HRGC and HRMS Analysis of PCDD/PCDF, PCBs and Toxaphenes in Environmental Samples.

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The toxicity of PCDDs and PCDFs in a wide range of environmental samples such as drinking water, soils, incinerator stack emissions, industrial effluents, and humans has necessitated quantitative determination to lower levels. The importance of this method is evidenced by the vast amount of research and literature published over the last 20 years. The analysis requires effective sampling techniques, separation of CDDs/CDFs from bulk matrices and coextractives. For ultimate low level detection and quantitation of PCDD/Fs, PCBs and toxaphenes in environmental samples the major requirements are specificity, reliability and reproducibility. One of the most accurate techniques for obtaining quantitative information is by High Resolution Gas Chromatography combined with High Resolution Mass Spectrometry (HRGC/HRMS).

We have performed a series of experiments at 10,000 resolution (10% valley definition) to mass resolve many of the components within the complex sample matrix. In accordance with the 1613 EPA protocol[1], two ions for each analyte and isotopically labelled standard are monitored, a total of 51 ions in five groups. Identification relies on predefined isotope ratio values and retention time limits. Calibration is performed via isotope dilution. The analysis was performed on the CONCEPT mass spectrometer (Kratos Analytical), coupled with an HP 5890 GC fitted with a CTC autosampler. The analysis employed chromatographic separation on a DB-MS and a SP-2331 column.

Fifteen repeat injections of a water sample were performed by unattended automated analysis. A maximum deviation of < 10% RSD on area ratio response was recorded on **each** congener. The native 2,3,7,8 TCDD quantitated to 50fg. All recorded isotope ratios fall within the defined tolerance values, allowing unambiguous identification (see tabulated results). Quantitative data obtained at 10,000 resolution on low levels are presented. These samples, as indicated, are from water and fly ash origins. For each congener a minimum detection limit has been determined based on 2.5x the noise value.

Table of Results

Number of each analyte in each injection represents: $\frac{\text{Area of analyte}}{\text{Area of corresponding } ^{13}C_{12}\text{ - labelled internal standard}}$

Analyte	Inj #1	Inj #2	Inj #3	Inj #4	Inj #5	Inj #6	Inj #7	Inj #8	Inj #9	Inj #10
2,3,7,8-TCDD	0.0559	0.0524	0.0573	0.0451	0.0481	0.0514	0.0468	0.0532	0.0487	0.051
2,3,7,8-TCDF	1.363	1.321	1.328	1.237	1.317	1.217	1.345	1.238	1.288	1.334
1,2,3,7,8-PeCDD	0.450	0.397	0.458	0.434	0.406	0.459	0.401	0.07	0.441	0.432
1,2,3,7,8-PeCDF	0.674	0.706	0.657	0.574	0.538	0.609	0.655	0.342	0.661	0.649
2,3,4,7,8-PeCDF	1.505	1.501	1.529	1.487	1.459	1.454	1.507	1.542	1.490	1.537
1,2,3,4,7,8-HxCDD	0.884	0.906	0.828	0.871	0.843	0.893	0.899	0.836	0.823	0.839
1,2,3,6,7,8-HxCDD	0.364	0.375	0.328	0.385	0.346	0.371	0.407	0.351	0.371	0.360
1,2,3,7,8,9-HxCDD	1.099	1.093	1.008	1.102	1.042	1.030	1.080	1.011	1.023	1.022
1,2,3,4,7,8-HxCDF	5.0371	5.465	4.829	5.445	5.346	5.559	5.576	5.282	5.248	4.905
1,2,3,6,7,8-HxCDF	2.789	2.842	2.546	2.773	2.759	2.597	2.774	2.407	2.589	2.375
1,2,3,7,8,9-HxCDF	3.434	3.446	3.346	3.628	3.449	3.425	3.679	3.227	3.504	3.493
2,3,4,6,7,8-HxCDF	0.445	0.455	0.400	0.467	0.441	0.457	0.455	0.403	0.436	0.439
1,2,3,9,6,7,8-HpCDD	9.231	9.021	9.722	9.515	9.341	9.699	9.442	9.627	9.520	9.686
1,2,3,4,6,7,8-HpCDF	8.481	8.736	8.285	8.697	8.480	8.676	8.631	8.645	8.805	8.548
1,2,3,4,7,8,9-HpCDF	0.651	0.660	0.616	0.672	0.692	0.695	0.661	0.676	0.693	0.662
OCDD	8.708	8.531	8.922	8.673	8.893	8.744	8.399	9.003	9.323	9.435
OCDF	2.022	2.008	2.077	2.016	2.078	2.055	1.969	2.104	2.327	2.159

