

A ROBUST SCREENING METHOD FOR DIOXINS AND FURANS BY ION TRAP GC-MS/MS IN A VARIETY OF MATRICES

John D. Ragsdale, Meredith Conoley

Thermo Finnigan, 2215 Grand Avenue Parkway, Austin, Texas 78728

Introduction

The purpose is to develop a screening method utilizing GC-MS/MS and minimal sample preparation to screen for the 17 2,3,7,8-chlorine substituted dioxins and furans at part-per-trillion (ppt) levels in a variety of matrices. If one can reduce the amount of time spent on sample preparation and still have ppt detection limits then the method can be an effective screening tool which saves the analyst and the laboratory time and money.

Methods and Materials

USEPA Method 1613¹ was followed for the compounds, concentrations and most of the sample preparation. For the sample preparation only the sulfuric acid wash was performed. The gas chromatographic condition were altered slightly to accommodate split injections(split ratio 15:1). A shorter and narrower column (SGE BPX-5, 0.15 mm ID, 0.25 micron film, 25M) was used to resolve both the 2,3,7,8 TCDD/TCDF isomer in a single injection. A PolarisQ(Thermo Finnigan, Austin) external source ion trap mass spectrometer with the buffer gas option (2 ml/min)² connected to a TRACE GC(Thermo Finnigan, Milan) and a AS2000 (Thermo Finnigan, Milan) liquid autosampler. All standards were purchased from Cambridge Isotope Laboratories.

Table 1. GC Conditions (40 min total)

150 °C	1 min	
20 °C/min	200 °C	1.5 min
3 °C/min	300 °C	1.67 min

Table 2. MS/MS Parameters for Furans

Compound	Precursor	Width (amu)	Product Ions Range	Isolation Time (ms)	Collision Energy (V)	Collision Time (ms)
TCDF	306	5	237-247	16	4.00	30
PeCDF	340	5	272-282	16	4.00	30
HxCDF	374	5	306-318	16	4.25	30
HpCDF	410	5	340-350	16	4.50	30
OCDF	444	5	375-385	16	5.00	30

ANALYSIS II

Table 3. MS/MS Parameters for Dioxins

Compound	Precursor	Width (amu)	Product Ions Range	Isolation Time (ms)	Collision Energy (V)	Collision Time (ms)
TCDD	322	5	253-263	16	3.50	30
PeCDD	356	5	288-298	16	3.50	30
HxCDD	390	5	322-332	16	3.50	30
HpCDD	426	5	357-367	16	4.00	30
OCDD	460	5	391-401	16	4.00	30

Results and Discussion

The results of this methodology can be seen in the included figures. There are four important concepts to be addressed in this screening methodology, sample cleanup, chromatographic resolution,

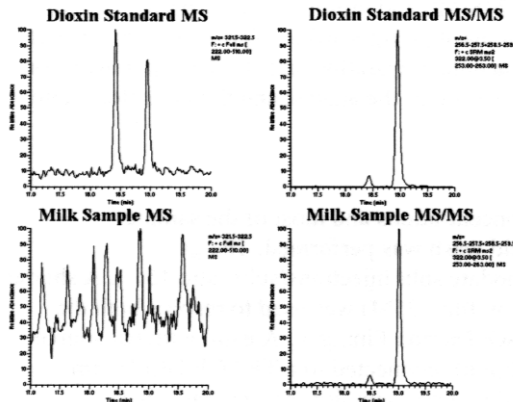


Figure 1. This shows the improvement in the detectivity of the TCDD from full scan to MS/MS

