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High Sensitivity Analysis of Dioxins By Using a Multi Dimensional GC System (MDS-6890 Solvent-Cut System) with a Large Volume Injector

Recently, dioxin is being analyzed in a wide variety of materials. In addition to conventional environmental samples such as fly ash and exhaust gas, biological and water samples such as blood, breast milk, and tap water are being analyzed. Because the dioxin concentrations in these samples are extremely low, ultra high sensitivity is one of the critical features required for analytical systems. Higher sensitivity in analysis is obtained by improving the performance of the mass spectrometer as well as improving the injection techniques for the gas chromatograph. The PTV (Programmable Temperature Vaporizer) inlet is an example of such injection techniques. The PTV inlet selectively eliminates solvents at the sample injector, allows for large volume sample injection, and concentrates the compounds of interest onto the GC column.(1) However, the PTV inlet does not support solvents whose boiling point is higher than that of toluene because it is designed to separate solvents from compounds in question by controlling the injector temperature alone. Also, contamination builds up rapidly inside the injector. To address these problems, we investigated the analysis of dioxins by using a multi-dimensional gas chromatograph (MD-GC) with a large-volume injector as a high-sensitivity analytical method for dioxins.

The MD-GC connects two or more columns in series, providing an enhancement over a single column separation. It combines different types of columns to maximize the selection power and sample load, optimizing at high speed the analytical conditions for samples with a wide-ranging concentration level.(2)

Figure 1 shows an outline of the MD-GC system developed by SGE that we used for our experiment. It features a split/splitless injector. The path splits into two after the pre-column, and one part is connected to the purge while the other is connected to the analytical column through the restricting column. A cold trap is attached to the tip of the analytical column to capture components in question, resulting in a narrow peak bandwidth in the chromatogram. The column flow rate is controlled by the pressure balance between the injector and makeup gas. Purge and coolant valves as well as the GC oven are controlled in scheduled operation under optimum conditions. Operating conditions including

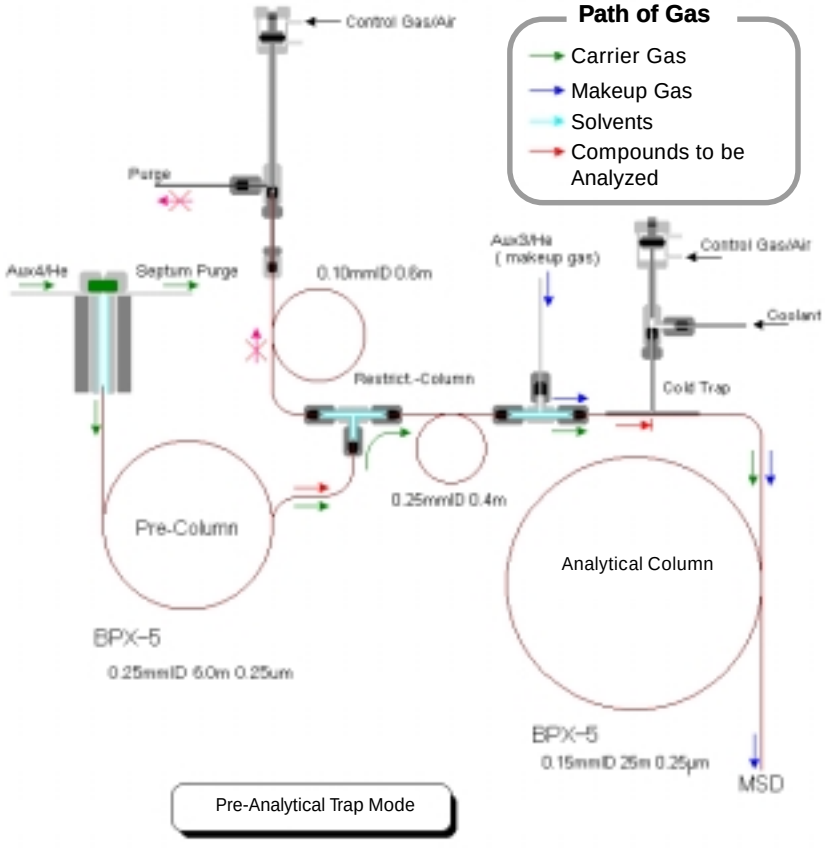

Figure 1. MDS-6890 Solvent Cut System - An Outline

pressure balance are computed by SGE programs. Figures 2 and 3 shows time programs for the pressure balance and the GC oven temperature respectively. For 8 minutes after a sample is injected, the purge line is open, eliminating early-eluting solvents as the GC oven temperature increases. When the purge line is closed, the eluted components are directed to the analytical column, and captured at the cold trap. When all components are eluted at the pre column, the purge line is opened again, and the GC oven temperature is reduced to 180°C. The cold trap is turned off immediately, and through rapid thermal desorption by the GC oven temperature, the components which have been captured are introduced to the analytical column where they are separated and analyzed. The analytical conditions used for our experiment were intended to support biological samples such as blood. Therefore, the analytical column was apolar, and the samples were grouped according to the isotope for high sensitivity MS analysis. One analytical cycle, incorporating sample concentration, separation, and analysis, took less than 50 min.

