

INVESTIGATION OF SOUTH AFRICAN SOIL AND SEDIMENT FOR PCDD AND PCDF CONTAMINATION USING GAS CHROMATOGRAPHY – HIGH RESOLUTION TIME OF FLIGHT MASS SPECTROMETRY

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Introduction

South Africa has no established gas chromatography–high resolution mass spectrometry (GC–HRMS) facility for polychlorinated dibenzo-p-dioxin (PCDD) or polychlorinated dibenzofuran (PCDF) analysis. This situation is not as a result of a lack of need; indeed in developing countries there is probably a greater need for strict control of effluent and waste disposal, but results from a shortage of finance available for the purchase of specialized scientific equipment, and also a shortage of skilled personnel needed for the optimum use and maintenance of such technology. The need for environmental monitoring is essential to ensure sustainable growth without exposing the population to dangerous toxins. This lack of GC–HRMS facilities in South Africa (and other developing countries) has led us to develop an alternative solution that is affordable, easy to manage and aligned to the country's needs^{1,2}, and which can be used for rapid sample screening.

With the acquisition of HRMS capability this investigation has been extended, and we report now on the investigation of South African soil and sludge samples using gas chromatography – high resolution time of flight mass spectrometry (GC-HRT).

Materials and methods

The GC-HRT system used in this study at the LECO Separation Science Laboratory, University of Pretoria, South Africa was a Pegasus HRT (LECO Corporation, St Joseph, MI, USA). The GC column used for this study was an Rxi-5Sil MS (Restek Corporation, Bellefonte, PA, USA). One set of analyses was performed on a Pegasus HRT system at the Life Sciences and Chemical Analysis Laboratory, LECO Corporation. The Pulsed Electron Impact Source (PEIS) work described was done on this instrument.

The systems were tuned on the 414 ion from the conventional perfluorotributylamine (PFTBA) mass calibrant. This is different from the standard tuning procedure and is an attempt to improve the signal intensity at the higher mass range. All instrument functions and data processing were managed with the *LECO ChromaTOF HRT* software (version 1.42). Manual review of all peak identifications and integrations was performed using this software. Library searching was performed using a PCDD/F *user* library compiled from PCDD/F standards. US EPA Method 1613 calibration and verification solutions (EPA-1613CVS), labelled calibration solutions (EPA-1613LCS), internal standard spiking solution (EPA-1613ISS) and cleanup standard stock solution (EPA-1613CSS) were chosen for spiking and calibration purposes. These solutions were purchased from Wellington Laboratories (Guelph, Canada) and contained the seventeen native and corresponding mass-labelled PCDD/F congeners in nonane. The isomer specificity and window defining standard (EDF-4147 *GC Retention Time Window Defining Solution and Isomer Specificity Test Standard*) was purchased from Cambridge Isotope Laboratories (Massachusetts, USA).

Sample extraction was performed using a Fluid Management Systems (FMS, Watertown, MA, USA) TRP 2 system, following standard procedures recommended for the instrumentation³.

Results and discussion

The Pegasus HRT system uses a novel folded flight path technology to achieve high resolution (up to 50 000 FWHM) and routinely achieves mass accuracy of 1 ppm or better.

