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The Analysis of Dioxins and Furans Using HRGC-High Resolution MS with the AutoSpec-*Ultima* NT

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Abstract

This application note gives examples of the performance of the Waters Micromass AutoSpec *Ultima* NT and describes QuanLynx Application Manager, the most advanced quantification software for dioxin and furan analysis, illustrating why this combination is the market leader in the field.

Introduction

'Dioxins' refers to a group of chemical compounds that share certain similar chemical structures and biological characteristics. Several hundred of these toxic compounds exist and are members of three closely related families: the polychlorinated dibenzop-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and certain polychlorinated biphenyls (PCBs).

Sometimes the term dioxin is also used to refer to the best studied and one of the most toxic dioxins, 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD). PCDDs and PCDFs are not created intentionally, but are produced inadvertently by a number of human activities. Natural processes also produce PCDDs and PCDFs.

Over the past decade, regulatory environmental agencies and industries have worked together to dramatically reduce dioxin emissions. Because dioxins are extremely persistent compounds, levels of dioxins still exist in the environment from both man-made and natural sources and will take years to decline.

The detection and quantification of dioxins is a particularly demanding analysis due to the low level of regulatory exposure limits and the variety of complex sample matrices encountered. High Resolution Gas Chromatography (HRGC), coupled with High Resolution Mass Spectrometry (HRMS) offers the high sensitivity, selectivity, and quantitative dynamic range for this application and as such, is the technique of choice.

This application note gives examples of the performance of the Waters Micromass AutoSpec *Ultima* NT and describes QuanLynx Application Manager, the most advanced quantification software for dioxin and furan analysis, illustrating why this combination is the market leader in the field.

Regulatory Considerations

Across the world, there are many different legislative methods for dioxin and furan analysis, including US

EPA method 1613, European method EN1948, Canadian EPS1/RM/19 and other variants of these.

In the UK and across much of Europe, there is no specific legislative method for the analysis of dioxins and furans. In UK-based laboratories, for example, methods using the extraction and clean-up processes of US EPA method 1613 and the labeled internal standard mixtures of US EPA method 23 are employed for the analysis of all environmental samples other than those obtained by air emission sampling.

The general common factor is the use of labeled internal standards for quantification and determination of recoveries, the use of resolutions in excess of 10,000 resolving power (5% height, 10% valley definition) coupled with a 60 m GC column, either DB5, SP2331 or similar.

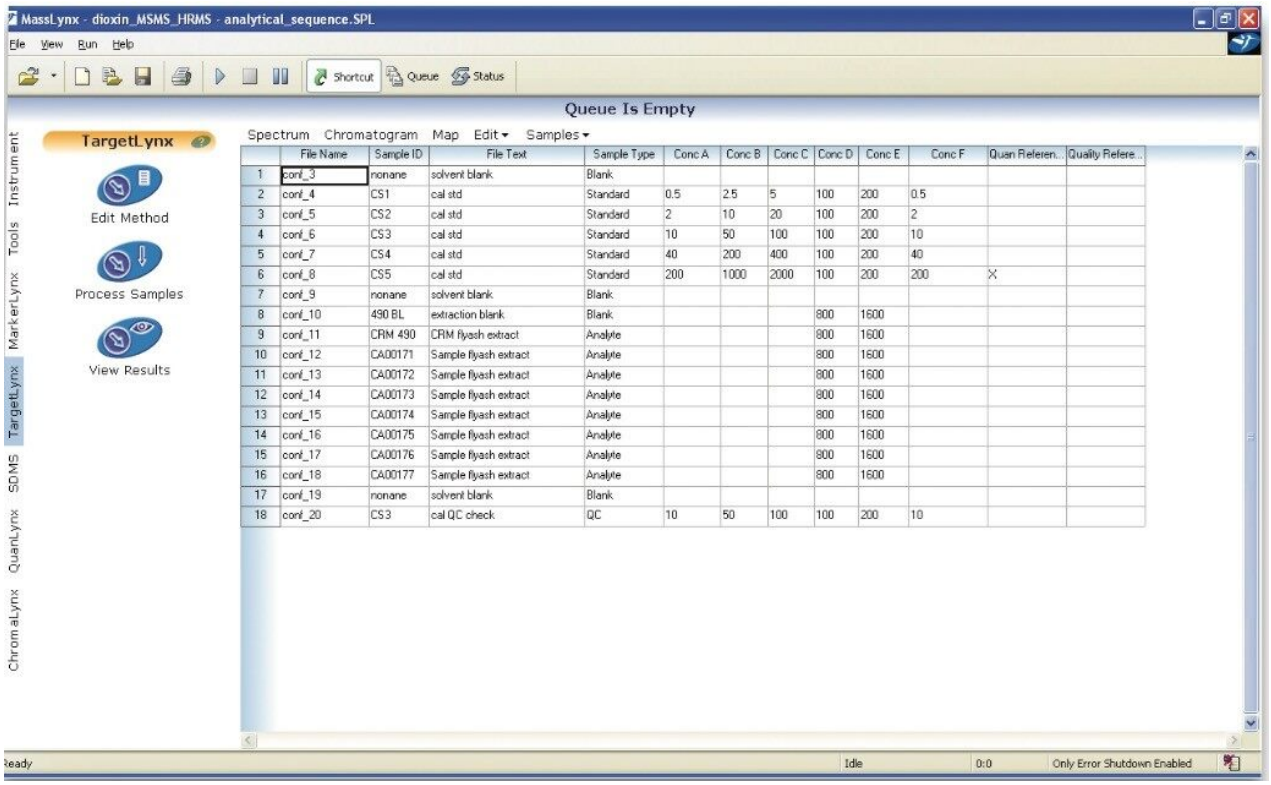
While the procedures and results described in this application note are intended to show the performance of the AutoSpec *Ultima* NT for dioxin and furan analysis, this could be as easily applied following any legislative method explicitly.

