The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans Using GCxGC-TOFMS

Peter Gorst-Allman LECO Africa, Kempton Park, South Africa • Jayne de Vos NMISA, Pretoria, South Africa

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are ubiquitous byproducts of industrial processes and incineration. The high toxicity of these compounds necessitates their analytical determination and control. In South Africa (SA) there is no established dedicated dioxin laboratory to handle these demanding measurements.

We have been actively investigating alternatives to the existing, regulatory approved, gas chromatography-high resolution mass spectrometry (GC-HRMS) method, which might prove to be more practical for PCDD and PCDF analysis in SA and other third world countries lacking a dedicated facility. This investigation has focused on the use of comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC-TOFMS) for dioxin and other persistent organic environmental contaminants.

Comprehensive two-dimensional gas chromatography (GCxGC) coupled to Time-of-Flight mass spectrometry (TOFMS) can play a significant role in handling samples where complexity and sensitivity are key issues. The increased peak capacity of GCxGC, coupled with the powerful deconvolution software available in the ChromaTOF software package used to operate LECO Pegasus and TruTOF systems, allows the coelution always present in complex samples to be minimized. Where it does occur the software handles this in such a way that compound identification and quantitation are not compromised. Also the focusing effect of the modulator permits an increase in detectability, such that the low levels for PCDD analysis, as described in EPA Method 1613, can be readily achieved.

2. Experimental Conditions

Samples

The five standard sample mixtures analyzed in this investigation (1613CS1, 1613CS2, 1613CS3, 1613CS4 and 1613CS5) were purchased from Wellington Laboratories. Each standard contained the 17 native PCDD and PCDF components mandated for analysis by EPA Method 1613, as well as 16 [13C]-labeled congeners and 3 labeled recovery and clean-up standards. A complete list of the components contained in the standards is shown below. The four "real world" samples analyzed were supplied by the Environmental Analysis Laboratory of the Environmental Protection Agency in Taiwan. These samples were fly ash (Sample 1), sediment (Samples 2 and 4), and a prepared test sample (Sample 3). Extraction, clean up and GC-HRMS analysis of these samples were performed by the same laboratory. We would like to thank Dr David Jui-Hwa Peng and his group for this work.

Analysis Conditions

A number of considerations were important in choosing the column set to be used for the GCxGC analysis of the PCDD/F mixture. The column set should provide good separation of all the components, it should be thermally robust with the ability to handle the elevated temperatures needed for successful chromatography of the less volatile components, and it should make good use of the total chromatographic space of the analysis. The final column set used, and the conditions for the analyses are shown below.

Detector:
LECO Pegasus® 4D Time-of-Flight Mass Spectrometer
Acquisition Rate: 50 spectra/second
Acquisition Delay: 15 minutes
Stored Mass Range: 160 to 500 u
Transfer Line Temp.: 280°C
Source Temperature: 250°C
Detector Voltage: -1900 Volts
Mass Defect Setting: - 40
Column 1:
Rxi-5SilMS, 30 m x 0.25 mm ID, 0.25 µm film thickness
Column 2:
Rtx-200, 1.5 m x 0.18 mm ID, 0.2 µm film thickness
Column 1 Oven:
80°C for 1 min, to 220°C at 20°C/min, to 240°C at 2°C/min, to 250°C at 1°C/min, to 260°C at 5°C/min, to 270°C at 1°C/min.
Column 2 Oven:
90°C for 1 min, to 230°C at 20°C/min, to 250°C at 2°C/min, to 260°C at 1°C/min, to 270°C at 5°C/min, to 280°C at 1°C/min
Modulation Period: 4 seconds
Modulator Temp Offset: 30°C
Inlet: Splitless at 250°C
Injection: 2 µL
Carrier Gas:
Helium, 1.5 mL/min corrected constant flow

Data Processing with ChromaTOF using isotope dilution techniques requires careful set up for optimal results. The procedure used for data processing is described in an Application Note on the LECO Africa website (www.lecoafrica.co.za) entitled Data Processing with Isotopes as Internal Standards.[1] The Ave RF Quantitation Mode was used for all calculations.

