

Validation of a novel HRGC/HRMS instrument and the TACO user Interface in respect to USEPA methods 1613 and 8290

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Quality assurance for dioxin/furan analysis gained importance during the last years due to various national reference methods¹⁻⁵, accreditation regulations and the global ISO 9000 quality standards. The number of samples to be measured, as well as the requested amount of documentation, verification and quality control increased and ask for automated instrumentation.

The present paper describes the validation of the QUANTUM HRGC/HRMS instrument with the integrated TACO (Target Compound analysis software) according to USEPA methods 1613 and 8290 in a routine environment.

The system coordinates the instrument control of the high resolution mass spectrometer, the gas chromatograph and the autosampler. It includes automated instrument setup routines and takes care of data acquisition, data evaluation and quantification according to the predefined methods⁶. These methods also determine quality control parameters relating to the mass spectrometer and derived from the data evaluation. System performance parameters can be checked against method dependent limits and may stop batch processing via feedback control. TACO automatically documents quality charts and generates reports that integrate text and graphics in a flexible user defined format.

Figure 1 is a plot that documents the MID peak jumping accuracy and the selected resolution using PFTBA reference ions, as requested in the corresponding MID descriptor. The plot is generated automatically during batch operation. Jumping accuracy and resolution at full and decreased accelerating voltage are transferred into quality charts as given in figure 2. For stability validation an initial calibration was

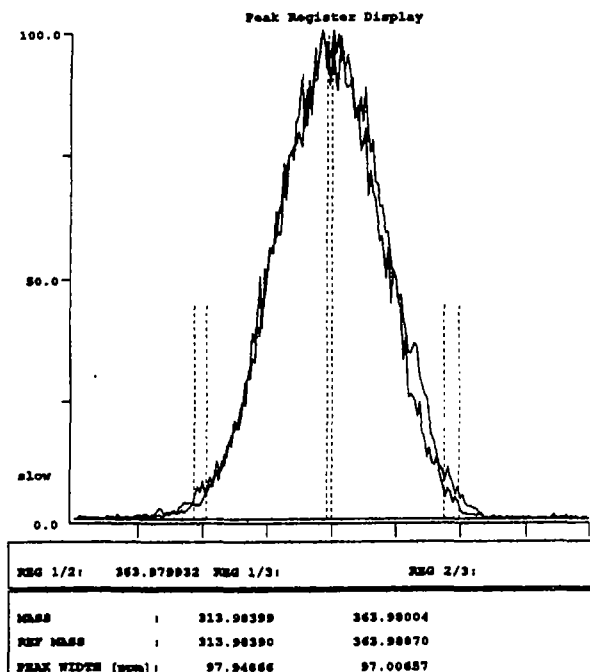


Fig. 1: Plot of the MID peak jumping accuracy

Quality-Chart of: Instrument parameter: Resolution at reduced Ua

First Value: 1993-04-02-15:43.00
 Last Value: 1993-04-08-19:51.00
 AVG ± STD

Instrument: QUANTUM
 Reporting Date: 09-Apr-93
 10:52:12

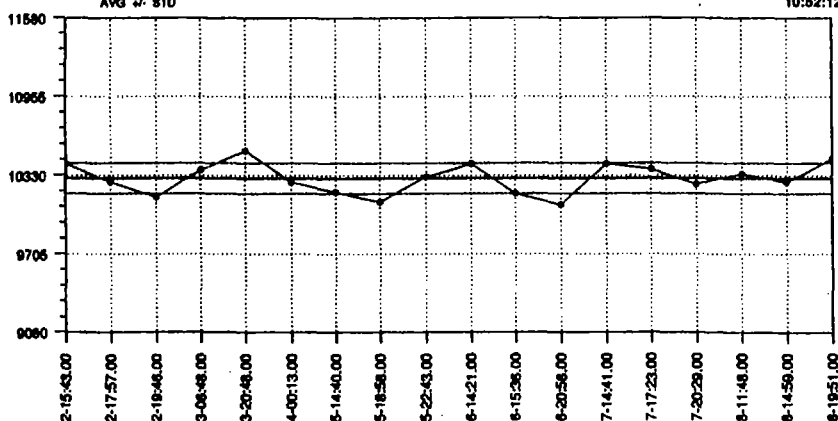


Fig. 2: Quality chart of resolution at reduced accelerating voltage



INC Summary Report

Date: 02-Apr-1993
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Calculated response factors for CS 1 to Cs 5

