APPLICATION OF LARGE VOLUME INJECTION IN GC USING PTV INJECTOR FOR DIOXIN ANALYSIS

Yawei Wang[1], Qinghua Zhang[1], Guibin Jiang[1*]，Qing He[2]

[1]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, The Chinese Academy of Sciences, Beijing 100085, PR China
[2]Focus Technology Co., Ltd-Service Center of ATAS in China, Beijing, 100012

Introduction

The level of dioxin in the environment is normally pg/g or pg/L or less. To achieve the ultra low limit of detection, many techniques have been adopted to improve the detectability[1]. Very often concentrating the diluted sample extract is used to increase the amount in the injection. Traditional split/splitless injection technique for capillary gas chromatography (GC) requires the injection volume less than 2 μL. The sample extract needs to be concentrated to about 10 to 20 μL in a small vial under a gentle nitrogen flow. This operation is very tedious and difficult to control. Sometimes loss of sample can't be avoided and the recovery will be affected. Programmed temperature vaporizing injectors (PTV) have been shown to be eminently suited for large volume sample introduction in capillary GC and have been considered to replace the off-line concentration step[2]. Large volume injection (LVI) using PTV injectors is based on selective evaporation of the sample solvent from the liner of the PTV injector while simultaneously trapping the less volatile components in the cold liner. During this stage of the sampling process solvent vapours are discharged via the opened split exit of the injector. When solvent elimination, the split exit is closed and the components are transferred to the column in the splitless mode by rapid temperature-programmed heating of the injector. LVI is quite suitable for dioxins or other persistent organic pollutants (POPs) analysis due to their semi-volatile property. The aim of this work is to evaluate the performance of the injection with LVI by comparing the widths and skews of peaks

Materials and Methods

TCDD Column Performance Check Solution (ED935) was purchased from Cambridge Isotope Lab (Andover, MA, USA). An Agilent 6890 GC/5973 MSD (Avondale, PA, USA) equipped with a OPTIC 3 PTV injector[3] (ATAS International, Veldhoven, The Netherlands, see figure 1 for the schematic diagram) was used. GC separation was performed on a DB-5MS column (30m×0.25 mm i.d.×0.25 μm film) with helium as carrier gas at a constant flow rate of 1 ml/min. All injections were carried out manually. The injection volume of 1 μL with split/splitless injector and 5, 10, 25,50 μL and 100 μL with LVI was studied. The injection amount was 182 pg each for 1,4,7,8-TetraCDD, 1,2,3,4-TetraCDD, 1,2,3,7/1,2,3,8-TetraCDD, 2,3,7,8-TetraCDD, and 364 pg each for 1,2,7,8-TetraCDD, 1,2,6,7-TetraCDD per injection. The splitless injector was held at 280 ℃ and the splitless time was 1.5 min and the purge flow was 50 ml/min. After solvent elimination with split flow of 50 ml/min at 40 ℃, the PTV was heated at 10 ℃/s to 280 ℃ and the splitless time was

1.5 min and the purge flow was 25 ml/min. The oven temperature program for all separations was as follows: 80 ℃ (0.5 min) with 8 ℃/min to 220 ℃, then with 2 ℃/min to 270 ℃ (5 min). The MS was operated on EI mode at 70 eV and the source temperature was 250 ℃. The data were acquired by selective ion monitoring (SIM) mode and ions of 322 and 334 were recorded for native and ^{13}C-labeled congeners. The peak areas and peak widths were calculated by ChemStaion Integrator of the Agilent MSD Enhanced ChemStation.

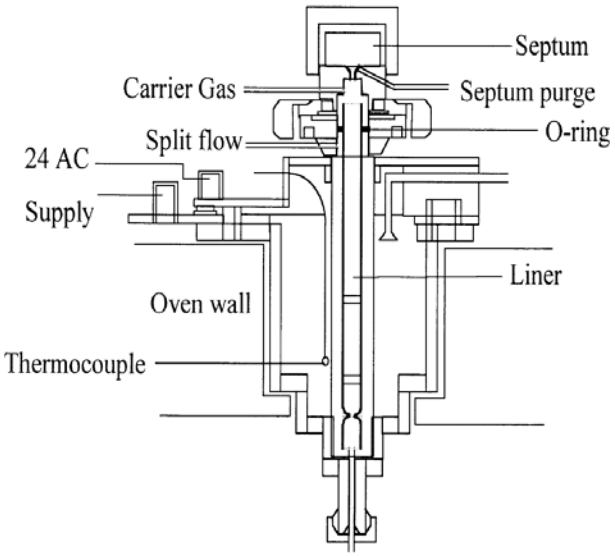


Figure 1. Schematic diagram of the large volume injector[3]

