Rapid dioxin analysis using accelerated solvent extraction (ASE), multi-column sample cleanup and Rtx-Dioxin2 gas chromatography column.

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Introduction

One of the main aims of many dioxin analysis laboratories is to reduce sample turnaround times to the absolute minimum [1]. Often shorter times between sample receipt and reporting of results can attract a premium price for the analysis. It is generally accepted that the GC-MS portion of dioxin/PCB analysis is not the rate determining step in the overall scheme. Therefore, sample extraction and clean up is the obvious step to investigate for time-saving purposes. The use of accelerated solvent extraction (ASE) and multi column cleanup has been investigated for soil, sediment, air sampling media (XAD-2 resin) and fly-ash samples. For water samples the ASE step is replaced with a liquid/liquid separatory funnel extraction.

Environmental analyses regularly require the use of two GC-MS runs to produce dioxin results that may be relied upon. The use of the classical 5MS type column coupled with the more polar 2331 type to produce final results is typical. The innovative capillary GC column, Rtx-Dioxin2 [2], has offered the possibility of performing a dioxin analysis in a single GC-MS run. The analysis of the WHO-12 PCB (PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) congeners has also been investigated using this column.

Methods and Materials

ASE Extraction.

Dionex ASE 200 Accelerated Solvent Extractor.

An extraction pressure of 1500psi, pre-heat time 0 minutes, heat time 7 minutes, temperature 150°C, static time 10 minutes, 40% flush, 60 seconds purge. One cycle using toluene as the extraction solvent. For fly-ash samples, the same program was used except for extraction temperature (200°C), number of cycles (2) and extraction solvent (5% CH_3COOH in toluene).

Silica cleanup column

Multi-layered silica columns were prepared in 25mm i.d. glass columns (ACE glass). Packed into the column (in order) are silanised glass wool, Na_2SO_4, neutral silica gel, base modified (KOH) silica gel, neutral silica gel, acid modified (H_2SO_4) silica gel, neutral silica gel and Na_2SO_4. The columns are conditioned with hexane (200mL) prior to sample cleanup.

Florisil column

Into a Pasteur pipette (150mm) are packed silanised glass wool, Florisil (Supelco, 60/100 mesh PR, approximately 1.0g) and Na_2SO_4. The columns are conditioned with dichloromethane (DCM) and then DCM in hexane (2%) and placed in an oven at 130°C for at least 16 hours prior to use.

Alumina column

Into a Pasteur pipette (150mm) are packed silanised glass wool, aluminium oxide (activated, basic, Brockman I, standard grade, ~150 mesh, 58Å, approximately 2.0g) and Na_2SO_4. The columns are conditioned with and DCM in hexane (2%) and the hexane and placed in an oven at 130°C for at least 16 hours prior to use.

GC-MS

Micromass (Waters) AutoSpec Ultima NT coupled with an Agilent 6890 gas chromatograph equipped with a Shimadzu SIL 5000 Auto Injector (CTC GC-PAL). Data system with MassLynx 4.0 software.

The AutoSpec was operated at minimum 10,000 resolution (10% valley definition) in EI+ mode. Electron energy of approximately 33eV was used with trap current of 650µA and a source temperature of 280°C.

An Rtx-Dioxin2 (40m x 0.18mm i.d. x 180µm df, Restek Corp.) was installed into the split/splitless injector of the GC.
GC oven temperature programs were utilised as follows;

PCDD/F analysis	PCB analysis
140°C (2.4 min)	140°C (2 min)
13.2°C/min to 220°C	52°C/min to 200°C
2.3°C/min to 260°C	3.9°C/min to 235°C
6.6°C/min to 310°C (4 min)	6.5°C/min to 300°C (1 min)
	60°C/min to 320°C (5 min)
Constant flow 0.72mL/min)	Constant flow 0.72mL/min)
280°C injector temp., 1µl splitless injection, 2 min purge time, 30mL/min purge flow	280°C injector temp., 1µl splitless injection, 2 min purge time, 30mL/min purge flow

Sample Extraction and Cleanup

After ASE or liquid/liquid extraction the sample extracts are concentrated (TurboVap, Zymark) and then applied to the top of the multi-layered silica column. Hexane is eluted through the column and collected. The extract is once again concentrated and applied to the top of the Florisil column. The column is eluted with DCM in Hexane (2%) and then with DCM. Both elutions are collected separately.

The DCM/Hexane fraction (WHO-PCBs) is then concentrated and applied to the alumina column. Hexane is eluted and discarded. DCM in hexane (2%) is then eluted and collected. This is then concentrated into auto-sampler vials, internal standard added and analysed for PCBs.

The DCM in hexane fraction from the Florisil is concentrated into auto-sampler vials, internal standard added and analysed for PCDD/Fs.

The above cleanup procedure is summarised in Figure 1.

