

## Comparison of High Resolution and Low Resolution Mass Spectrometer Performance in an Ambient Air Round-Robin Study

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### Summary

A round-robin study was conducted to determine the state-of-the-art performance of laboratories for the analysis of ambient air sample extracts for the chlorinated dibenzo-p-dioxins (dioxins) and the chlorinated dibenzofurans (furans). Of the 18 laboratories that took part in the investigation 12 used high resolution mass spectrometers (HRMS), one used a tandem quadrupole Finnigan TSQ 70, four used low resolution quadrupole mass spectrometers (LRMS), and one laboratory used an ion trap. Average detection limits were 10 times lower for the laboratories that employed HRMS compared to LRMS systems. Average concentrations reported for the 2,3,7,8-substituted congeners were comparable for LRMS and HRMS for a high-concentration sample, but most LRMS laboratories were unable to achieve acceptable performance for toxic congener analysis of a low-concentration sample.

### Description of Round-Robin Study

Hi-Vol air samples (teflon-coated glass fibre filter and polyurethane foam plug) were collected in two areas: one known to have relatively low ambient air concentrations of dioxins/furans, and the other area suspected of having much greater ambient air concentrations. Samples from the "high" area were extracted without spiking and pooled, as were the samples from the "low" area - so two pooled sample extracts were obtained. The "high" sample was spiked with an extract of dioxins/furans from municipal incinerator fly ash to ensure the concentrations of dioxins/furans were at least ten times greater than concentrations in the "low" sample. Aliquots of the pooled "high" and "low" concentration samples were sent to the various laboratories that participated in the round-robin study.

Eighteen laboratories from the U.S.A. and Canada participated in the study. Each laboratory received two replicates of the "high" sample and two replicates of the "low" sample. All samples were numbered so that laboratories were not aware they received

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replicates. In addition, calibration, spiking, and recovery standards were supplied to each laboratory.

### Results and Discussion

Table 1 shows a summary of the results received from 13 HRMS (including MS-MS) laboratories, and from five LRMS laboratories (high concentration sample only).

**Table 1: Summary of Round-Robin Study Results (High Concentration Sample)**

	HRMS Results			LRMS Results		
	mean DL	mean conc.	%rsd	mean DL	mean conc.	%rsd
2378-TCDD	3.3	47.4	110	48	271	73
total TCDD	-	2170	24	-	2033	26
12378-5CDD	8	218	22	140	283	18
total 5CDD	-	5690	12	-	4810	36
123478-6CDD	7.4	373	51	110	334	16
123678-6CDD	6.7	691	72	97	672	24
123789-6CDD	7.0	732	42	88	756	23
total 6CDD	-	8460	41	-	7620	21
1234678-7CDD	10	3480	12	75	4186	27
total 7CDD	-	6200	15	-	7037	21
OCDD	23	3750	26	180	4552	22
2378-TCDF	2.9	252	52	48	250	62
total TCDF	-	1650	25	-	1804	30
12378-5CDF	5.0	99.6	12	53	203	83
23478-5CDF	5.3	220	19	41	218	8.2
total 5CDF	-	2170	15	-	1640	54
123478-6CDF	6.7	461	28	48	468	40
123678-6CDF	5.6	258	35	45	253	18
123789-6CDF	5.7	199	75	49	398	20
234678-6CDF	5.8	238	67	54	297	52
total 6CDF	-	2390	10	-	2048	41
1234678-7CDF	8.3	1080	13	74	1288	28
1234789-7CDF	8.1	127	24	93	133	34
total 7CDF	-	1860	18	-	1728	33
OCDF	16	846	140	150	2752	128

DL = mean reported detection limit in total picograms per sample.

All results are total picograms per sample; %rsd = % relative standard deviation.

Only the data from the high concentration sample are shown in Table 1 because the results for the low concentration sample were poor for the LRMS laboratories. The results for congener group totals only - for the low concentration sample - are shown in Table 2.

**Table 2: Comparison of HRMS and LRMS Results for Congener Group Totals in the Low Concentration Sample**

	HRMS Results		LRMS Results	
	N	mean	N	mean
total TCDD	26	52.9	-	nd
total 5CDD	26	105	-	nd
total 6CDD	26	300	3	287
total 7CDD	26	569	7	964
OCDD	26	826	8	1170
total CDD	26	1850	8	2120
total TCDF	26	250	-	nd
total 5CDF	26	191	1	26
total 6CDF	26	243	3	231
total 7CDF	25	164	5	192
OCDF	26	103	2	564
total CDF	26	945	6	468
total CDD+CDF	26	2790	8	1990

means are calculated using only the positive values reported.

N = number of positives reported in two replicates by all laboratories

(maximum value of N is 26 for HRMS labs and 10 for LRMS labs).

nd = not detected

The performance of LRMS laboratories seems comparable to the HRMS laboratories in Table 2 for the hexa- to octachlorinated congeners, but if the isomer-specific data are compared it can be seen the performance is much worse. This can be seen by comparing the number of times the 2,3,7,8-substituted congeners were detected. There are 17 2,3,7,8-substituted congeners, and two replicates were analyzed by each of five LRMS laboratories. Therefore, the total number of times a 2,3,7,8-substituted congener could have been detected by all five LRMS laboratories is 170 (17 x 2 x 5). The actual number reported was 24, or

14% of the maximum possible. For the HRMS laboratories, the percent reported 2,3,7,8-substituted congeners is 88% (we are assuming there were no false positives reported). Most of the positives reported by LRMS laboratories for the 2,3,7,8-substituted congeners were the hepta- and octachlorinated congeners, so if the total toxicity equivalency values for HRMS and LRMS laboratories were compared, there would be a much greater difference between HRMS and LRMS performance for the low concentration sample. This also points out the dangers in rapid screening procedures that are based on total congener group methods rather than isomer-specific methods.

### Conclusions

For determination of the chlorinated dioxins/furans in ambient air, both HRMS and LRMS systems can achieve comparable performance in the analysis of relatively high level samples. For low concentration samples, the performance of LRMS systems was not acceptable, especially for the determination of the 2,3,7,8-substituted congeners. There was considerable variation in the performance of some of the participating laboratories, but in general the laboratories that employed HRMS detection achieved comparable results. When outliers are removed, the average overall percent relative standard deviation for reported results from HRMS laboratories is 13% for the high concentration sample, and 22% for the low concentration sample.