Experimental

In preparation for the analyses, the AutoSpec *Ultima* NT was tuned to in excess of 10,000 resolutions at electron energy of 30 eV, before calibration over the mass range for the experiment was acquired. The experiment used was a standard EPA1613 five-function voltage selected ion recording (VSIR) acquisition system. The calibration is performed on a daily basis and by keeping a hardcopy record of the per-fluorokerosene (PFK) peaks during calibration, a permanent record of instrument resolution is maintained which is essential for the level of auditing in a modern accredited laboratory.

First, a single function survey injection was performed to determine the acquisition time windows for the multifunction analysis.

Next, a sample list was set up to include a solvent blank injection of nonane, a CS1 to CS5, five-point calibration using standard EPA1613 standard sets. After the calibration, more nonane solvent blank injections were included, before the sample extract injections were to be performed. The sample list is shown in Figure 1.



	File Name	Sample ID	File Text	Sample Type	Conc A	Conc B	Conc C	Conc D	Conc E	Conc F	Quan Referen...	Quality Refere...
1	conl_3	nonane	solvent blank	Blank								
2	conl_4	CS1	cal std	Standard	0.5	2.5	5	100	200	0.5		
3	conl_5	CS2	cal std	Standard	2	10	20	100	200	2		
4	conl_6	CS3	cal std	Standard	10	50	100	100	200	10		
5	conl_7	CS4	cal std	Standard	40	200	400	100	200	40		
6	conl_8	CS5	cal std	Standard	200	1000	2000	100	200	200	X	
7	conl_9	nonane	solvent blank	Blank								
8	conl_10	490 BL	extraction blank	Blank				800	1600			
9	conl_11	CRM 490	CRM flyash extract	Analyte				800	1600			
10	conl_12	CA00171	Sample flyash extract	Analyte				800	1600			
11	conl_13	CA00172	Sample flyash extract	Analyte				800	1600			
12	conl_14	CA00173	Sample flyash extract	Analyte				800	1600			
13	conl_15	CA00174	Sample flyash extract	Analyte				800	1600			
14	conl_16	CA00175	Sample flyash extract	Analyte				800	1600			
15	conl_17	CA00176	Sample flyash extract	Analyte				800	1600			
16	conl_18	CA00177	Sample flyash extract	Analyte				800	1600			
17	conl_19	nonane	solvent blank	Blank								
18	conl_20	CS3	cal QC check	QC	10	50	100	100	200	10		

Figure 1. Sample list for dioxin and furan analysis.

The samples were spiked with labeled internal standards similar to those used for US EPA method 23, having one labeled standard for each level of chlorination for each group of congeners i.e. ^{13}C-2,3,7,8-TCDF and ^{13}C-TCDD for the tetra dioxins and tetra furans. ^{13}C-1,2,3,4-TCDD and ^{13}C-1,2,3,7,8,9-HxCDD were added as recovery standards.

The sample list was then started and the data acquired and processed automatically using QuanLynx 4.0.

GC Conditions

Column:	J&W DB5-ms, 60 m,0.25 mm ID, 0.25 µm
Flow rate (He):	1 mL/min constant flow
Oven program	140 °C, hold 4 min, 9 °C/min to 220 °C, 1.4 °C/min to 260 °C, 4 °C/min to 310 °C hold 6 min

Injection volume:	1 µL splitless
Injector temperature:	280 °C
Purge time:	4 mins
Purge flow:	30 mL/min

MS Conditions

Ionization mode:	Electron impact (EI+)
Acquisition mode:	Voltage SIR (quantitative analysis)
Resolution:	10,000 (5% height, 10% valley definition)
Electron energy:	30 eV

All acquisition and data processing was performed using MassLynx 4.0 and QuanLynx 4.0 Software.