Acquired : 02-Apr-93

	CS 1	CS 2	CS 3	CS 4	CS 5	MEAN	%RSD
Native Congeners							
2378-TCDF	1.078	1.005	0.969	1.005	1.029	1.017	3.5
2378-TCDD	1.152	1.240	1.119	1.115	1.140	1.153	3.9
12378-PeCDF	0.967	0.973	1.009	1.043	1.074	1.013	4.0
23478-PeCDF	1.022	0.980	0.965	1.045	1.036	1.010	3.1
12378-PeCDD	1.126	1.024	1.070	1.117	1.223	1.112	6.0
123478-HxCDF	1.018	0.944	0.977	1.019	1.072	1.006	4.3
123678-HxCDF	0.968	0.983	1.011	1.047	1.076	1.017	3.9
234678-HxCDF	1.041	0.943	0.962	0.995	1.019	0.992	3.6
123789-HxCDF	1.017	0.978	1.005	1.039	1.063	1.020	2.8
123478-HxCDD	1.117	0.968	1.013	1.025	1.063	1.037	4.8
123678-HxCDD	1.063	0.928	0.947	0.977	0.984	0.980	4.7
123789-HxCDD	1.043	0.984	0.987	0.993	0.996	1.000	2.2
1234678-HpCDF	1.247	1.006	0.966	1.073	1.099	1.078	9.0
1234789-HpCDF	1.039	0.974	0.994	1.037	1.051	1.019	2.9
1234678-HpCDD	1.029	1.008	1.019	1.056	1.075	1.037	2.4
OCDF	1.500	1.417	1.595	1.648	1.711	1.574	6.6
OCDD	1.296	1.193	1.205	1.304	1.324	1.264	4.3
Surrogate Std's							
2378-TCDF 13C12	1.705	1.693	1.697	1.722	1.790	1.721	2.1
2378-TCDD 13C12	1.084	1.096	1.012	1.115	1.157	1.093	4.3
12378-PeCDF 13C12	1.262	1.370	1.350	1.393	1.542	1.383	6.6
23478-PeCDF 13C12	1.329	1.503	1.409	1.348	1.598	1.437	7.0
12378-PeCDD 13C12	0.740	0.850	0.809	0.815	0.852	0.813	5.0
123478-HxCDF 13C12	1.470	1.592	1.495	1.550	1.494	1.520	2.9
123678-HxCDF 13C12	1.577	1.732	1.688	1.723	1.735	1.691	3.5
234678-HxCDF 13C12	1.506	1.646	1.565	1.605	1.594	1.583	2.9
123789-HxCDF 13C12	1.219	1.323	1.261	1.310	1.353	1.293	3.7
123478-HxCDD 13C12	0.834	0.910	0.859	0.900	0.905	0.882	3.4
123678-HxCDD 13C12	0.942	1.005	0.984	1.024	1.062	1.003	4.0
1234678-HpCDF 13C12	1.090	1.286	1.282	1.283	1.290	1.246	6.3
1234789-HpCDF 13C12	0.951	1.009	1.001	1.002	1.067	1.006	3.7
1234678-HpCDD 13C12	0.773	0.799	0.784	0.809	0.831	0.799	2.5
OCDD 13C12	0.395	0.398	0.411	0.408	0.460	0.414	5.7
Cleanup Std							
2378-TCDD 37Cl4	2.010	2.021	1.801	2.041	2.160	2.007	5.8

Fig. 3: Summary report of the initial calibration



VER Summary Report

Date: 06-Apr-1993

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VER3_1613c_VER_2

Vial 2 1071:40 Verification standard CS

Native Congeners

Compound Name	Calculated Amount	Amount Low li	Amount High 1	Amount Status
2378-TCDF	9.0	8.8	11.3	PASS
2378-TCDD	8.9	8.3	11.7	PASS
12378-PeCDF	48.3	39.2	60.8	PASS
23478-PeCDF	46.8	39.2	60.8	PASS
12378-PeCDD	48.4	39.7	60.3	PASS
123478-HxCDF	49.6	32.8	60.2	PASS
123678-HxCDF	49.4	41.6	58.4	PASS
234678-HxCDF	48.7	41.5	58.5	PASS
123789-HxCDF	49.4	42.6	57.4	PASS
123478-HxCDD	49.8	40.8	59.2	PASS
123678-HxCDD	49.6	41.2	58.5	PASS
123789-HxCDD	46.7	32.2	67.8	PASS
1234678-HpCDF	48.0	40.7	59.3	PASS
1234789-HpCDF	49.2	40.8	59.2	PASS
1234678-HpCDD	48.3	40.8	59.2	PASS
OCDF	99.8	71.6	139.7	PASS
OCDD	95.2	79.7	125.4	PASS

