

Precision and Accuracy of Ion Abundance Ratio Measurements

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The typical qualitative method used in the GC/MS identification of chlorinated dibenzo-p-dioxins and dibenzofurans is based on a comparison of the isotopic ratio of selected ions in the molecular ion region to their theoretical abundance ratios. USEPA analytical methods provide theoretical abundance ratios and control limits to be used in the identification of chlorinated dibenzo-p-dioxins and dibenzofurans present in environmental samples. Quality assurance requirements in USEPA method 8280, 8290, and 1613 specify that all calibration standard ion ratios must be within the control limits before the analysis of samples may proceed. 1-3)

It is assumed that the calculated ion abundance ratios of the standard are indicative of the mass spectrometer's ability to generate ion abundance ratios that will positively identify chlorinated dibenzo-p-dioxins and dibenzofurans if they are present in the sample and free from interferences. However, single measurements are usually not adequate in judging the normal distribution and variability involved in the measurement process. Typically, statistical measurement of the precision and accuracy of the measurement process is focused on the qualitative aspect of the analytical method through the analysis and control charting of spiked QC sample results (i.e., PAR, LCS, MS/MSD samples). Often overlooked is the ability of the mass spectrometer to consistently produce accurate ion abundance measurements within the required limits of the method.

In order to evaluate the ability of the analytical methods to produce consistent ion abundance ratios, data was collected from standards analyzed on a Finnigan MAT 95 HRGC/HRMS over the period from January 1993 to March 1994. The analyses were performed in a commercial analytical laboratory operating under routine conditions. Factors that might affect the measurement process such as ion source condition, GC column condition, source tuning, and electron multiplier condition were varied as would be expected in a production laboratory with a medium to high sample load consisting of mixed matrices from various sources. The GC/MS mass assignment accuracy was checked prior to standard analysis by locking on PFK ion m/e 304.9824 and jumping to m/e 380.9760 by reducing the accelerating voltage. Ion abundance ratios were calculated using the ions specified in USEPA methods 8290 and 1613 and compared to the control limits in the methods. The ratios for each native and labeled compound in the standards were compiled in a database and used to develop precision and accuracy estimates.

