JEOL USA, Inc.
11 Dearborn Road
Peabody, MA 01960
978-536-2270 ms@jeol.com

A Simplified, Low-Cost Analytical Method for Dioxins: GC/MS Analysis of Dioxins with GCmate and a Large-Volume Injector

The Japanese government, through various guidelines and the JIS standard, regulates analytical methods for dioxins from preliminary treatment to data acquisition to data processing. The guidelines specify a high resolution gas chromatograph – high resolution mass spectrometer system (HRGC/HRMS) as a final analytical instrument and a resolution of 10,000 for the mass spectrometer.

These methods, however, are quite costly if executed as the government recommends. Since the Law Concerning Special Measures Against Dioxins went into effect in January 2000, dioxin samples to be analyzed are expected to multiply in a few years to come. Researchers are concerned that the high cost of analysis per sample will affect the scope and quality of their studies. As a result, simplified methods for dioxin analysis are in dire need to streamline the analytical process and reduce the cost.

There are different steps involved to simplify the process: 1) simplified sampling; 2) simplified preliminary treatment; 3) compact, low priced instruments; and 4) efficient data processing. As a mass spectrometer manufacturer, JEOL identifies a simplified analytical method for dioxins as a compact, low priced analytical system:

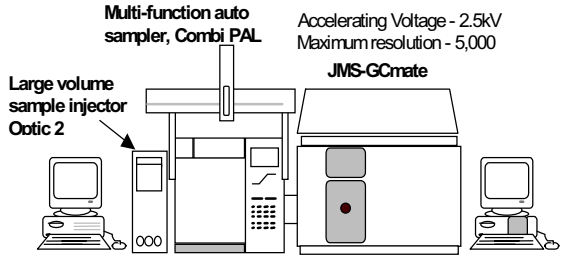

Figure 1

Basic Concept of Simplified Analytical Method for Dioxins

1) Compact (low-priced) analytical system
   - ▶ Lower cost
   - ▶ Smaller footprint
   - ▶ Enhanced ease in operation
2) That achieves the same level of performance as HRGC/HRMS for samples with fewer interferences, and
3) Acquires a reasonable level of information (rough concentration levels) from samples with many interferences
   - ▶ Matrix components eliminated by the injector or the GC column

In addition to the above, the criteria should include “resistance to contamination”, “matrix removing capability of GC/MS to simplify the clean-up process”, and “speedy and efficient data processing”.

Focusing on item 1) above, we experimented with an analytical method for dioxins using a GCmate GC/MS system with a large volume PTV injector, and will discuss the results below.

Figure 1 is an external view of the system used for our experiment. It features a compact double-focusing mass spectrometer (the GCmate) as a detector, a large volume PTV injector (Optic2) connected to the back injector port of an Agilent 6890, and a multi functional auto sampler (CombiPAL).

Table 1 shows the analytical conditions. To maximize the sensitivity, we used a capillary column with relatively small column back, CP-Sil88, and increased the resolution of the mass spectrometer as much as possible (R=3,000). It is typical in dioxin analysis to use separate columns for the tetra- through hexachloro compounds and the hepta- through

Table 1. Analytical Conditions

GC Conditions

Column	CP-Sil88 60m x 0.25mm, Film Thickness 0.1μm
Oven Temp	100° C (1.5 min) ->20° C/min -> 180° C (0 min) -> 4° C/min -> 270° C (27 min
Injection	Optic 2 used 5 μL

MS Conditions

Resolution	3,000
Switching	Electric Field
Detector Voltage	600 V
Pre amp	X 100
Attenuator	1/16
Cycle Time	0.44 sec
Ionization Voltage	40 V