Surrogate Standards

Compound Name	Calculated Amount	Amount Low li	Amount High 1	Amount Status
2378-TCDF 13C12 STD	98.7	71.0	129.0	PASS
2378-TCDD 13C12 STD	93.8	82.0	118.0	PASS
12378-PeCDF 13C12 STD	83.0	66.7	133.3	PASS
23478-PeCDF 13C12 STD	87.3	80.0	125.0	PASS
12378-PeCDD 13C12 STD	91.7	62.4	137.6	PASS
123478-HxCDF 13C12 STD	97.8	71.4	128.6	PASS
123678-HxCDF 13C12 STD	99.7	65.3	134.7	PASS
234678-HxCDF 13C12 STD	98.4	73.4	126.6	PASS
123789-HxCDF 13C12 STD	93.2	75.4	124.6	PASS
123478-HxCDD 13C12 STD	94.5	81.8	118.3	PASS
123678-HxCDD 13C12 STD	99.9	79.3	120.7	PASS
1234678-HpCDF 13C12 STD	99.4	86.1	113.8	PASS
1234789-HpCDF 13C12 STD	95.3	60.0	140.0	PASS
1234678-HpCDD 13C12 STD	98.6	68.7	145.5	PASS
OCDD 13C12 STD	193.9	94.6	422.8	PASS

Cleanup Standard

Compound Name	Calculated Amount	Amount Low li	Amount High 1	Amount Status
2378-TCDD 37C14 STD	8.5	7.1	12.9	PASS

Internal Standard

Compound Name	Actual Time	Area	Height	S/N
1234-TCDD 13C12 STD	34:38	591814.	61521.	676
123789-HxCDD 13C12 STD	51:56	419007.	91314.	1255