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3. Results and Discussion

The five standard solutions were first run using the conditions described above. An example of the GCxGC-TOFMS Chromatogram for the 1613CS4 standard mixture is shown in Figure 1 below. Abbreviations used to indicate the PCDDs/Fs include: 2378 = 2,3,7,8; Te = tetra; Pe = penta; Hx = hexa; Hp = hepta; O = octa; C = chloro; DF = dibenzofuran; DD = dibenzo-p-dioxin.

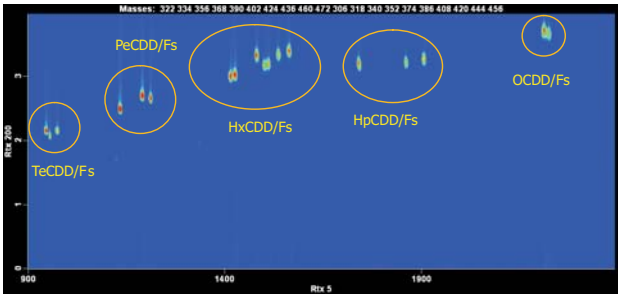

Figure 1. Selected Ion Chromatogram GCxGC-TOFMS results for the 1613CS4 standard mixture.

These results were then used to set up the Calibration Tables for unknown sample component determination, as described in Reference 1. A Calibration Table was created for each separate group of PCDD/F components (tetrachloro, pentachloro, hexachloro, heptachloro and octachloro).

Even at the lowest levels mandated by EPA Method 1613 (0.5 pg/µl for 2378-TeCDF and 2378-TeCDD) it is an easy matter to obtain accurate quantitation. To demonstrate this, Figure 2 shows a plot of the masses used for area quantitation for the 2378-TeCDF (318 for the label and 306 for the native). As can be seen even the 306 mass which represents the 2378-TeCDF at 0.5 pg/µl shows a clearly defined peak which can be easily quantified. It should be noted that there is practically no separation of the native and labeled material, with the peak apexes for the two components almost coinciding.

Confirmation of accurate quantitation, even at the lowest level, is shown by the excellent correlation co-efficient obtained from the calibration curve for 2378-TeCDF (0.99975). This is shown in Figure 3.

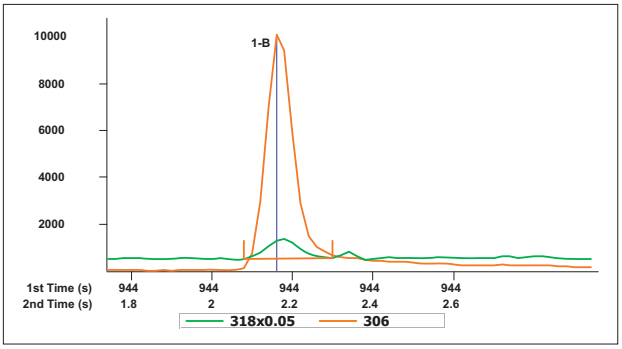

Figure 2. Masses used for area calculation for 2379-TeCDF (0.5 pg/µl).

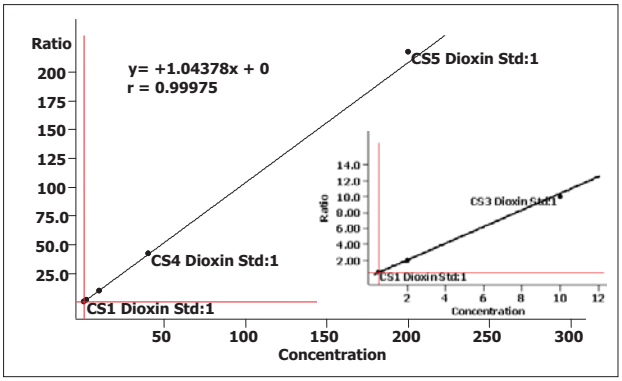

Figure 3. Calibration Table for 2,3,7,8-Tetrachlorodibenzofuran (2378-TeCDF).

After running the unknown samples, the various PCDD/F components could be quantified directly by using the appropriate Calibration Table.

An example of a chromatogram for Sample 1 is shown in Figure 4.