Analyte	Inj #11	Inj #12	Inj #13	Inj #14	Inj #15	Mean	%RSD
2,3,7,8-TCDD	0.0530	0.0615	0.0540	0.0535	0.0468	**0.0519**	**8.48**
2,3,7,8-TCDF	1.421	1.195	1.359	1.299	1.181	**1.296**	**5.32**
1,2,3,7,8-PeCDD	0.490	0.435	0.412	0.424	0.439	**0.432**	**5.92**
1,2,3,7,8-PeCDF	0.681	0.635	0.663	0.647	0.602	**0.640**	**6.74**
2,3,4,7,8-PeCDF	1.598	1.536	1.591	1.521	1.485	**1.516**	**2.73**
1,2,3,4,7,8-HxCDD	0.892	0.862	0.872	0.907	0.865	**0.868**	**3.31**
1,2,3,6,7,8-HxCDD	0.376	0.361	0.378	0.360	0.361	**0.366**	**4.95**
1,2,3,7,8,9-HxCDD	1.084	1.109	1.054	1.095	1.099	**1.063**	**3.51**
1,2,3,4,7,8-HxCDF	5.300	5.304	5.176	5.014	5.089	**5.261**	**4.24**
1,2,3,6,7,8-HxCDF	2.623	2.787	2.491	2.576	2.500	**2.629**	**5.72**
1,2,3,7,8,9-HxCDF	3.523	3.549	3.286	3.533	3.506	**3.469**	**3.42**
2,3,4,6,7,8-HxCDF	0.440	0.463	0.440	0.428	0.434	**0.440**	**4.37**
1,2,3,9,6,7,8-HpCDD	9.193	9.802	9.406	9.603	8.922	**9.449**	**2.79**
1,2,3,4,6,7,8-HpCDF	8.559	8.771	8.519	8.475	8.494	**8.587**	**1.62**
1,2,3,4,7,8,9-HpCDF	0.647	0.671	0.627	0.625	0.612	**0.657**	**4.18**
OCDD	9.371	8.441	8.624	8.919	8.573	**8.837**	**3.74**
OCDF	2.255	1.948	1.957	1.976	1.915	**2.058**	**5.62**

Internal Standards:

$^{13}C_{12}$-2,3,7,8-TCDD
$^{13}C_{12}$-2,3,7,8-TCDF
$^{13}C_{12}$-1,2,3,7,8-PeCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-OCDD

These have been calculated to 0.5fg, and quantified levels as low as 2fg recorded. Under these conditions levels of 10fg of the native tetra derivatives with a S/N > 8: 1 were obtained.

A similar experiment using calibration standard CS-2 was performed at 30,000 resolution. The loss in sensitivity is compensated by the increase in specificity. This increased resolution has the benefit that less clean-up may be required so reducing analysis time. Quantitation levels achievable would be expected to be of the order of 50fg under these conditions. Data has been acquired at 30,000 resolution and a direct comparison of peak areas of repeat injections at 10 and 30,000 resolution performed illustrated a linearity of response. This method has now been adapted to target other components of interest.

Toxaphenes, a complex mixture of over 670 polychlorinated camphenes (PCCs) are present in similar concentrations to PCBs in freshwater samples and marine mammals. Quantitation is difficult due to poor characterisation, the complex nature of the PCC mix and the difficulty of chromatographic separation even by HRGC. Analysis can be performed by HR electron capture negative ion mass spectrometry, using methane as the moderating gas to reduce component fragmentation.[2] M^- ions for the hexa-chlorinated components and $(M\text{-}Cl)^-$ ions for the hepta through deca-chlorinated compounds are commonly monitored.[2-3]

An experiment at 1000 resolution was performed on a 50pg (total of all components) toxaphene standard. The results suggest detection limits of a single congener to be in