Table 1

Theoretical vs Observed Ion Abundance Ratios and Their Control Limits

Analyte	EPA			EPA		Mean \pm 3s	
	Theoretical Ratio	Mean Ratio	%D	Control Limits Lower	Control Limits Upper	Control Limits Lower	Control Limits Upper
¹³ C-1,2,3,4-TCDD	0.77	0.78	-1.1	0.65	0.89	0.74	0.82
¹³ C-2,3,7,8-TCDD	0.77	0.77	-0.6	0.65	0.89	0.74	0.81
2,3,7,8-TCDD	0.77	0.77	-0.6	0.65	0.89	0.70	0.85
¹³ C-1,2,3,7,8-PeCDD	1.55	1.62	-4.4	1.32	1.78	1.47	1.76
1,2,3,7,8-PeCDD	1.55	1.60	-3.5	1.32	1.78	1.49	1.71
¹³ C-1,2,3,4,7,8-HxCDD	1.24	1.28	-3.6	1.05	1.43	1.20	1.36
¹³ C-1,2,3,6,7,8-HxCDD	1.24	1.28	-3.5	1.05	1.43	1.20	1.37
¹³ C-1,2,3,7,8,9-HxCDD	1.24	1.28	-3.1	1.05	1.43	1.20	1.36
1,2,3,4,7,8-HxCDD	1.24	1.29	-3.7	1.05	1.43	1.18	1.39
1,2,3,6,7,8-HxCDD	1.24	1.28	-3.3	1.05	1.43	1.19	1.37
1,2,3,7,8,9-HxCDD	1.24	1.28	-3.3	1.05	1.43	1.20	1.36
¹³ C-1,2,3,4,6,7,8-HpCDD	1.04	1.05	-1.3	0.88	1.20	0.99	1.11
1,2,3,4,6,7,8-HpCDD	1.04	1.05	-1.4	0.88	1.20	0.97	1.14
¹³ C-OCDD (IS)	0.89	0.90	-0.9	0.76	1.02	0.85	0.95
OCDD	0.89	0.89	0.5	0.76	1.02	0.85	0.95
¹³ C-2,3,7,8-TCDF	0.77	0.80	-3.8	0.65	0.89	0.76	0.84
2,3,7,8-TCDF	0.77	0.78	-1.4	0.65	0.89	0.71	0.85
¹³ C-1,2,3,7,8-PeCDF	1.55	1.60	-3.3	1.32	1.78	1.43	1.78
¹³ C-2,3,4,7,8-PeCDF	1.55	1.61	-3.7	1.32	1.78	1.42	1.79
1,2,3,7,8-PeCDF	1.55	1.61	-3.8	1.32	1.78	1.49	1.73
2,3,4,7,8-PeCDF	1.55	1.60	-3.5	1.32	1.78	1.48	1.73
¹³ C-1,2,3,4,7,8-HxCDF	0.51	0.51	-0.3	0.43	0.59	0.48	0.54
¹³ C-1,2,3,6,7,8-HxCDF	0.51	0.51	-0.1	0.43	0.59	0.48	0.54
¹³ C-2,3,4,6,7,8-HxCDF	0.51	0.51	0.0	0.43	0.59	0.48	0.54
¹³ C-1,2,3,7,8,9-HxCDF	0.51	0.51	0.2	0.43	0.59	0.48	0.54
1,2,3,4,7,8-HxCDF	1.24	1.26	-2.0	1.05	1.43	1.17	1.36
1,2,3,6,7,8-HxCDF	1.24	1.26	-1.8	1.05	1.43	1.17	1.35
2,3,4,6,7,8-HxCDF	1.24	1.26	-1.8	1.05	1.43	1.16	1.36
1,2,3,7,8,9-HxCDF	1.24	1.26	-2.0	1.05	1.43	1.17	1.36
¹³ C-1,2,3,4,6,7,8-HpCDF	0.44	0.44	0.4	0.37	0.51	0.41	0.46
¹³ C-1,2,3,4,7,8,9-HpCDF	0.44	0.43	1.3	0.37	0.51	0.41	0.46
1,2,3,4,6,7,8-HpCDF	1.04	1.06	-1.5	0.88	1.20	0.93	1.18
1,2,3,4,7,8,9-HpCDF	1.04	1.05	-1.3	0.88	1.20	0.94	1.17
OCDF	0.89	0.90	-1.4	0.76	1.02	0.84	0.96