Results and Discussion

Figures 2 and 3 show the calibration curves for 2,3,7,8-TCDD and OCDD illustrating excellent quantitative linearity.

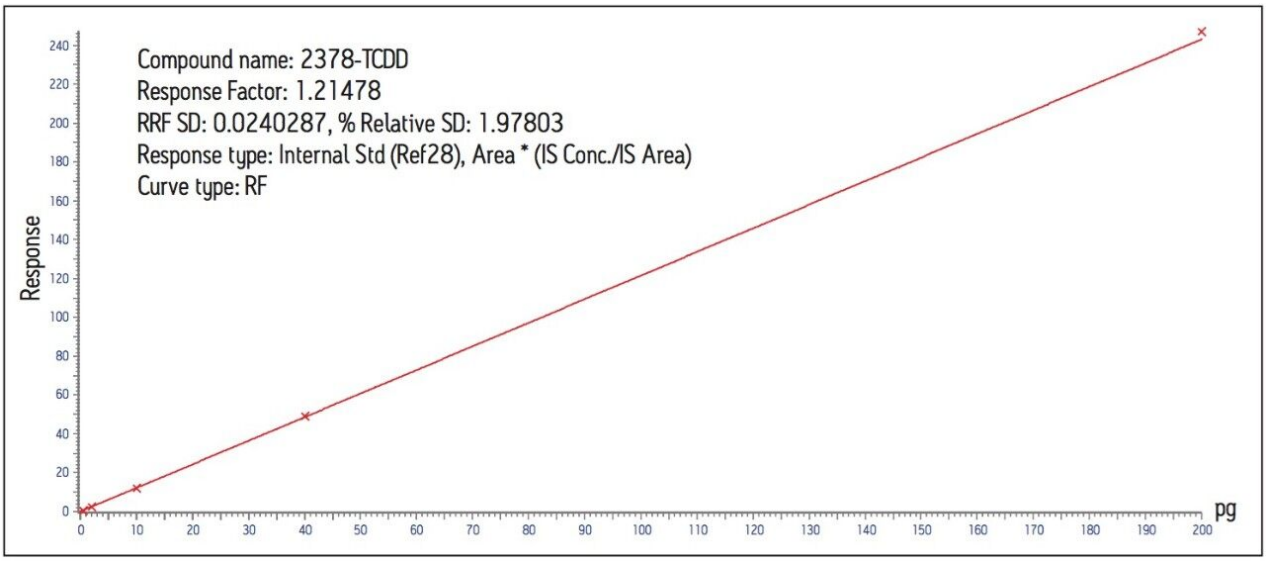


Figure 2. Calibration curve for 2, 3, 7, 8-TCDD.

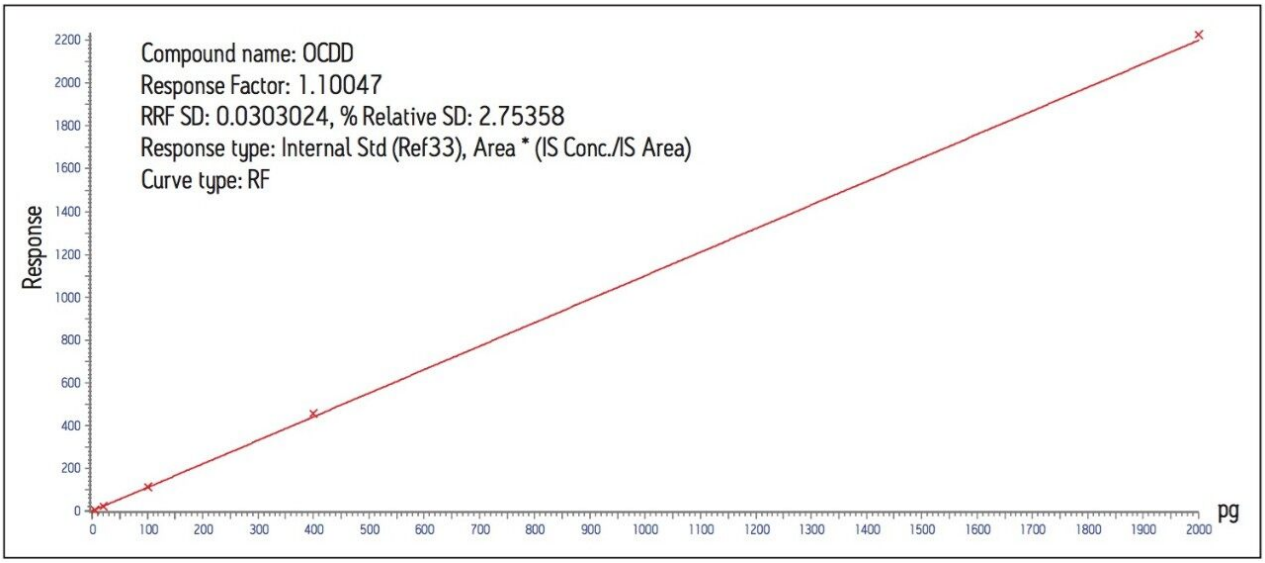


Figure 3. Calibration curve for OCDD.