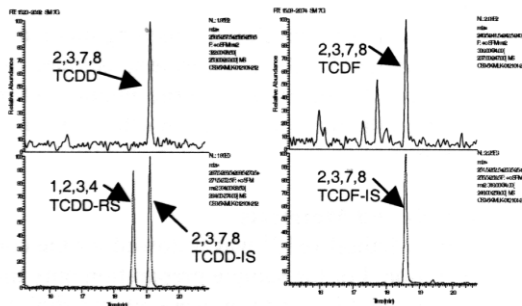


Figure 2. This shows the detectivity of the TCDD and TCDF in the milk extract at 8 ppt

detectivity, and quantitation. From figure 1 we can see that with out the sample cleanup the compounds cannot be determined with full scan, but with MS/MS the compounds are easily detected. In figure 2 we can easily detect the components in the milk matrix at 8 ppt. Figure 3 demonstrates the ability to separate the tetra chlorinated dioxins and furans from the normally interfering isomers. Tables 4 and five demonstrate the precision of the method which not only allows the screening to be performed at ppt levels but also allows the screened sample to be quantified.

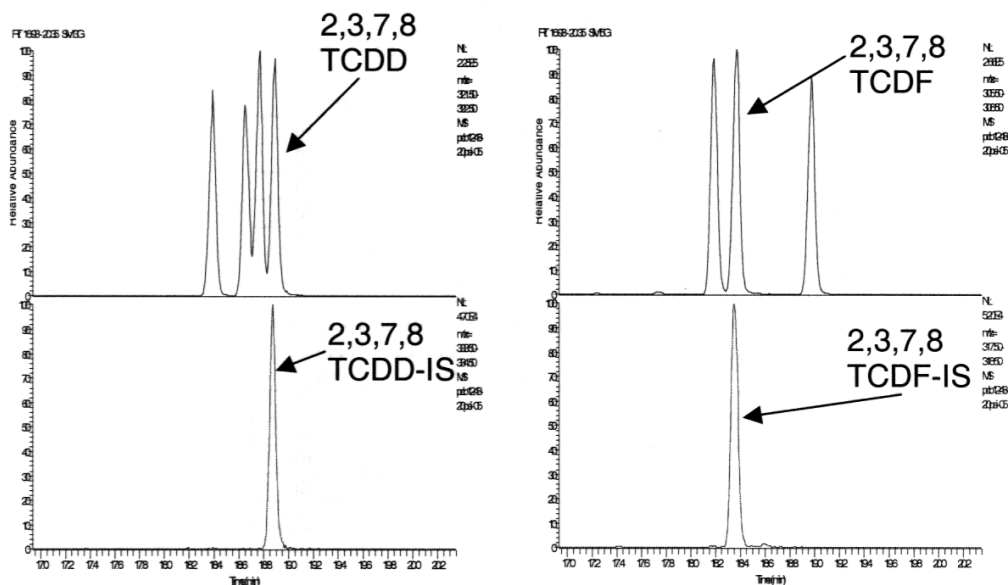


Figure 3. A demonstration of the chromatographic resolution that allows this methodology to screen for the dioxins and furans in a single injection

Table 4. Calibration Summary for Dioxins

COMPOUND	% RSD
2,3,7,8-TCDD	10.8
1,2,3,7,8-PeCDD	6.4
1,2,3,4,7,8-HxCDD	6.9
1,2,3,6,7,8-HxCDD	9.1
1,2,3,7,8,9-HxCDD	8.7
1,2,3,4,6,7,8-HpCDD	4.9
OCDD	5.2

ANALYSIS II

Table 5. Calibration Summary for Furans

COMPOUND	%RSD
2,3,7,8-TCDF	17.4
1,2,3,7,8-PeCDF	5.5
2,3,4,7,8-PeCDF	6.2
1,2,3,4,7,8-HxCDF	3.5
1,2,3,6,7,8-HxCDF	4.0
2,3,4,6,7,8-HxCDF	5.6
1,2,3,7,8,9-HxCDF	6.4
1,2,3,4,6,7,8-HpCDF	4.5
1,2,3,4,7,8,9-HpCDF	5.8
OCDF	5.4

References

1. Method 1613, Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, US EPA, November 1994
2. Grabic R., Novak J., Packakova V.; "Optimization of a GC-MS/MS Method for the Analysis of PCDDs and PCDFs in Human and Fish Tissue." *J. High Resol. Chromatogr.* 23, 595-599 (No. 10, 2000)