Fig. 4: Verification report for a single injection

VERIFICATION STATISTICS

	Apr-03 04:37	Apr-03 21:19	Apr-05 20:31	Apr-06 14:23	Apr-06 20:58	Apr-07 14:44	Apr-07 20:32	Apr-08 12:05	Apr-08 19:54	MEAN	%RSD
Native Congeners											
2378-TCDF	9.6	9.5	9.4	9.0	9.0	9.3	9.2	9.5	9.6	9.4	2.2
2378-TCDD	9.2	9.0	9.2	8.8	8.9	9.3	9.2	9.0	9.0	9.1	1.7
12378-PeCDF	48.9	49.4	49.6	48.9	48.3	51.0	49.0	50.0	48.2	49.3	1.7
23478-PeCDF	48.8	48.3	47.7	47.8	46.8	46.9	46.9	47.2	48.0	47.6	1.4
12378-PeCDD	52.5	49.1	49.8	47.2	48.4	48.2	48.3	48.4	48.8	49.0	2.9
123478-HxCDF	50.0	48.9	49.8	48.9	49.6	50.1	49.8	49.2	50.4	49.6	1.0
123678-HxCDF	50.0	49.7	50.3	48.5	49.4	49.9	49.6	49.3	49.9	49.6	1.0
234678-HxCDF	49.1	49.2	49.3	48.8	48.7	48.3	49.1	49.5	49.9	49.1	0.9
123789-HxCDF	50.2	49.6	50.1	49.4	49.4	50.7	50.9	50.8	51.8	50.3	1.5
123478-HxCDD	50.6	50.0	50.4	49.9	49.8	50.4	49.3	50.3	49.8	50.0	0.8
123678-HxCDD	49.5	49.6	50.1	49.3	49.6	48.8	50.3	50.1	49.6	49.7	0.9
123789-HxCDD	48.4	50.3	49.0	47.2	46.7	47.1	47.9	47.7	48.0	48.0	2.2
1234678-HpCDF	48.6	47.1	47.2	47.3	48.0	47.6	48.0	47.3	47.2	47.6	1.0
1234789-HpCDF	48.6	49.5	50.3	49.4	49.2	48.4	50.8	49.1	50.3	49.5	1.5
1234678-HpCDD	49.0	49.7	49.5	48.3	48.3	48.7	49.1	49.3	50.2	49.1	1.2
OCDF	99.3	101.3	104.1	99.8	99.8	100.9	102.4	100.8	101.9	101.2	1.4
OCDD	91.6	95.9	96.8	95.0	95.2	95.7	96.7	94.0	94.7	95.0	1.6
Surrogate Std's											
2378-TCDF 13C12	101.5	98.8	100.3	100.0	98.7	98.6	99.6	99.7	102.0	99.9	1.1
2378-TCDD 13C12	93.4	92.6	94.9	94.8	93.8	89.5	91.4	93.2	93.6	93.0	1.7
12378-PeCDF 13C12	86.7	96.2	95.1	92.8	83.0	79.7	93.6	90.8	91.4	89.9	5.9
23478-PeCDF 13C12	86.3	96.4	95.4	87.4	87.3	85.1	87.2	87.0	98.0	90.0	5.3
12378-PeCDD 13C12	85.2	98.0	90.8	94.3	91.7	87.7	91.0	96.0	91.6	91.8	4.0
123478-HxCDF 13C12	99.5	97.2	101.3	98.7	97.8	95.1	94.4	99.5	100.5	98.2	2.3
123678-HxCDF 13C12	99.7	98.1	100.4	100.2	99.7	101.0	103.4	101.6	108.4	101.4	2.8
234678-HxCDF 13C12	99.0	97.7	101.6	98.4	98.4	100.9	96.8	98.7	101.8	99.3	1.7
123789-HxCDF 13C12	94.4	96.3	96.6	94.4	93.2	91.2	91.8	93.1	94.7	94.0	1.8
123478-HxCDD 13C12	96.5	96.1	97.7	94.7	94.5	93.4	91.5	92.9	95.1	94.7	1.9
123678-HxCDD 13C12	98.7	96.6	99.2	100.5	99.9	101.2	99.9	100.3	103.5	100.0	1.8
1234678-HpCDF 13C12	100.8	99.8	101.5	96.6	99.4	102.5	99.3	104.1	112.5	101.8	4.2
1234789-HpCDF 13C12	96.9	98.4	94.0	92.4	95.3	98.1	95.5	101.1	98.5	96.7	2.6
1234678-HpCDD 13C12	97.9	97.4	98.5	98.0	98.6	98.8	97.6	101.5	97.9	98.5	1.2
OCDD 13C12	186.1	198.7	190.3	185.5	193.9	202.8	193.7	200.8	197.9	194.4	3.0
Cleanup Std											
2378-TCDD 37Cl4	8.7	8.7	8.9	8.6	8.5	8.6	8.6	8.7	8.8	8.7	1.1

Fig. 5: Verification statistics for all injections

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performed in accordance to USEPA method 1613 (Fig. 3). MID-window-check, GC-performance check and the verification solution were integrated into the routine batch which was acquired at noon and night under TACO control over a period of one week. TACO created the requested documentation for individual runs (Fig. 4). The verification statistics (Fig. 5) demonstrate that all verification runs were within USEPA method 1613 limits for all congeners within this period. There was no retune of the QUANTUM instrument during this week.

References

- ¹ USEPA Office of Water, Method 1613 Revision A; Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Washington, DC 1990
- ² USEPA Office of Solid Waste and Emergency Response, Draft Method 8290 ; Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans by HRGC/HRMS, Washington, DC 1990
- ³ Canadian EPS Report 1/RM/19 February 1992; Reference Method for the Determination of Polychlorinated Dibenzo-para-dioxins and Polychlorinated Dibenzofurans in Pulp and Paper Mill Effluents
- ⁴ VDI-Richtlinien, Entwurf VDI 3499; Messen von Emissionen; Messen von Reststoffen. Messen von polychlorierten Dibenzodioxinen und -furanen im Rein- und Rohgas von Feuerungsanlagen mit der Verduennungsmethode. Bestimmung in Filterstaub, Kesselasche und in Schlacken.
- ⁵ VDI-Richtlinien, Entwurf VDI 3498; Messen von Immissionen; Messen von Innenraumluft. Messen von polychlorierten Dibenzo-p-dioxinen und Dibenzofuranen - LIB-Filterverfahren
- ⁶ Schubert R, Pesch R, Pfaff H, Schroeder E; An Integrated Concept of Automated Instrument Control, Quality Assurance and Data Reporting for Dioxin/Furan Analysis. Chemosphere, Vol. 27, Nos. 1-3, pp 25-32, 1993