Table 1 shows a summary of the calibration curves. It can be seen that the RRF % relative standard deviations are well within the regulatory limits of <15% (US EPA method 1613 and most European methods) and <10% (Japanese and some other methods).

60m DB5-ms calibration curve summary

Congener	RRF Mean	RRF %Rel SD	LOD (pg)	LOD (pg/g-WHO-TEQ)	WHO-TEF
2378-TCDF	1.017	3.457	0.011	0.00011	0.1
12378-PeCDF	0.956	2.805	0.015	0.000075	0.05
23478-PeCDF	0.934	5.707	0.015	0.00075	0.5
123478-HxCDF	1.196	2.769	0.02	0.0002	0.1
123678-HxCDF	1.218	1.782	0.019	0.00019	0.1
234678-HxCDF	1.068	4.224	0.022	0.00022	0.1
123789-HxCDF	0.929	5.873	0.026	0.00026	0.1
1234678-HpCDF	1.458	4.447	0.021	0.000021	0.01
1234789-HpCDF	1.124	3.992	0.027	0.000027	0.01
OCDF	1.186	3.92	0.035	0.00000035	0.0001
2378-TCDD	1.077	1.267	0.009	0.0009	1
12378-PeCDD	1.006	3.851	0.021	0.0021	1
123478-HxCDD	1.043	3.559	0.039	0.00039	0.1
123678-HxCDD	0.992	2.405	0.041	0.00041	0.1
123789-HxCDD	1.025	4.312	0.039	0.00039	0.1
1234678-HpCDD	0.987	0.837	0.033	0.000033	0.01
OCDD	1.05	4.643	0.03	0.0000003	0.0001
		Total WHO-TEQ		0.005	
Total TEQ detection limit based upon 10g of sample.					

Table 1. Summary of calibration curve results.

Similarly, the Total WHO-TEQ LOD falls well below the regulatory level required for dioxin analysis illustrating the unmatched sensitivity of the AutoSpec *Ultima* NT.

The results from the quantitative data processing are stored and displayed for ease of review in the QuanLynx browser.

Figures 4 and 5 show views of the QuanLynx browser for the hexa-furans in a calibration curve standard and in a real sample respectively.