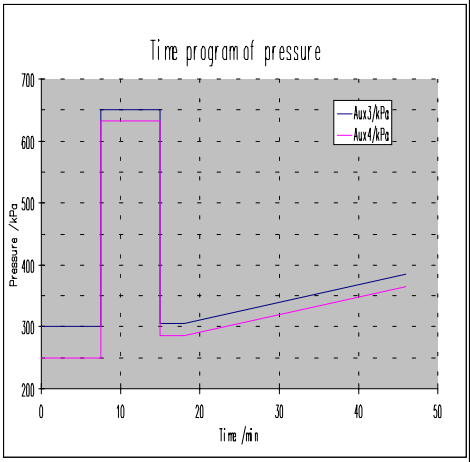

Figure 2. Pressure Program

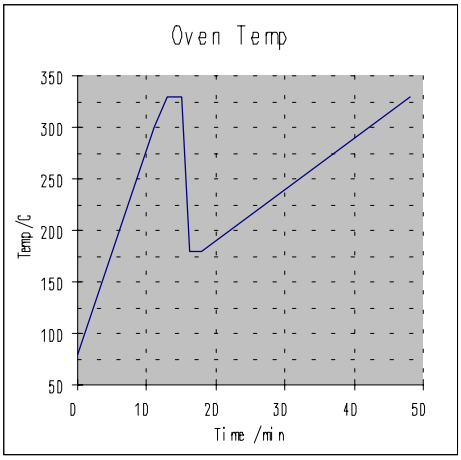

Figure 3. Oven Temperature Program

We analyzed a standard dioxin sample, and will discuss the results below. A JMS-700D was used as a mass spectrometer and NK-CS2-C from Wellington Laboratories was diluted to 1/50000 with toluene as a standard sample. This standard sample thus had two concentration levels: 1 fg/µL for the fully native compound, and 2 fg/µL for the labeled compound. A single injection volume was 10 µL. The absolute quantities of the injected compound were therefore 10 fg and 20 fg respectively. The carrier gas flow rate at the analytical column was low at 0.37 mL/min due to the small inner diameter of 0.15 mm. The resolution was 10,000, and the switching time was 100 msec per channel. Figure 4 shows the SIM chromatogram of 2, 3, 7, 8-TeCDD at m/z 321.8936. The peak was extremely sharp at a high S/N ratio of 39. The peak form, separation, and detection sensitivity were also satisfactory in the other isotopes. The successful analysis was due to the peak bandwidth reduced by the cold trap and the high vacuum in MS resulting from the thin analytical column. The system, capable of analyzing samples at a concentration of 1 fg, is expected to be a powerful tool for high sensitivity analysis of various samples. We will continue reporting on the linearity and reproducibility in relation to the injection volume and the practical application of the system in the next issue.

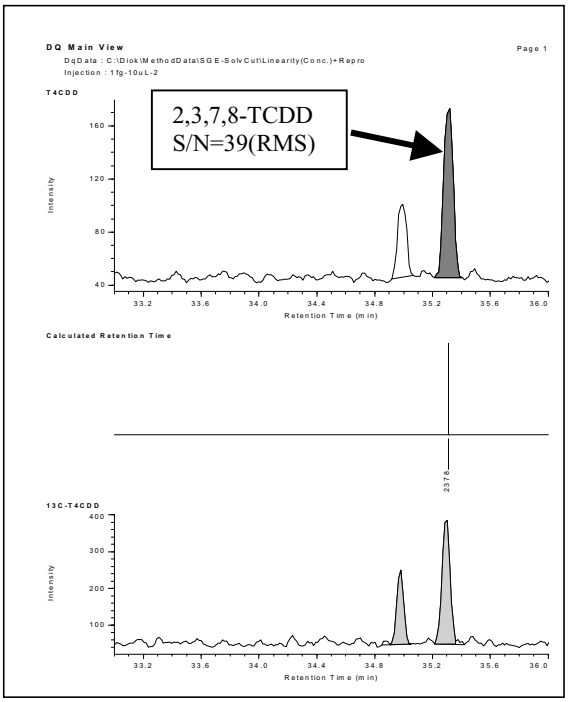

Figure 4. SIM Chromatograms for 2,3,7,8-TCDD (1 fg, 10 µL)

References:

1. Onodera, et al., (1999), Proceedings of the 8th Environmental Chemistry, 100, p 206-207.
2. W. Dale Snyder, (1990), Capillary Gas Chromatography, Volume 3, Chapter 5, p 1-36.