LVI) – making use of the concurrent solvent recondensation effect - were carried out.

Typically dioxin/furan sample extracts after cleanup range from 10 to 100 ml and are concentrated in the last sample preparation step to final volumes prior to injection of 8 – 25 ul. In this context injecting slightly higher volumes can help to enhance the analytical sensitivity[2], whereas injections of large volumes can reduce or even omit the final concentration step of the sample preparation.

Materials and Methods

All experiments were carried out on a DFS High Resolution GC/MS and on a Quantum GC triple quadropole MS. Both MS systems were coupled to a TRACE GC Ultra™ gas chromatograph equipped with a SSL and PTV injector (PTV with large volume injection mode). All samples were injected using a TriPlus™ autosampler.

A 30 m TRACE™ TR-5MS, 0.25 mm I.D., 0.1 um film was used on both MS systems. For the PTV LVI BKF the backflush option was installed on the GC by coupling the analytical column to a 2 m x 0.53 mm (deactivated) pre-column. PTV LVI experiments were carried out with and without attaching a precolumn. A PTV liner with glas wool and a 100 ul syringe with a side hole in the needle was used for injecting large volumes.
All experiments with large volume splitless (SSL LVI) were carried out with a 2 m x 0.53 mm (deactivated) pre-column attached via a pressfit connector, a liner with glas wool at the bottom and a merlin cap attached to the split/splitless injector.

For the experiments dioxin/furan calibration standards (Welington Lab. Inc., Canada) and different types of food and feed sample extracts were employed. Standards and sample extracts were diluted according to the different LVI experiments up to a factor of 1/80 in toluene or hexane.

Results and Discussion

Injection of increased volumes (4 – 20 ul)
Up to 20 ul of sample were injected in PTV splitless mode (or more correct PTV *delayed* splitless mode) and using the SSL injector with concurrent solvent recondensation technique (SSL LVI, Fig. 1) with very good peak

shapes. For the PTV splitless mode no pre-column for analyte refocusing was necessary. Crucial parameters are the initial oven temperature and the isothermal time for the initial PTV temperature.

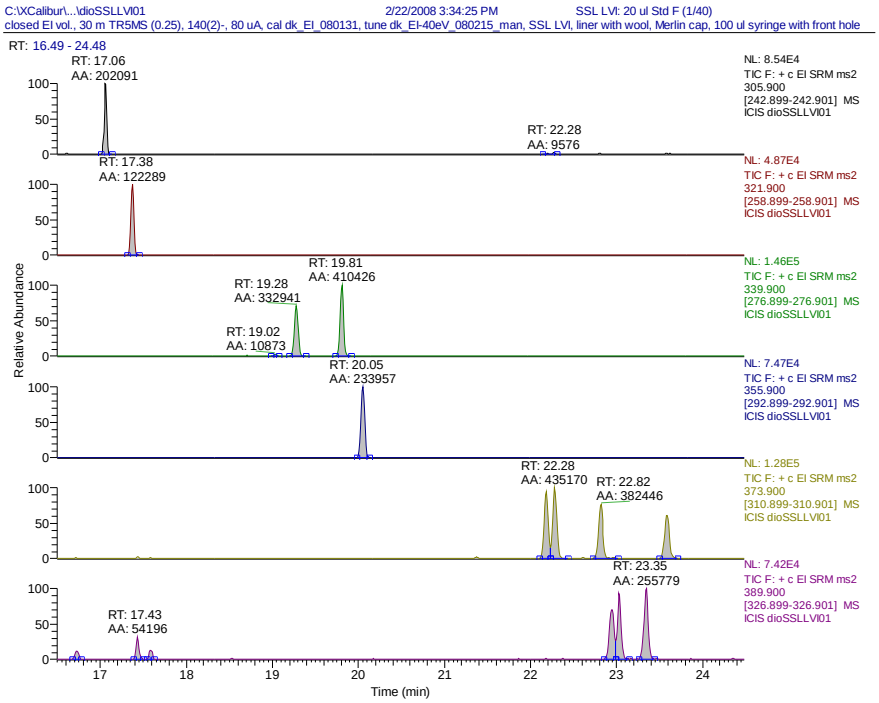

Fig. 1: 20 ul injected in SSL LVI (concurrent solvent evaporation) native tetra to hexa dioxins/furan mass traces

Large volume injections (20 – 80 ul)

Large volume injection analysis methods were developed for up to 80 ul of dioxins/furans in toluene and partly in hexane (up to 40 ul). Even at 80 ul optimum recoveries for all dioxin / furan congeners were achieved. For all LVI modes the evaluation of the analyte recovery is crucial for the overall method performance. This is due to the reason that during the first step of a PTV LVI injection the split line remains open at a low injector temperature and is only closed for evaporation/transfer of the analytes to the analytical column in the second injection phase. This recovery check was performed comparing 1 ul injections of a standard with LVI injections (e.g. 80 ul) of the same but diluted (e.g. 1/80) standard (Fig. 2).