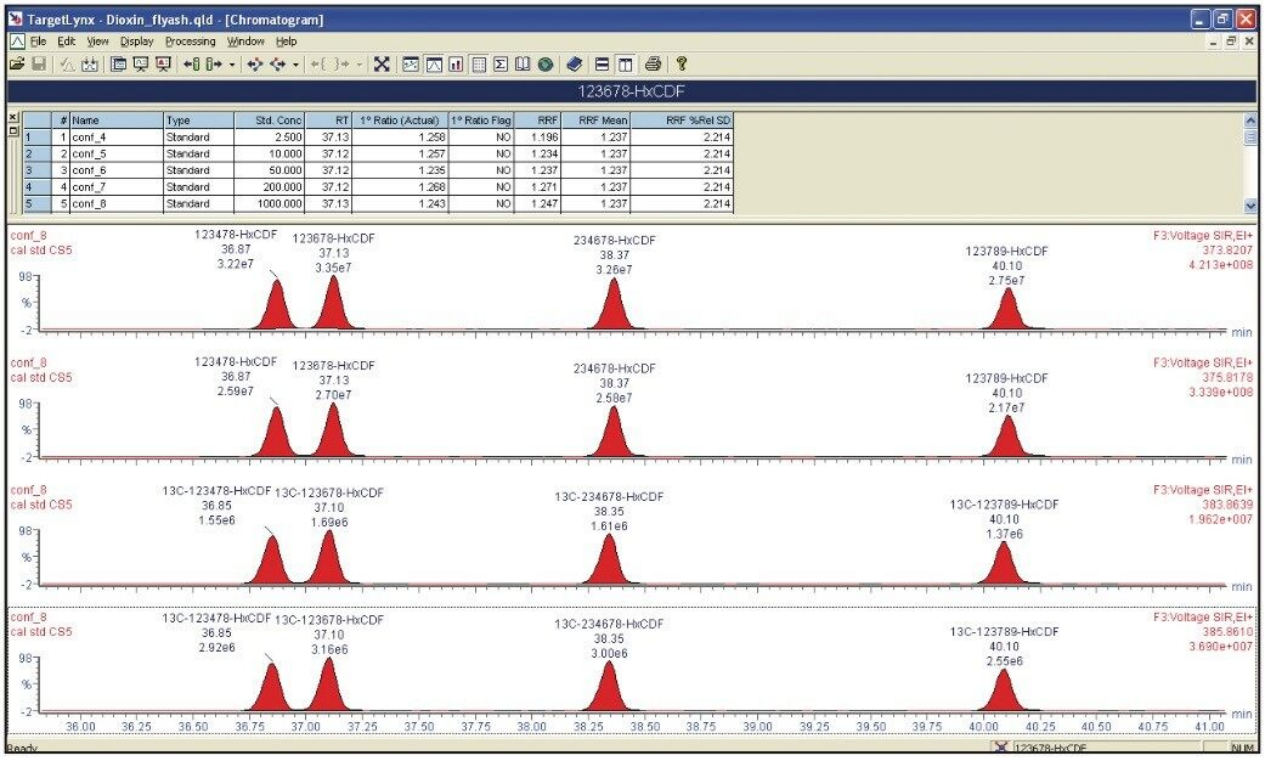
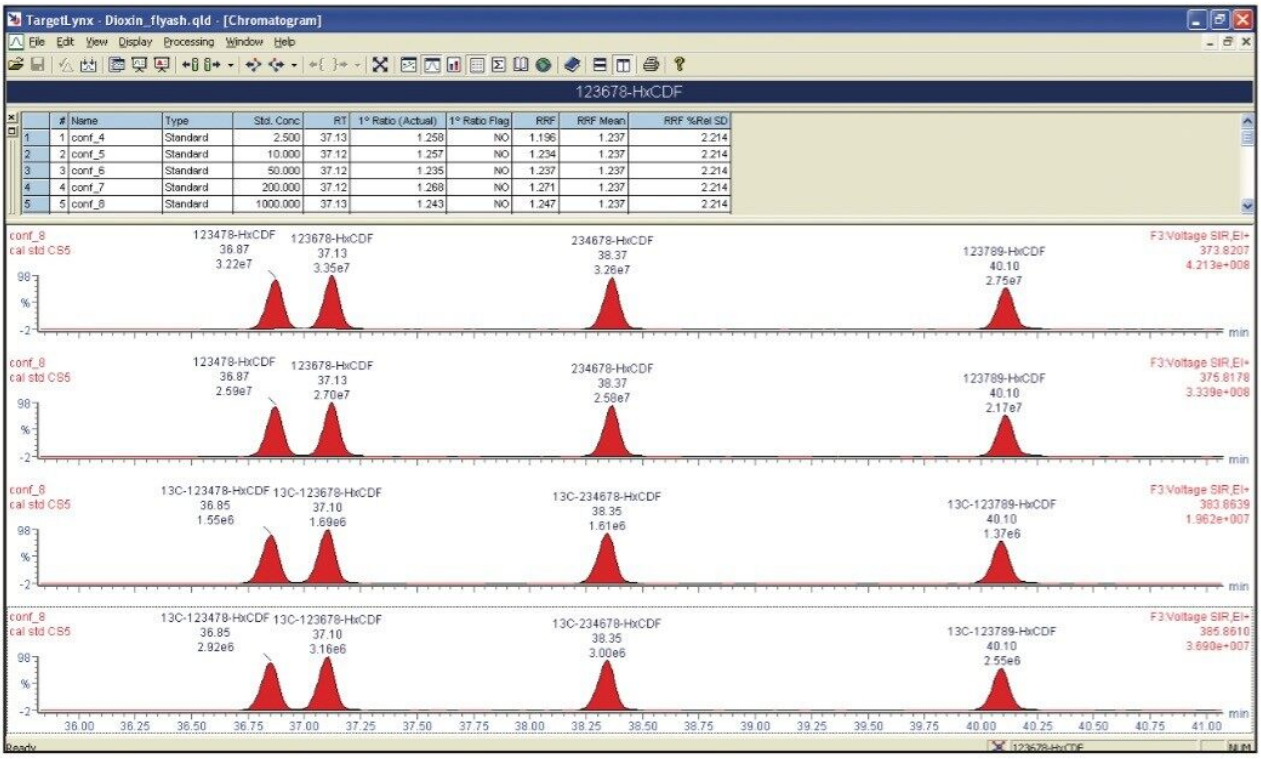


Figure 4. QuanLynx browser display of hexa-furans in calibration standard.



#	Name	Type	Std. Conc	RT	1° Ratio (Actual)	1° Ratio Flag	RRF	RRF Mean	RRF %Rel SD
1	conf_4	Standard	2.500	37.13	1.258	NO	1.196	1.237	2.214
2	conf_5	Standard	10.000	37.12	1.257	NO	1.234	1.237	2.214
3	conf_6	Standard	50.000	37.12	1.235	NO	1.237	1.237	2.214
4	conf_7	Standard	200.000	37.12	1.268	NO	1.271	1.237	2.214
5	conf_8	Standard	1000.000	37.13	1.243	NO	1.247	1.237	2.214

Figure 5. QuanLynx browser display of hexa-furans in sample.