Table 2. SIM Grouping

Group 1 (18~23 min.)			
319.8966	321.8936	333.9338	TeCDD
Group 2 (23~26.5 min.)			
303.9016	305.8987	317.9389	TeCDF
339.8597	341.8567	351.9000	PeCDF
353.8576	355.8546	367.8949	PeCDD
Group 3 (26.5~30.1 min.)			
339.8597	341.8567	351.9000	PeCDF
373.8207	375.8178	385.8610	HxCDF
389.8157	391.8127	401.8559	HxCDD
Group 4 (30.1~33.7 min.)			
373.8207	375.8178	385.8610	HxCDF
389.8157	391.8127	401.8559	HxCDD
407.7818	409.7788	419.8220	HpCDF
Group 5 (33.7~40 min.)			
373.8207	375.8178	385.8610	HxCDF
407.7818	409.7788	419.8220	HpCDF
423.7767	425.7737	435.8169	HpCDD
Group 6 (40~55 min.)			
441.7428	443.7398	453.7830	OCDF
457.7377	459.7348	469.7780	OCDD

Table 3. S/N at 0.05 μg/L

	Isomer	S/N
TeCDD	2378	10. 1
PeCDD	12378	2. 9
HxCDD	123478	4. 5
HxCDD	123678	3. 3
HxCDD	123789	2. 7
HpCDD	1234678	11. 6
OCDD	12346789	\
TeCDF	2378	10. 3
PeCDF	12378	6. 6
PeCDF	23478	12. 8
HxCDF	123478	17. 3
HxCDF	123678	17. 9
HxCDF	123789	20. 4
HxCDF	234678	12. 5
HpCDF	1234789	2. 6
OCDF	12346789	\

octachloro compounds in order to detect all isomers. However, since our objective is to "simplify" dioxin analysis, we focused on specifically on efficient analysis of the toxic 2, 3, 7, 8-substituted isomers, forgoing quantitative analysis of the other isomers. Thus, we used the same column, CP-Sil88, to analyze the 2, 3, 7, 8 isomers in a single injection by the SIM grouping technique. Table 2 is a time table of the SIM grouping designed for the experiment, which, although complicated, is designed to maximize sensitivity.

Figure 2 shows the chromatograms of 2, 3, 7, 8-TCDD and 2,3, 7, 8-TCDF acquired when a standard toluene solution of 0.05 μg/L was analyzed under the conditions above. Table 3 shows S/N ratios of the peaks of other 2,3, 7, 8 isomers. The results were satisfactory at S/N~5 for all isomers except for OCDD and OCDF. The injection volume being 5 μL for all samples, the absolute injected quantity volume of the isomers was 250 fg. It is known that OCDD and OCDF in columns with high polarity do not satisfy the sensitivity requirement due to their long retention time. In our experiment, the sensitivity decreased by a magnitude of 1 to 2. However, since the toxic equivalence of these isomers was extremely small at 0.0001 compared to the other 2, 3, 7, 8 isomers, we concluded that the sensitivity decline at this level was negligible when evaluating dioxins in the total-TEQ. We therefore decided to analyze OCDD and OCDF at lower sensitivity to achieve a simplified analytical method.

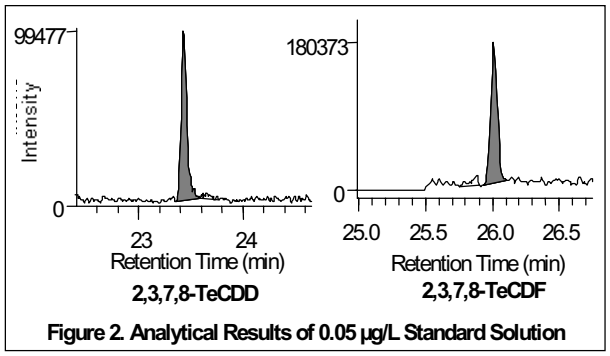

Figure 2. Analytical Results of 0.05 µg/L Standard Solution

To evaluate the system, especially the combination of a large volume injector and SIM at a resolution of 3,000, fly ash samples were analyzed. For comparison, the same samples were analyzed in SIM at a resolution of 500 (resolution level of a quadrupole mass spectrometer). Figure 3 compares the results. It was expected that the fly ash samples would have a relatively high concentration. In fact, the results of native compounds were more or less the same at R=500 and R=3,000. However, the chromatogram of ^{13}C added as an internal reference showed an increased baseline and interfering peaks at R=500, which were not present at R=3,000. While the fly ash samples in our experiment had relatively high concentration and were cleaned thoroughly, it is obvious that the results at R=3,000 were superior.