Figure 1 - Theoretical vs Observed Ion Ratio for 2,3,7,8-TCDD

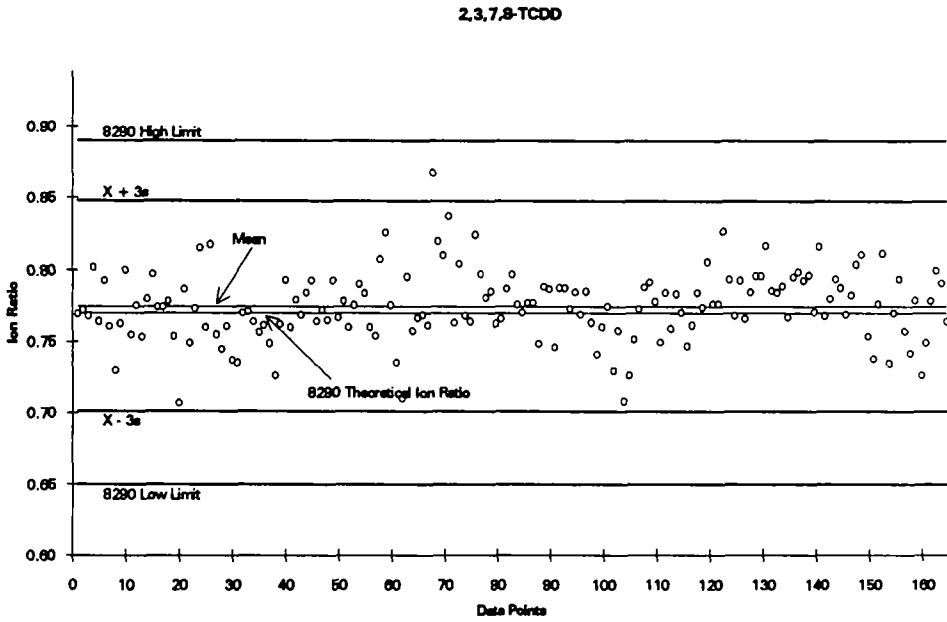
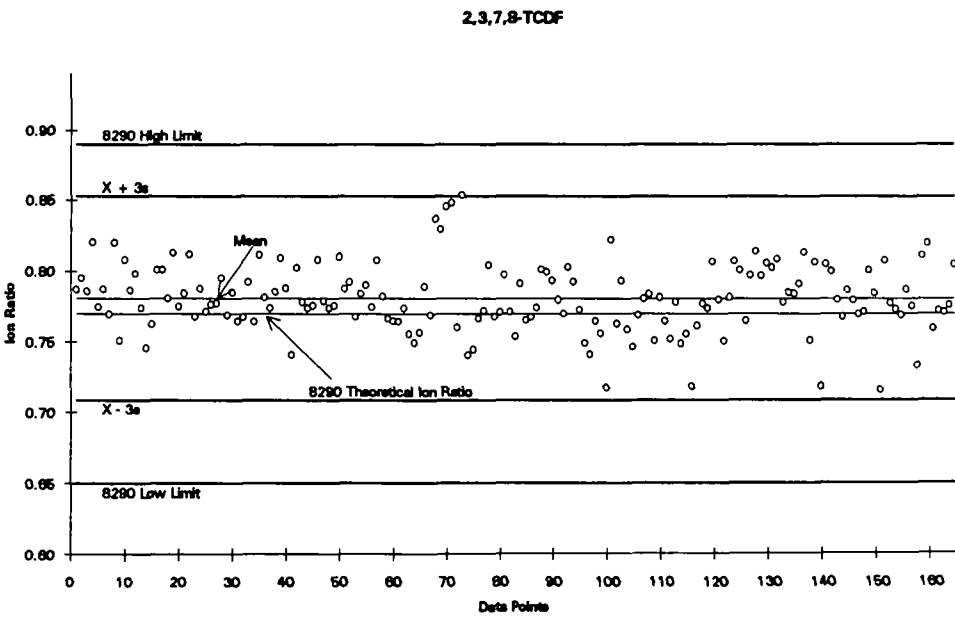


Figure 2 - Theoretical vs Observed Ion Ratio for 2,3,7,8-TCDF



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The statistical mean and control limits calculated from the ratio data exhibit good correlation with the EPA theoretical ion abundance's and control limits (Table 1). The mean ion ratio for all compounds is within $\pm 5\%$ of the EPA theoretical ratio in all cases. The calculated control limits of ± 3 standard deviations are within the EPA $\pm 15\%$ limit (Figures 1 and 2). The data indicates that the MAT 95 is capable of producing consistently accurate ion ratios within the limits specified by the EPA methods. By monitoring the ion ratio measurement process on a regular basis the laboratory can be confident the qualitative as well as the quantitative results are within control.

References

- 1) USEPA Office of Solid Waste and Emergency Response, SW-846 Method 8280 ; The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans, Washington, DC 1986
- 2) USEPA Office of Solid Waste and Emergency Response, SW-846 Draft Method 8290 ; Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans by HRGC/HRMS, Washington, DC 1990
- 3) USEPA Office of Water Regulations and Standards Industrial Technology Division, Method 1613 ; Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Washington, DC 1990