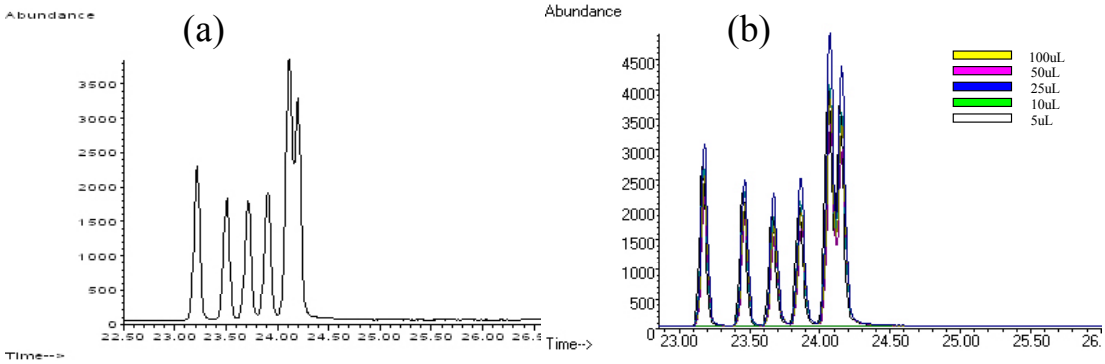
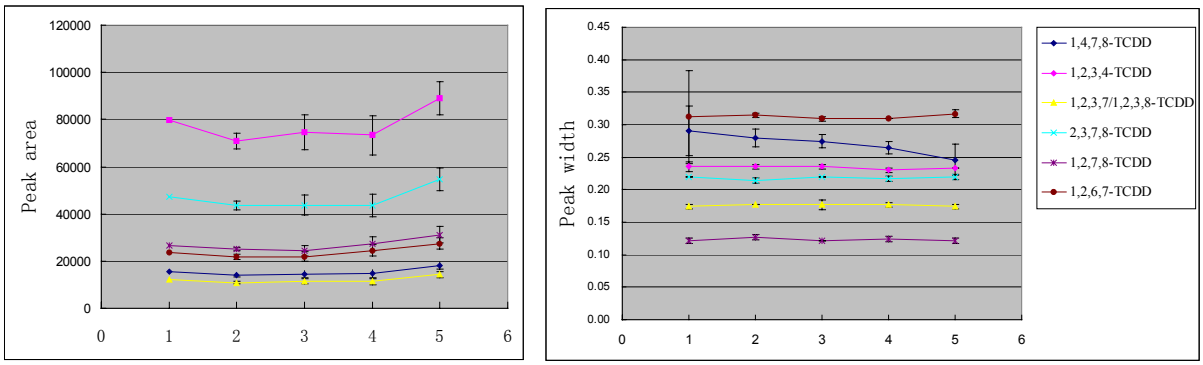


Figure 2 (a) The chromatography of the column check standard by GC-low resolution mass spectrometry using split/splitess injection. From the left to right: 1,4,7,8- TetraCDD, 1,2,3,4- TetraCDD, 1,2,3,7/1,2,3,8- TetraCDD, 2,3,7,8- TetraCDD, 1,2,7,8- TetraCDD, 1,2,6,7- TetraCDD. (b) The chromatography of different injection volume with PTV injector.

Results and Discussion

Comparing to that with the traditional split/splitless injection, the peak responses were enhanced a little bit with the LVI (Figure 2). The peak areas and peak widths had no obvious changes with the injection volume increasing from 5 µL to 100µL besides the shape and symmetry of the peaks remained almost same (Figure 2 (b) and Figure 3). The separation performance was not affected with LVI on PTV injector compared to that on the traditional split/splitless injection. The results showed that LVI with PTV injector is a promising technique to improve detectability in dioxin analysis.



(a) (b)

Figure 3. The comparison of peak areas (a) and peak widths (b) of six target compounds with different injection volumes: 1. 5 µL; 2. 10 µL; 3. 25 µL; 4. 50 µL; 5. 100 µL.

References

1. Sing, S.B. and Kulshrestha, G.. *J Chromatogr. A.* 1997, 774, 97-109.
2. Mol, H.G.J., Henriks, P.J.M., Janssen, H.G. and Cramers, C.A. *J. High Resol. Chromatogr.*, 18, 124-128.
3. Janssen, H.G., Mol, H. and Cramers, C. A. *ATAS Chromatography Technical Notes* No 1.