Figures 6 and 7 show data for the tetrafurans and hexa-dioxins in the real sample.

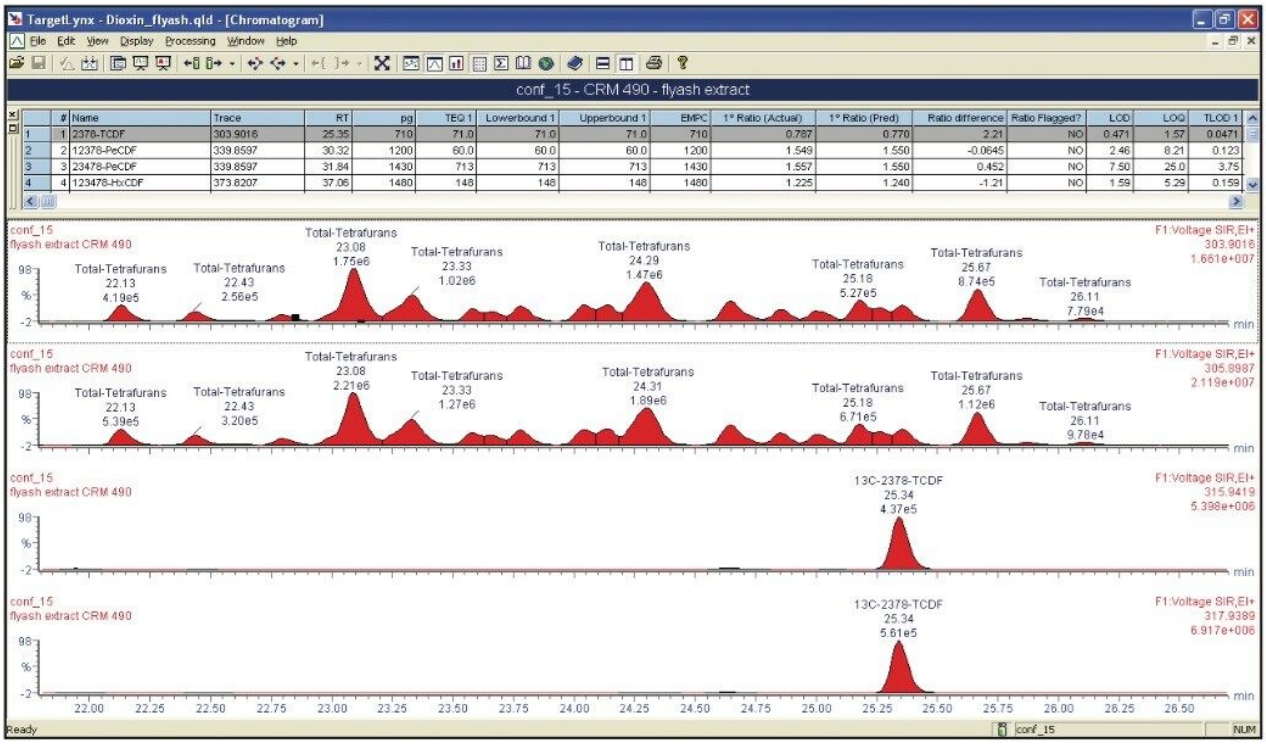


Figure 6. Tetra-furan results from sample.

