

THE APPLICATION OF HYBRID MS/MS AND HRMS
TO THE ANALYSIS OF FISH SAMPLES FOR PCDD/F's

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ABSTRACT

Low resolution MS/MS of dioxins and furans on a CONCEPT hybrid mass spectrometer has been used to analyze fish extracts which were heavily contaminated with PCB's. The samples were also analyzed by EPA method 8290 on a 2 sector CONCEPT mass spectrometer and the quantitative data from the two analyses were very similar.

INTRODUCTION

The mass spectrometric method of choice for the determination of polychlorinated dioxins and furans in environmental and biological samples uses high resolution selected ion monitoring, as described in detail by EPA Method 8290. Key features of this method include:

- (1) Extensive sample cleanup prior to mass spectral analysis.
- (2) High resolution (10000) mass spectroscopy to separate the dioxins and furans from any remaining interfering compounds.
- (3) After an initial multi-point isomer specific internal standard calibration, the calibration is checked daily by a single injection of a medium level (10pg TCDD) standard.
- (4) Using isotope ratio measurements to positively identify a dioxin/furan.

A number of workers have reported the use of MS/MS on hybrid or triple quadrupole mass spectrometers for dioxin analysis. Monitoring loss of -COC1 by MS/MS gives greater specificity than

10000 resolution HRSIM. This specificity is highly desirable for fish samples heavily contaminated with PCB's. Since a coeluted PCB ion at m/z 357.8444 interferes with m/z 357.8516 for PeCDD and a resolution of 50000 is required to resolve them. In this study we have used MS/MS on a hybrid CONCEPT ISQ to analyze heavily contaminated fish samples which had previously been analyzed by method 8290 on a two sector CONCEPT IS. As the same sample and standard solutions were used for both analyses, we have been able to critically assess the utility of MS/MS for this type of analysis.

EXPERIMENTAL

High resolution data were obtained on a CONCEPT IS under standard EPA 8290 conditions. MS/MS data were obtained on a CONCEPT ISQ hybrid mass spectrometer. It is of EBQQ geometry, that is a double-focusing, forward geometry sector instrument (MS1-identical to a CONCEPT IS), followed by a quadruple collision cell and a second quadruple for fragment ion analysis.

MS1 as operated at 1000 resolution and MS2 at a peak width of 1.5amu. Parent ions were selected by changing the accelerating voltage on MS1's ion source and the appropriate daughter ion was selected by adjusting the voltages on the analytical quadruple. The transitions to be monitored were split into five groups of eight and the cycle time for eight transitions was one second. The Argon collision gas pressure was set to give approximately 50% attenuation of the parent ion signal.

RESULTS

(1) Calibration

17 native dioxin and furan isomers are used in the initial calibration, but we will discuss in detail results obtained for five of these. Shown below are the calibration data obtained by SIM and MS/MS of the EPA standards.

SIM [MS/MS] Relative Response Factors

Compound	Conc. TCDD pg/ul				
	200	50	10	5	2.5
2,3,7,8TCDD	.8895 [.5719]	.8706 [.5634]	.8335 [.6848]	.8152 [.9288]	.8269 [1.3655]
1,2,3,7,8PeCDF	1.2463 [1.033]	1.1086 [1.0626]	1.2799 [1.313]	1.0481 [1.8943]	1.2645 [2.1766]
1,2,3,4,7,8HxCDD	.9970 [.4069]	.9983 [.5253]	.9868 [.7403]	.8467 [1.4584]	1.0378 [2.1984]
1,2,3,4,6,7,8HpCDF	1.5336 [1.2261]	1.5312 [1.0585]	1.5750 [1.4175]	1.3557 [1.9442]	1.6019 [2.4514]
OCDD	1.0672 [.4795]	.8201 [.4650]	.9503 [.4679]	.8097 [.5927]	1.3676 [.7083]

The SIM data gives response factors which are independent of analyte concentration, whereas the MS/MS response factors are linearly dependent on concentration and therefore average response factors could not be used with the MS/MS data. Three days after the initial MS/MS calibration data were obtained we injected the 10pg/ul standard and obtained response factors which were within 20% of those in the table above.

(2) Isotope ratio's

If a MS/MS method is to be used, then measured isotope ratio's must be close to their predicted values. For TCDF the m/z 304 (M) to m/z 241 (M-COC1) and m/z 306 (M+2) to m/z 243 (M+2-COC1) transitions were monitored. Theory predicts that the 243/241 ratio should be 1 : 1.03 and the 5 standard solutions gave ratio's of 1 to .997, 1, 1.11, 1.14 and .977, which is within the tolerance limits of +/- 15% suggested by EPA.

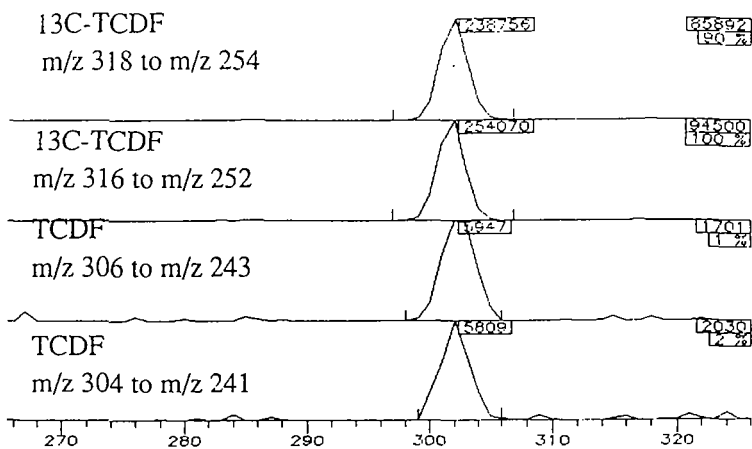
(3) Sample analysis

Four fish extracts which had been analyzed by SIM were also analyzed by MS/MS, the two sets of data are compared for one sample below.

Compound	Conc pg/g	SIM	MS/MS
2,3,7,8 TCDD		6.12	6.24
2,3,7,8 TCDF		17.21	4.94
1,2,3,7,8 PeCDD		ND	1.77
1,2,3,7,8 PeCDF		6.66	21.29
2,3,4,7,8 PeCDF		14.94	13.77
1,2,3,4,7,8 HxCDD		1.31	0.2
1,2,3,6,7,8 HxCDD		5.17	2.3
1,2,3,7,8,9 HxCDD		3.93	1.54
1,2,3,7,8,9 HxCDF		13.89	12.05
2,3,4,6,7,8 HxCDF		5.10	3.16
1,2,3,4,6,7,8 HpCDD		10.5	21.16
1,2,3,4,6,7,8 HpCDF		12.88	14.16
1,2,3,4,7,8,9 HpCDF		10.50	9.39
OCDD		16.8	13.96
OCDF		8.29	8.35

ND means not determined because of unresolved interferences from PCB's.

Quite good agreement between the two techniques is shown by these data and the greater selectivity of the MS/MS technique is advantageous for this sample. In an earlier study (1) the ultimate detection limits for SIM was found to be 10fg and for MS/MS 350fg. This means that a S/N ratio of approximately 20 to 1 for a 2ul injection of the lowest standard is easily obtained as shown below.



CONCLUSIONS

MS/MS on a hybrid mass spectrometer has been shown to give similar data to that obtained by high resolution mass spectrometry, but with better selectivity.

REFERENCES

- (1) Moore, C., Moncur, J., Wright, B., unpublished data.