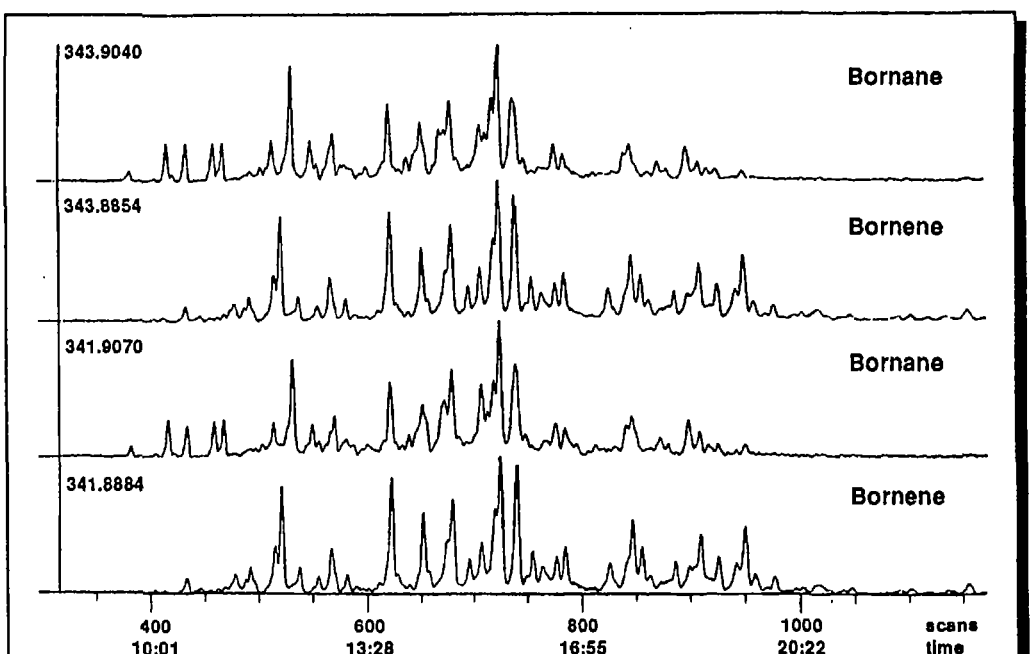

Figure 1: 24,000 resolution SIM analysis of toxaphene standards

the low fg range. Using the high resolution SIM procedure at a resolution of > 24,000, the bornenes and bornanes were separated although further chromatographic improvements would clearly be beneficial (Figure 1).

Working at higher resolutions: a). eliminates the necessity for corrective calculations to compensate for interferences occurring from coeluting halogenated organic compounds and b). leads to better detection, as it is not necessary to monitor the response from other interferences occurring at low resolution, enabling increased analysis time on analyte ions.

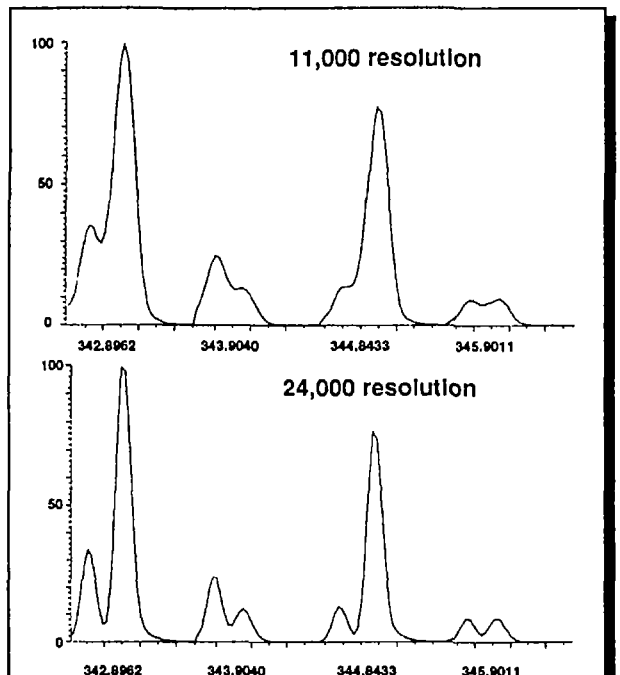

Figure 2: Toxaphene standards analysed by HRSIM at differing resolutions. The higher resolution shows separation of bornanes and bornenes (bornenes occur at lower mass than the bornanes)

An HRSIM[4] experiment (profile data) was performed at 11,000 and 24,000 resolution. This involves sweeping the ESA across a selected region of each ion. This technique clearly illustrates situations in which components co-elute and are insufficiently mass resolved (Figure 2). The inherent improvement of specificity with increased resolution is illustrated. The higher resolution analysis was performed on 1 ng total sample. Additionally it allows identification of a false positive result recorded if the isotope ratios pass the EPA criteria and false negative results which can be generated if an interfering component distorts the isotope ratios such that the result falls outside the required values and the peak is rejected. This method also serves to confirm experimental resolution, lock mass stability and identification.

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