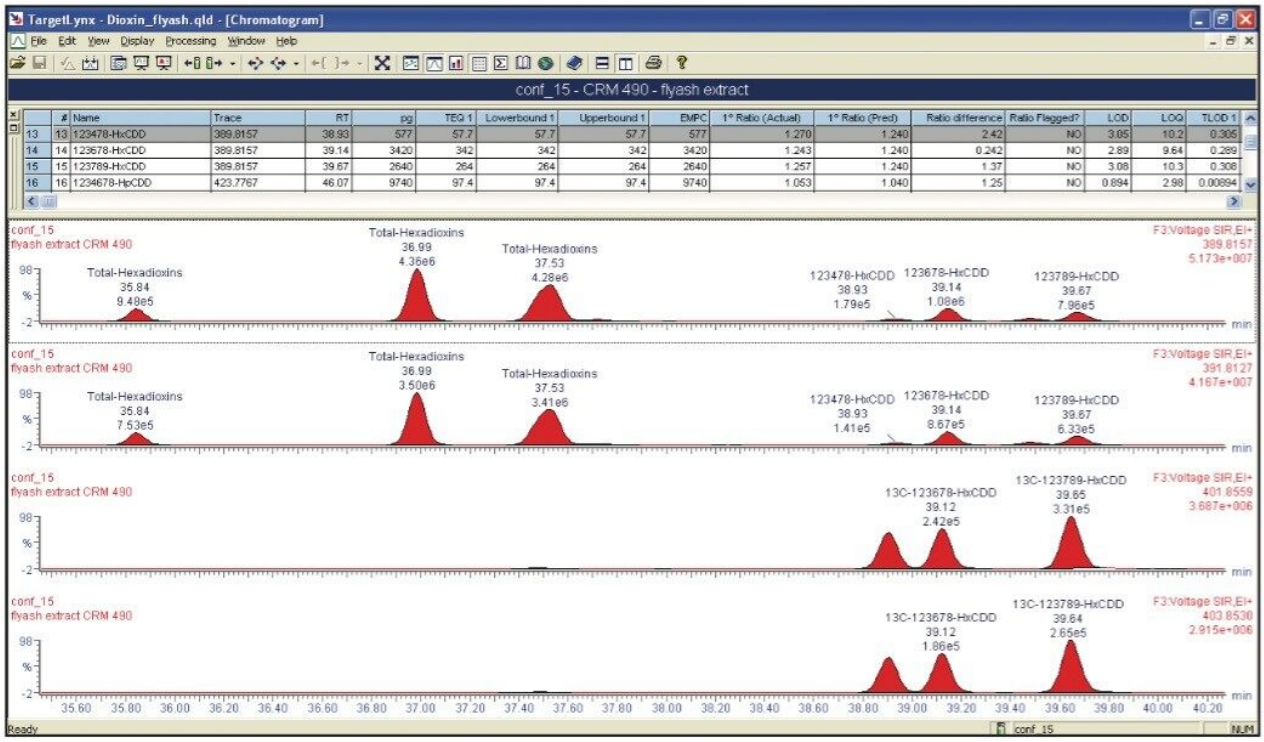


Figure 7. Hexa-dioxin results from sample.

Location and review of sample data is made easier using the numerous dioxin dedicated features included in QuanLynx. Figure 8 shows 'Congener Select', a drop-down menu provided to allow the user to quickly locate and view quantitative results for a particular congener.

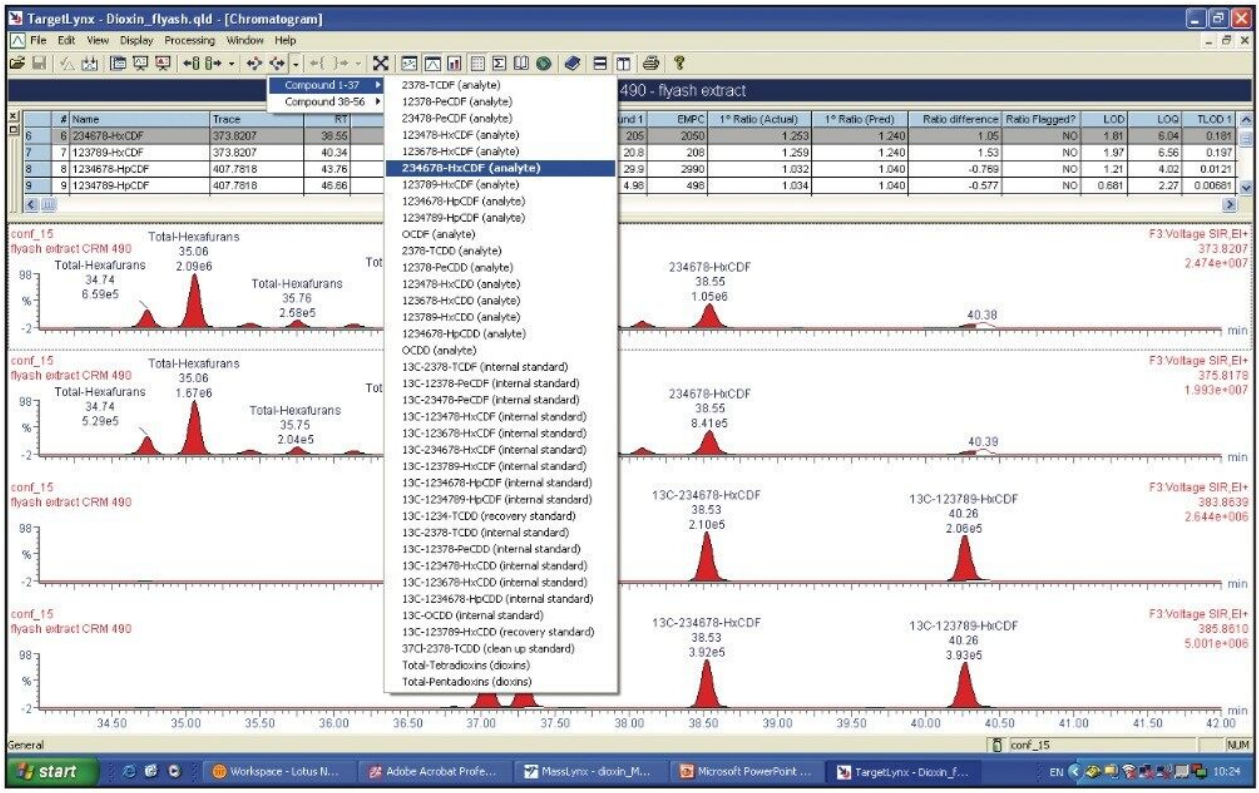


Figure 8. Congener Select functionality of QuanLynx browser.