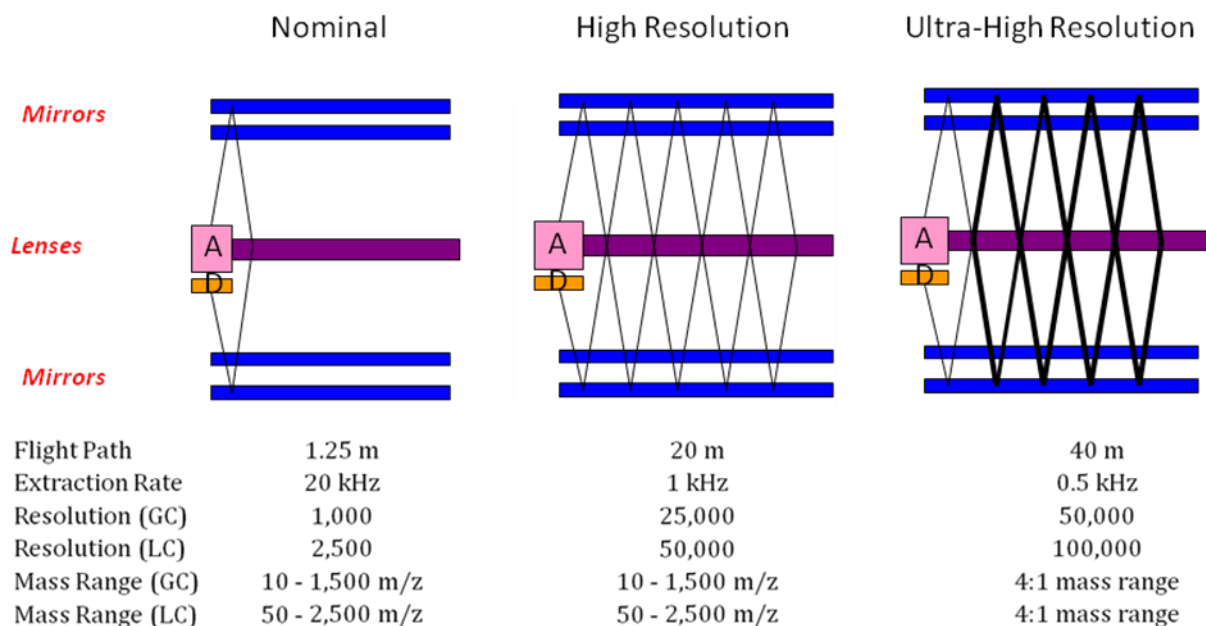


Figure 1: Diagram showing the properties of the folded flight path modes available on the Pegasus HRT.

The number of reflections of the ions between gridless mirrors can be controlled by the software to run the system in nominal, high or ultra high resolution mode. In this study analyses were performed in the high resolution mode.

Initial work focused on the confirmation of the chromatography using standards (Figure 2). Subsequent to this, limits of detection were investigated, and window defining and isomer specificity studies were undertaken. The limits of detection were determined using the new PEIS technology available on the Pegasus HRT systems. In this approach, signal intensity is increased over a limited mass range, thus providing a much lower limit of detection. This provides an enhancement of the detection limit by a factor of up to 40x, and using this approach a lower limit of detection for 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) of below 50 fg on column was established. This is well below the requirements of EPA Method 1613.

Once the methods and limitations of the approach had been defined using standards, calibration curves were produced using standard samples across the range covered by the commercially available EPA 1613 standard set. Satisfactory correlation co-efficients ($r \geq 0.999$) were obtained for all the components of the standard set.

The calibration information could then be used in the analysis of several real world samples. A typical chromatogram for a sediment sample is shown in Figure 3. Over 75 dioxins were located in this sample (Table 1) and quantitative values for the PCDD/Fs mandated for analysis by EPA Method 1613 are shown in Table 2. In addition to the PCDD/Fs identified in the sample, several other priority pollutants could also be detected and identified. Unlike HRMS using sector instruments, where the low levels necessary are obtained by using SIM, a target compound technique, HR-TOFMS, when not used in the PEIS mode, provides full range mass spectra for all the components of a sample. This allows identification of not only the target dioxins and furans, but also other compounds present in the sample. In this study this proved of particular interest, as in addition to the PCDDs and PCDFs numerous compounds from other pollutant classes were identified. Several polynuclear aromatic hydrocarbons (PAHs) were also detected and identified.

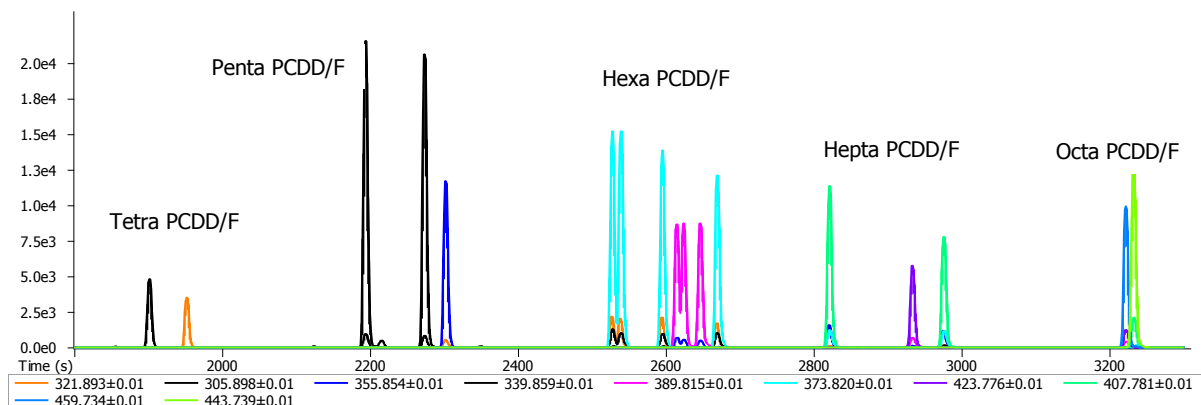


Figure 2: Extracted ion chromatogram (XIC) of a standard sample containing the 17 priority PCDD/F compounds mandated for analysis by EPA Method 1613.