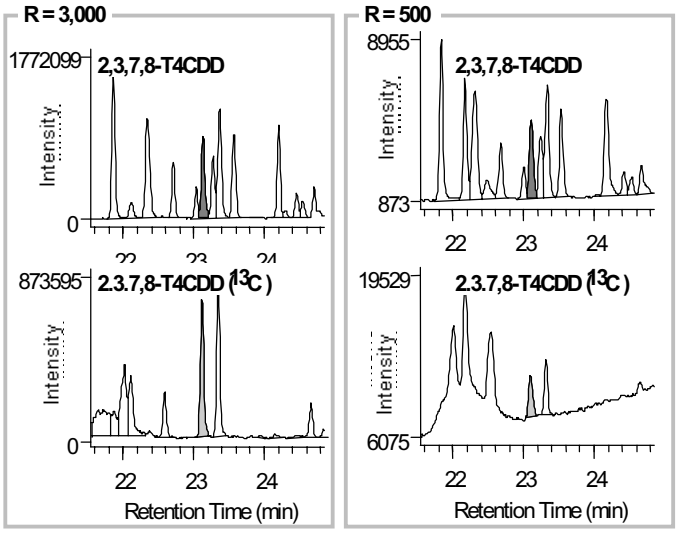

Figure 3. Fly Ash Analysis (TCDD)

Figure 4 shows the chromatograms of dioxins in soil samples. The soil samples, generally known for their low concentration and many matrix components, are difficult to clean, and are more susceptible to interference than other samples. As the figure demonstrates, the chromatogram at R=500 showed a rise and fluctuation in the base line as well as interfering peaks possibly caused by the increased matrix components, making it practically impossible to analyze 2, 3, 7, 8-TCDD, whereas the chromatogram at R=3,000 detected the peaks of 2, 3, 7, 8-TCDD despite the slight interference.

The system, combining a large volume injector GC-PTV with a small double-focusing mass spectrometer, achieved a sensitivity level that compared well with HRGC/HRMS. This system obtained analytical results equal to HRGC/HRMS from the high concentration ash samples. SIM at a resolution of 3,000 helped reduce the interference from the low-concentration soil samples.

The JMS-GCmate used in the experiment is a double-focusing mass spectrometer designed on the same principle as HRMS commonly used for dioxin analysis. The analytical conditions as well as the data acquired are fully comparable with HRGC/HRMS. The JMS-GCmate is therefore a powerful tool for "screening" as well as for "simplified analysis" of dioxins.

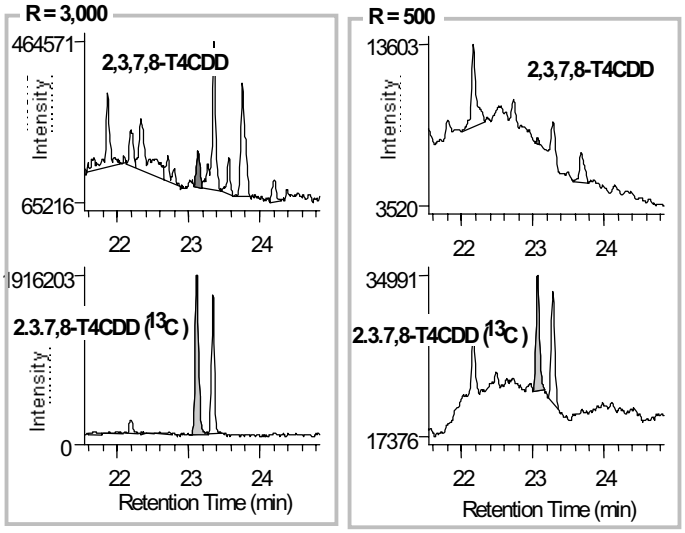

Figure 4. Soil Sample Analysis (TCDD)