After data acquisition and processing various options are available, including export of results in various forms for reporting purposes, storage of calibration for future use and/or acceptance and locking of the data set to prevent modification of processing results (see Figure 9).

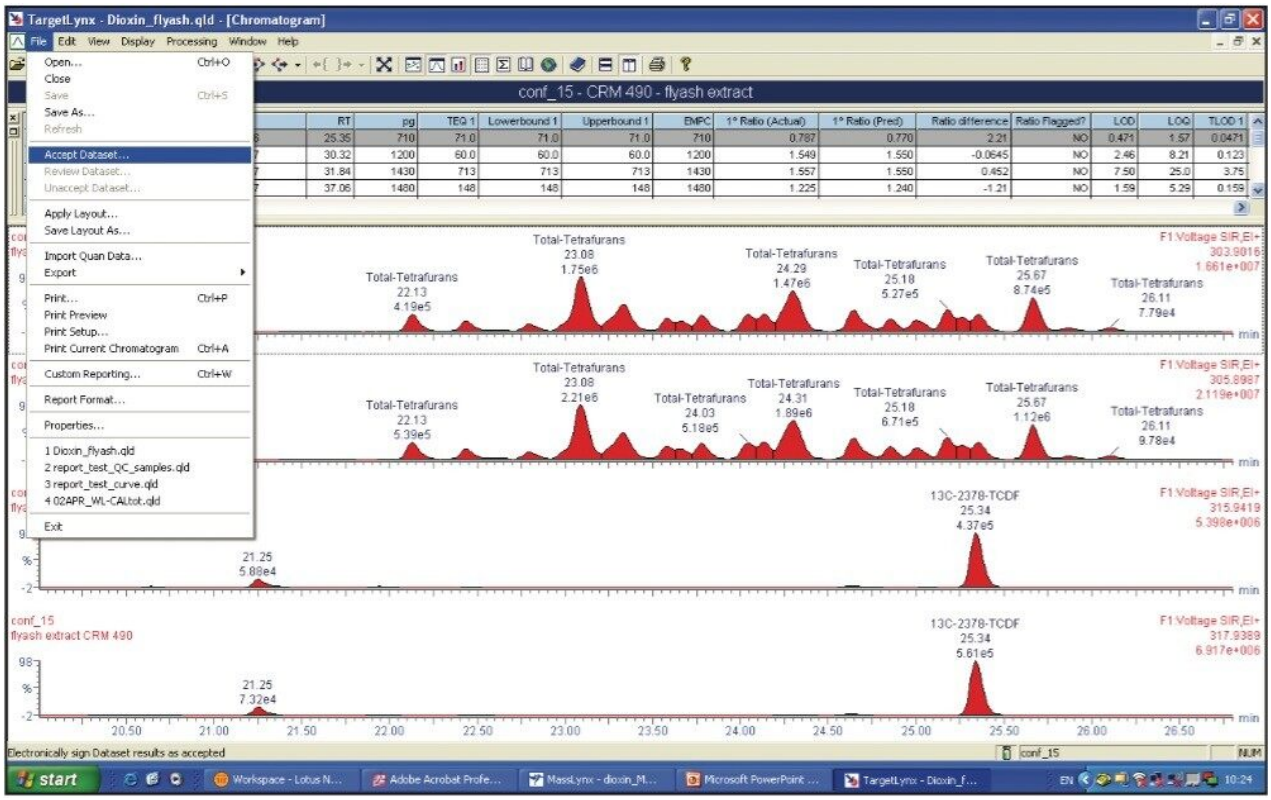


Figure 9. Acceptance and locking of quantification results.

Conclusion

High Resolution Gas Chromatography (HRGC) coupled with High Resolution Mass Spectrometry (HRMS) is the analytical technique of choice for analysis of dioxins and furans. The Micromass AutoSpec *Ultima* NT is the market-leading instrument of choice, offering the ultimate sensitivity, quantitative linearity, reproducibility necessary for regulatory dioxin and furan monitoring. In addition, MassLynx 4.0 and QuanLynx 4.0 give unprecedented automation, ease-of-use, data acquisition, and processing functionality with numerous features dedicated to dioxin and furan analysis.

Please see the Micromass website at www.micromass.co.uk for details of the latest technological developments and applications of the Micromass AutoSpec *Ultima* NT.

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