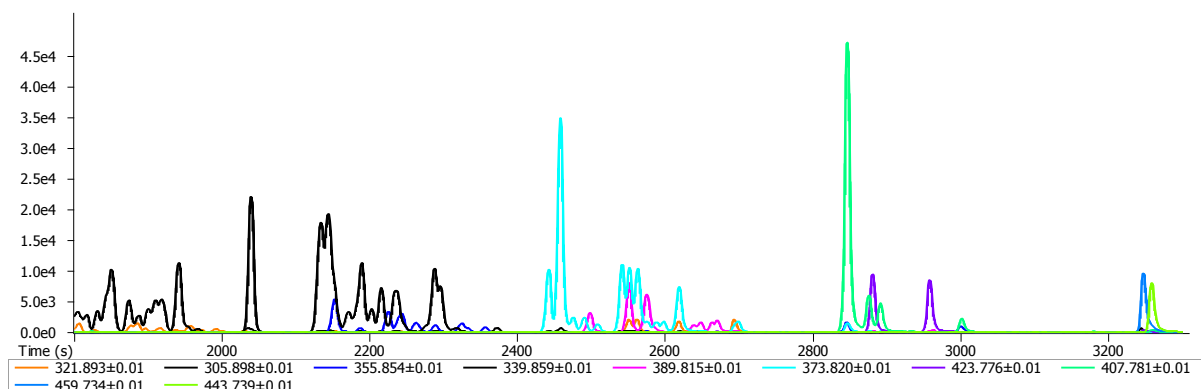


Figure 3: XIC showing a set of results (PCDD/Fs) for a typical sediment sample.

Table 1: Some PCDD/Fs identified in the sediment sample shown above.

Peak	Name	RT(s)	Quant S/N	Area	Peak	Name	RT(s)	Quant S/N	Area
1	TCDF	607.5	231	45522	35	PCDF	929.5	55	11679
2	TCDF	617.0	148	27060	37	12378-PCDD	931.5	256	45608
3	TCDF	626.0	70	9492	38	PCDD	953.5	100	27712
4	TCDF	636.0	1702	599207	39	PCDF	965.5	91	30171
5	TCDD	643.0	85	11796	40	HxCDF	1014.0	708	126499
6	TCDD	650.5	98	15172	41	HxCDF	1026.0	3895	1012971
7	TCDF	655.0	341	94019	42	HxCDF	1039.5	135	23815
8	TCDF	671.0	1193	503575	43	HxCDF	1050.5	264	64894
9	TCDF	683.5	419	87513	44	HxCDD	1055.5	402	122722
10	TCDD	684.5	245	93572	45	HxCDF	1065.0	135	32685
11	TCDD	700.5	71	15029	46	HxCDF	1091.0	683	124227
12	2378-TCDF	701.0	866	144124	47	HxCDD	1098.0	967	280421
14	TCDD	711.0	585	152418	49	123478-HxCDF	1099.5	533	45724

15	TCDF	714.0	1325	335836	51	123678-HxCDF	1109.0	760	53517
16	TCDD	720.5	146	58007	52	HxCDD	1118.0	742	252883
18	TCDD	738.0	67	16718	53	HxCDF	1129.5	99	18045
19	TCDD	757.5	25	7665	54	HxCDF	1138.5	121	24994
20	TCDF	761.5	100	30673	56	234678-HxCDF	1156.0	1093	170249
21	PCDF	820.0	2894	1493648	58	HxCDD	1173.0	40	5640
22	PCDD	824.0	681	204802	60	HxCDD	1181.5	162	36980
23	PCDD	844.5	64	17905	62	HxCDD	1202.5	240	107096
24	PCDF	846.0	1062	326860	64	123789-HxCDF	1228.0	209	40141
25	PCDF	856.0	54	5874	66	1234678-HpCDF	1379.0	5629	935138
27	12378-PCDF	864.5	672	67004	67	HpCDF	1410.0	667	208625
28	PCDD	867.0	324	68690	68	HpCDD	1417.0	1089	369451
29	PCDF	876.5	924	267925	69	HpCDF	1428.0	485	150041
30	PCDD	879.5	305	79188	71	1234678-HpCDD	1506.5	1038	185225
31	PCDD	891.5	147	34660	73	1234789-HpCDF	1557.0	264	46933
32	PCDD	908.5	176	48501	75	OCDD	1836.0	1410	251057
33	23478-PCDF	909.0	2043	440715	76	OCDF	1846.5	1091	190870

Table 2: Quantitative data for PCDD/Fs mandated by EPA Method 1613 in the sediment sample

Peak	Name	RT(s)	Quant		
			Mass	Concentration	Units
12	2378-TCDF	701.0	305.8982	133.39	pg/μl
27	12378-PCDF	864.5	339.8596	58.09	pg/μl
33	23478-PCDF	909.0	339.8592	340.5	pg/μl
37	12378-PCDD	931.5	355.8547	62.24	pg/μl
49	123478HxCDF	1099.5	373.8202	Out of range	pg/μl
51	123678HxCDF	1109.0	373.8207	Out of range	pg/μl
56	234678-HxCDF	1156.0	373.8206	171.91	pg/μl
64	123789-HxCDF	1228.0	373.8208	46.21	pg/μl
66	1234678-HpCDF	1379.0	407.7815	1316.6	pg/μl
71	1234678-HpCDD	1506.5	423.7763	470.9	pg/μl
73	1234789-HpCDF	1557.0	407.7814	89.99	pg/μl
75	OCDD	1836.0	459.7341	909.93	pg/μl
76	OCDF	1846.5	443.7396	496.22	pg/μl

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3. Obtainable from Mr P Germansderfer, FMS, Watertown, MA, USA