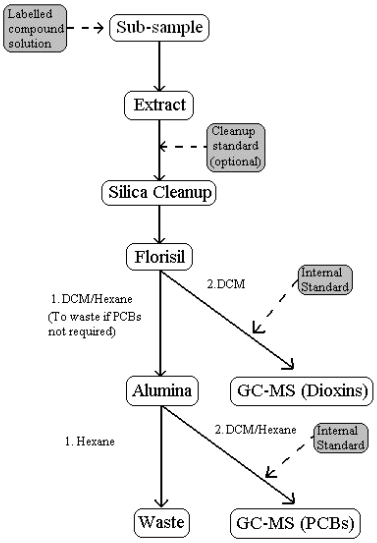

Figure 1. Flow diagram of cleanup procedure.

Results and Discussion

Analyses of the four certified reference materials listed below have yielded very good analytical results using only the Dioxin2 column. At present there appears to be only 1 co-elution interference of the 17 toxic PCDD/Fs. This is a co-elution of 1,2,3,7,8,9-HxCDF with 1,2,3,4,8,9-HxCDF.

	DX-1 (pg/g)		DX-3 (pg/g)	
Congener	Certified Range	Analysed (n=7)	Certified Range	Analysed (n=7)
2378-TCDD	210 – 316	284.8	78 – 164	131.2
12378-PeCDD	14 – 30	28.9	12 – 268	26.5
123478-HxCDD	16 – 30	21.1	10 – 30	19.4
123678-HxCDD	50 – 104	70.8	42 – 78	57.0
123789-HxCDD	29 – 77	40.4	21 – 53	35.2
1234678-HpCDD	452 – 816	743.0	372 – 630	594.7
OCDD	2999 – 4865	4546.3	2179 – 3955	3685.7
2378-TCDF	45 – 133	48.9	16 – 78	51.4
12378-PeCDF	25 – 53	38.8	18 – 52	37.6
23478-PeCDF	30 – 94	66.0	29 – 61	51.2
123478-HxCDF	438 – 990	699.0	286 – 588	468.9
123678-HxCDF	79 – 153	140.1	50 – 142	103.1
234678-HxCDF	0 – 70	60.6	8 – 70	51.9
123789-HxCDF	21 – 93	52.5	0 – 48	40.0
1234678-HpCDF	1601 – 3193	2648.6	1365 – 2481	2070.9
1234789-HpCDF	75 – 199	143.4	59 – 137	106.4
OCDF	4716 – 9528	8213.6	2547 - 5203	4608.3
PCB 77	-	-	1570 – 3550	3090
PCB 81	-	-	0 – 380	240
PCB 105	-	-	4630 – 7564	6280
PCB 114	-	-	42 – 526	330
PCB 118	-	-	6080 – 20880	15200
PCB 123	-	-	23 – 945	840
PCB 126	-	-	27 – 187	110
PCB 156	-	-	534 – 1718	1170
PCB 157	-	-	109 – 555	350
PCB 167	-	-	149 – 1025	750
PCB 169	-	-	0 – 27	20
PCB 189	-	-	55 – 315	230

DX-1 and DX-2 are sediment CRMs from NWRI, Canada

	BCR 529 (pg/g)		BCR 615 (pg/g)	
Congener	Certified Range	Analysed (n=7)	Certified Range	Analysed (n=7)
2378-TCDD	3900 – 5100	4600	22 – 32	25.83
12378-PeCDD	390 – 490	480	80 – 104	102.2
123478-HxCDD	900 – 500	1090	62 – 86	65.3
123678-HxCDD	4500 – 6300	4660	90 – 116	91.1
123789-HxCDD	2600 – 3400	2750	92 – 124	101.1
1234678-HpCDD	-	48200	740 – 1000	830.6
OCDD	-	23500	1550 – 1950	1813.1
2378-TCDF	65 – 91	75	58 – 114	78.3
12378-PeCDF	110 – 170	130	150 – 202	153.8
23478-PeCDF	290 – 430	330	105 – 145	114.9
123478-HxCDF	2900 – 3900	3600	182 – 224	188.4
123678-HxCDF	940 – 1240	1110	183 – 227	194.5
234678-HxCDF	330 – 410	400	115 – 145	136.5
123789-HxCDF	12 – 32	*500*	11.3 – 15.3	*39.3*
1234678-HpCDF	-	11500	660 – 840	674.6
1234789-HpCDF	-	1720	55 – 67	58.0
OCDF	-	47100	250 - 330	263.5

BCR 529 is a sandy soil CRM and BCR 615 is a fly-ash CRM.

As illustrated in figure 2, the separation of 2,3,7,8-TCDF from co-eluting congeners is much better than displayed by a classical 5MS type column. This allows for quantification without the need for a second analysis to confirm 2378-TCDF.