In addition an evaluation was carried out for the 80 ul PTV LVI method for dioxins/furans in toluene, comparing 80 ul PTV LVI injections of diluted standards and samples to conventional 1 ul injections with an SSL injector of the same but now undiluted set of standards and samples. Accordingly a dioxin/furan calibration curve was acquired in SSL (undiluted solutions) and PTV LVI mode (diluted solutions) and a number of different dioxin/furan food and feed sample extracts were injected in the same way. The possibility to use the 1 ul (SSL) calibration curve to evaluate data from sample extracts analyzed in PTV LVI mode was studied.

PTV LVI can probably be considered to be the most appropriate technique for injecting large volumes of dioxin/furan sample extracts and should be of comparable efficiency for many other POPs applications like PCBs and PBDEs. This is due to several reasons: POPs do not belong to the high volatile group of chemicals, ^{13}C labeled internal standards as used in isotope dilution technique would also correct for losses during the LVI injection process enhancing thus the method robustness, sample extracts are usually comparably “clean” as a thorough sample cleanup is typically used and finally PTV LVI can be seen as the most robust LVI method for dirty matrices.

Large volume injection techniques can help to automize the final concentration part of the sample preparation and thus increase the analytical productivity. The effort for final concentration of the sample extract after clean-up can be considerably reduced. The extent of reduction will depend on the overall required method detection limits and on the final sample extraction volume prior to concentration.

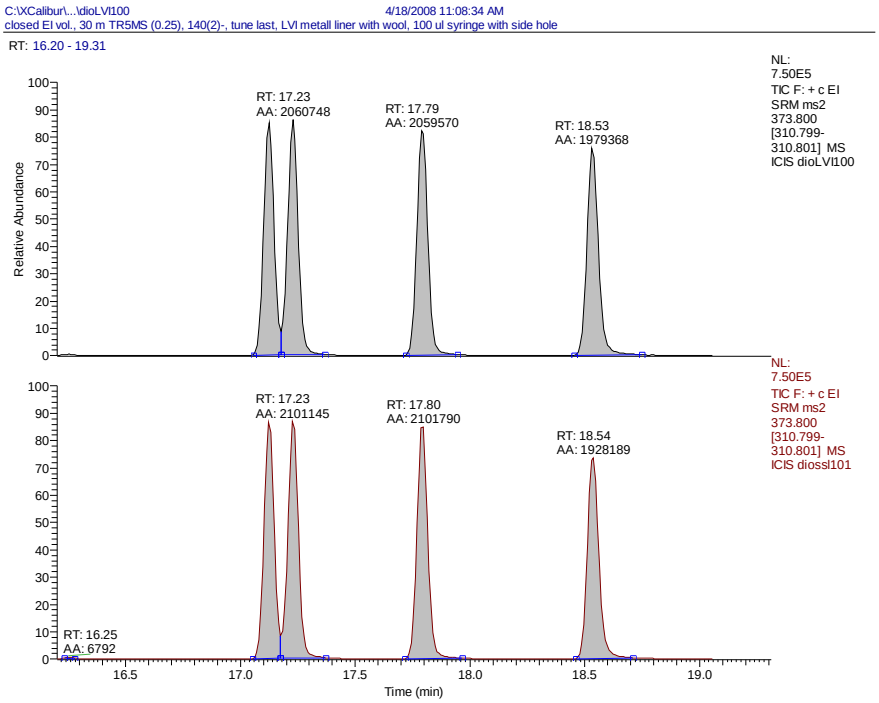

Fig. 2: *upper mass trace: EPA 1613 CS3 standard diluted 1/80 , 80 ul in PTV-LVI, hexafurans*
lower mass trace: EPA 1613 CS3 standard undiluted, 1 ul in PTV splitless, hexafurans

Large volume injection methods can also be the first step to an LC-GC coupling where extracts cleaned via LC could directly be introduced into the GC for concentration and analysis.

References

1: Hoh E., Mastovska K., *Journal of Chromatography A*, 2008; 1186: 2 - 15
2: Eppe G., Focant J.-F., Pirard C., De Pauw E.; *Talanta* 2004; 63: 1135