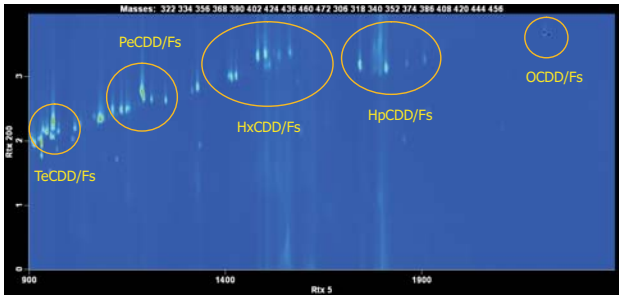

Figure 4. Selected Ion Chromatogram GCxGC-TOFMS results for Sample 1.

The quantitative values obtained for the different samples, together with a comparison of the values obtained using GC-HRMS are shown in Tables 1, 2, 3 and 4. The final result is expressed in ngTEQ/kg. This value is calculated using the measured amount of component present in the sample, the Total Equivalence Factor (TEF) of the component and the amount of sample analysed. The final value is then quoted in nanogram Total Equivalents (TEQ) / kilogram. This value expresses the overall "toxicity" of the sample and is based on different relative toxicities for the different components (the TEF in the Tables).

Table 1. Results obtained for Sample 1 showing a comparison with the values obtained using GC-HRMS.

Compound	Amount GC-HRMS (pg/µl)	Amount GCxGC-TOFMS (pg/µl)	WHO-TEF	ngTEQ/kg GC-HRMS	ngTEQ/kg GCxGC-TOFMS
2378-TeCDF	24.7	21.2	0.1	12.28	10.54
12378-PeCDF	42.7	45.6	0.05	10.62	11.34
23478-PeCDF	106.8	129.1	0.5	265.58	321.03
123478-HxCDF	92.6	100.0	0.1	46.05	49.73
123678-HxCDF	105.3	104.9	0.1	52.37	52.17
234678-HxCDF	196.9	173.9	0.1	97.93	86.49
123789-HxCDF	32.1	29.0	0.1	15.96	14.42
1234678-HpCDF	400.8	412.1	0.01	19.93	20.50
1234789-HpCDF	58.4	47.5	0.01	2.90	2.36
OCDF	232.1	265.5	0.0001	0.12	0.13
2378-TeCDD	3.2	2.6	1	15.91	12.93
12378-PeCDD	13.9	15.6	1	69.13	77.58
123478-HxCDD	13.6	13.3	0.1	6.76	6.61
123678-HxCDD	16.8	16.0	0.1	8.36	7.96
123789-HxCDD	12.1	9.4	0.1	6.02	4.67
1234678-HpCDD	122.7	77.0	0.01	6.10	3.83
OCDD	283.0	240.4	0.0001	0.14	0.12
			TOTAL	**636.17**	**682.43**

Table 2. Results obtained for Sample 2 showing a comparison with the values obtained using GC-HRMS.

Compound	Amount GC-HRMS (pg/µl)	Amount GCxGC-TOFMS (pg/µl)	WHO-TEF	ngTEQ/kg GC-HRMS	ngTEQ/kg GCxGC-TOFMS
2378-TeCDF	47.1	47.40	0.1	4.44	4.47
12378-PeCDF	20.0	14.30	0.05	0.94	0.67
23478-PeCDF	215.3	246.40	0.5	101.51	116.17
123478-HxCDF	217.0	235.20	0.1	20.46	22.18
123678-HxCDF	21.0	16.80	0.1	1.98	1.58
234678-HxCDF	19.6	15.50	0.1	1.85	1.46
123789-HxCDF	8.1	6.70	0.1	0.76	0.63
1234678-HpCDF	670.1	740.00	0.01	6.32	6.98
1234789-HpCDF	16.5	13.10	0.01	0.16	0.12
OCDF	850.5	921.30	0.0001	0.08	0.09
2378-TeCDD	68.4	73.10	1	64.50	68.93
12378-PeCDD	4.3	4.80	1	4.05	4.53
123478-HxCDD	6.5	7.60	0.1	0.61	0.72
123678-HxCDD	13.7	13.90	0.1	1.29	1.31
123789-HxCDD	10.2	10.60	0.1	0.96	1.00
1234678-HpCDD	197.1	124.30	0.01	1.86	1.17
OCDD	1000.1	943.10	0.0001	0.09	0.09
			TOTAL	211.88	232.11

Table 3. Results obtained for Sample 3 showing a comparison with the values obtained using GC-HRMS.