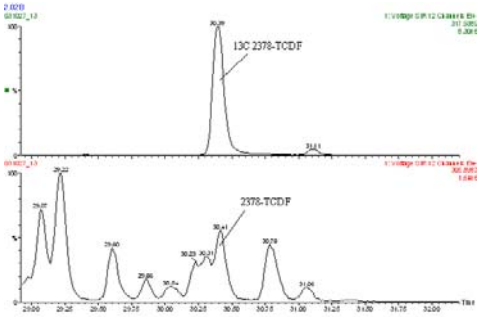

Figure 2i
60m DB5-MS TCDF specificity.

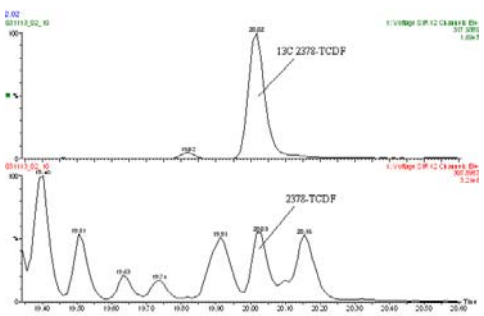

Figure 2ii)
40m Dioxin2 TCDF specificity.

The 2,3,7,8-TCDF results for the extract in Figure 2i (185 pg/g) were seen to be elevated by approximately 40% from the maximum of the certified range (45 – 133 pg/g) for the CRM. The results obtained from the repeat analysis in Figure 2ii were within the certified range at the lower end of the limits (46.8 pg/g).

In order to remove the requirement for changing the GC column between analyses, the Dioxin2 column was investigated for possible use in analysing PCBs. Whilst it is perfectly acceptable to use a 5MS type column for PCB analysis, column changeover may be an unnecessary step. Figure 3 shows the elution of WHO-12 PCB congeners from this column.

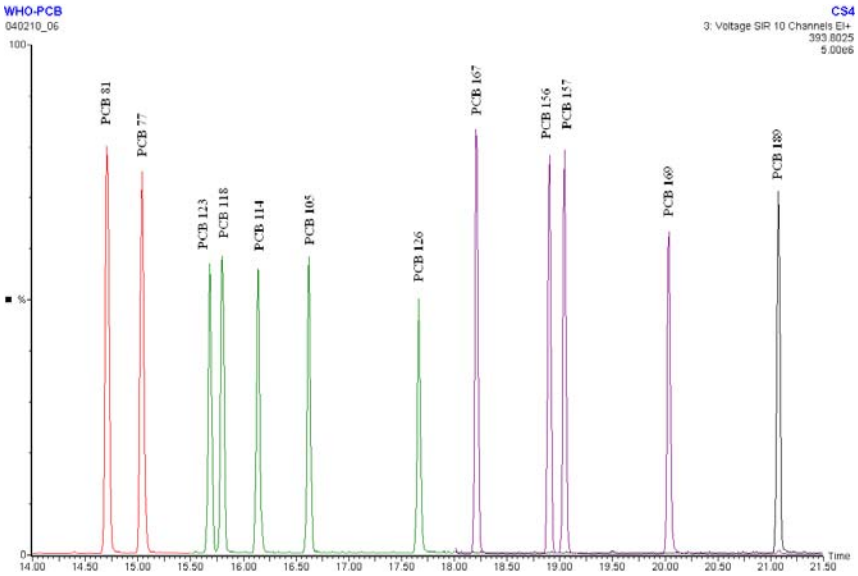

Figure 3: WHO-PCB elution from Rtx-Dioxin2 GC column.

No loss of resolution of the WHO-12 PCBs is evidenced on this column compared to the longer, and therefore lengthier analysis, 5MS type column. In fact some of the critical pairs (123/118 and 156/157) show more valley than may be obtained on the 5MS columns. With an analysis time of just over 21 minutes for PCB 189 and no evidence of co-elution affecting any of the PCBs, which may be confirmed by the CRM results, the Dioxin2 column has shown that it is a valuable analytical tool in the analysis of dioxins and PCBs.

Use of the Dioxin2 GC column coupled with ASE and multi-column cleanup it is possible for the laboratory to have analytical dioxin results for samples within 24 hours of receipt. The column has proven that it is able to offer a solution for a single run dioxin analysis and also WHO-PCB analysis. With no need for a column changeover at all, samples for dioxin and PCB analysis may be racked up on the autosampler and run one set after the other.

Acknowledgements
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References

1 Ray Fisher, Eric Aries, David R. Anderson, Nicholas Ordsmith, Keith Hall, LisaFitzpatrick and Fiona Barclay. 23rd International Symposium on Halogenated Environmental Organic Pollutants and POPs. Vol 61, pp21 – 24.
2 Frank Dorman. The Restek Advantage. Vol 4.