Compound	Amount GC-HRMS (pg/µl)	Amount GCxGC-TOFMS (pg/µl)	WHO-TEF	ngTEQ/kg GC-HRMS	ngTEQ/kg GCxGC-TOFMS
2378-TeCDF	37.3	42.3	0.1	3.73	4.23
12378-PeCDF	49.9	48.2	0.05	2.50	2.41
23478-PeCDF	50.7	49.3	0.5	25.35	24.65
123478-HxCDF	50.0	51.9	0.1	5.00	5.19
123678-HxCDF	49.8	45.2	0.1	4.98	4.52
234678-HxCDF	50.4	43.6	0.1	5.04	4.36
123789-HxCDF	71.6	65.6	0.1	7.16	6.56
1234678-HpCDF	46.9	47.5	0.01	0.47	0.48
1234789-HpCDF	52.1	42.9	0.01	0.52	0.43
OCDF	96.8	102.7	0.0001	0.01	0.01
2378-TeCDD	19.4	17.5	1	19.40	17.50
12378-PeCDD	75.3	76.7	1	75.30	76.70
123478-HxCDD	48.7	52.4	0.1	4.87	5.24
123678-HxCDD	51.4	56.1	0.1	5.14	5.61
123789-HxCDD	53.5	41.4	0.1	5.35	4.14
1234678-HpCDD	69.1	35.2	0.01	0.69	0.35
OCDD	95.9	101.5	0.0001	0.01	0.01
			TOTAL	165.52	162.39

Table 4. Results obtained for Sample 4 showing a comparison with the values obtained using GC-HRMS.

Compound	Amount GC-HRMS (pg/µl)	Amount GCxGC-TOFMS (pg/µl)	WHO-TEF	ngTEQ/kg GC-HRMS	ngTEQ/kg GCxGC-TOFMS
2378-TeCDF	10.1	17.7	0.1	4.90	8.59
12378-PeCDF	7.8	6.3	0.05	1.89	1.53
23478-PeCDF	18.8	13.7	0.5	45.63	33.25
123478-HxCDF	130.6	118.4	0.1	63.40	57.48
123678-HxCDF	24.0	21.0	0.1	11.65	10.19
234678-HxCDF	12.1	6.1	0.1	5.87	2.96
123789-HxCDF	9.7	8.0	0.1	4.71	3.88
1234678-HpCDF	465.5	489.7	0.01	22.60	23.77
1234789-HpCDF	32.9	29.2	0.01	1.60	1.42
OCDF	1388.9	1401.9	0.0001	0.67	0.68
2378-TeCDD	55.2	49.8	1	267.96	241.75
12378-PeCDD	5.3	9.3	1	25.73	45.15
123478-HxCDD	3.9	5.0	0.1	1.89	2.43
123678-HxCDD	16.7	13.2	0.1	8.11	6.41
123789-HxCDD	10.6	9.2	0.1	5.15	4.47
1234678-HpCDD	139.0	85.0	0.01	6.75	4.13
OCDD	724.0	703.0	0.0001	0.35	0.34
			TOTAL	478.86	448.42

4. Conclusions

As can be seen in Tables 1–4 there is excellent agreement between the ngTEQ/kg values obtained for the four samples using the accepted GC-HRMS technology and GCxGC-TOFMS. On the basis of these results it would appear that GCxGC-TOFMS provides an excellent screening tool for samples containing PCDD/Fs at levels normally encountered in environmental analysis. Indeed at the levels found in the samples analysed, GCxGC-TOFMS can be used not only as a screening technique but is capable of providing quantitative results comparable with GC-HRMS.

At much lower levels, as are to be expected in biological samples and which are well below the values mandated by EPA Method 1613, GC-HRMS is the method of choice.

This Application Note is also available in electronic format on the LECO Africa website (www.lecoafrica.co.za) in the Application Notes section.

5. References

[1]P Gorst-Allman, Data Processing with isotopes as internal standards, LECO Africa Website, www.lecoafrica.co.za , Application Notes Section.

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