

THE ANALYSIS OF SMOKESTACK SAMPLES FOR DIOXINS BY GC-MS AND GC-MS-MS

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A hybrid mass spectrometer has been used to show the potential of high resolution MS and hybrid MS-MS for dioxin analysis. The two methods have been compared in the determination of PCDDs and PCDFs, both offering a high degree of specificity to the analysis. Data obtained indicates that the two techniques are complementary and choice of methods will depend on the type of matrix interference.

Introduction

The determination of chlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in complex matrices often requires extensive sample clean-up prior to instrumental analysis. Samples may contain chemical interferences at concentrations several orders of magnitude greater than those of the PCDD and PCDF, placing heavy demands on the instrumentation.

Difficulties in the analysis of environmental samples make selectivity and sensitivity important considerations for the method of choice. Capillary column high resolution gas chromatography- high resolution mass spectrometry has been the "standard method" to date for the analysis of samples such as sediments, effluents and biological tissues. Tandem mass spectrometry (MS-MS) has been able to meet the requirements of selectivity but has not yet reached the ultimate detection levels of SIM. However, our MS-MS data do show some very useful features when it comes to the analysis of real samples.

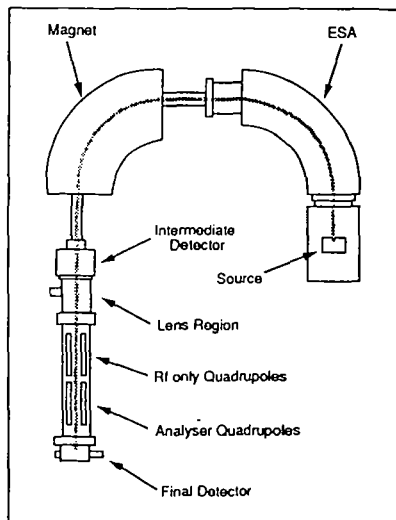


Figure 1: Schematic diagram of a CONCEPT 1 SQ hybrid GC-MS-MS instrument

Instrumentation

Figure 1 shows a diagram of the CONCEPT I SQ. It is of EBQQ geometry, that is a double-focusing, forward geometry sector instrument (MS1), followed by a quadrupole collision cell and a second quadrupole for fragment mass analysis (MS2).

A resolution of 10,000 (10% valley definition) is needed for dioxin analysis using selected ion monitoring (SIM). Figure 2 shows that the product of resolution and sensitivity remains relatively constant beyond 10,000 resolution. This indicates that the transmission of MS1 at 10,000 resolution is about 10% of that at 1,000 resolution. To circumvent the problem of sensitivity loss, encountered by monitoring at substantially reduced accelerating voltage, the ions to be monitored are split into groups of similar mass (tetra, penta, hexa, hepta and octa-chloro) and a different magnetic field strength is used for each group. By this means, mass discrimination amongst the groups is minimized. Figure 3 shows the analysis of equal concentrations of penta, hexa, hepta, and octa chloro compounds by this method.

MS-MS

For low resolution MS-MS to attain equal sensitivity to HRSIM, no less than 10% of the precursor ions originating in the source must reach the final collector (MS2) as fragment ions. Such sensitivities are not generally achieved in MS-MS, however, because of further losses in transmission through MS2 and because of ion losses in the collision process itself.

When these loss factors are taken into account, the detected ion currents at MS2 are typically between 1% and 0.5% of the source ions, leading to detection limits between 10 and 20 times poorer than the HRSIM mode of operation. Figure 4 and 5 show these limits at 2 ions/sec for HRSIM and 4 ions/sec for MS-MS.

Despite this reduced sensitivity, MS-MS may, however, provide superior results where heavily-polluted samples are to be analysed. In particular, PCBs (especially the hexa and hepta-chlorinated congeners) are known to interfere with the measurement of TCDDs and its ion fragments formed in the ion source. Additional interferences

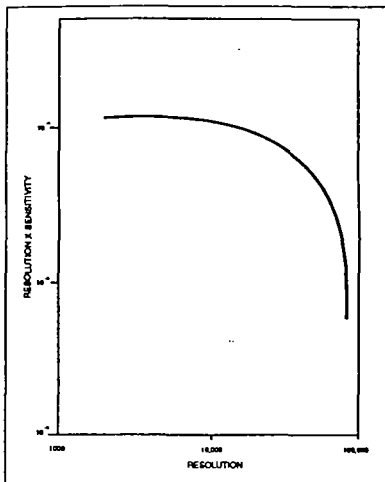


Figure 2: Curve of the product of resolution and sensitivity versus resolution for a CONCEPT instrument

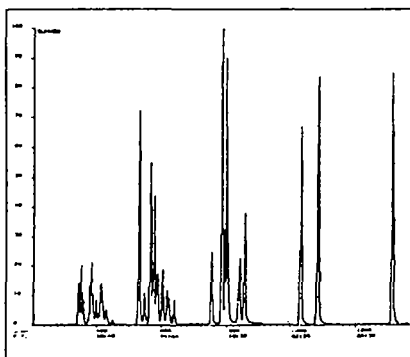


Figure 3: Analysis of penta, hexa, hepta and octa-chloro PCDDs by group selection in SIM

are often experienced from methyl and ethyl tetrachlorinated dibenzofurans, even when using SIM at 10,000 resolution. MS-MS constitutes the method of choice in these cases. In a case where the analyst has no knowledge of possible interfering peaks, it may be impossible to decide which approach is more appropriate so that both methods may be necessary.

Results

In the analysis of smokestack samples undertaken during the course of this work, the MS-MS conditions used are shown in table 1. Several standard solutions and blanks were run during the course of this investigation. The data obtained showed good linearity of response over the concentration range 500 pg to 350 fg and suggested an ultimate detection limit of 200 fg with 2:1 S/N ratio. All unknown samples were prepared in iso-octane, and 1 μ l injections of these solutions were injected into the GC.

For heavily-contaminated samples such as the smokestack sample of Figure 6, MS-MS shows clear, strong ions from components simultaneously eluting from the GC column. Many isomers are present, as is typical of real samples. The series shows all 5 groups from tetra to octa. Figure 7 shows the isomers of TCDD and TCDF

TABLE 1 MS-MS CONDITIONS

MS1 resolution	1,000
MS2 resolution	unit mass
Collision gas	argon
Pressure	set for 50% attenuation
Collision energy	160eV
Number of ions monitored	5 groups of 8 ions all COCl losses from native or ^{13}C spike
Precursor ion rate	8 ions/sec

included in Figure 6. Eight ions per second were monitored, four from the ^{13}C spike parent ions and four from the native parent ions; only the four native ions are shown.

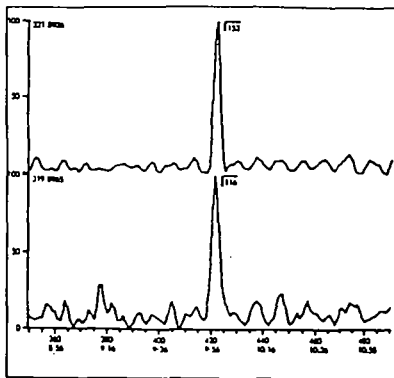


Figure 4: Analysis of 10 fg of TCDD by HRMS (10,000 RP)

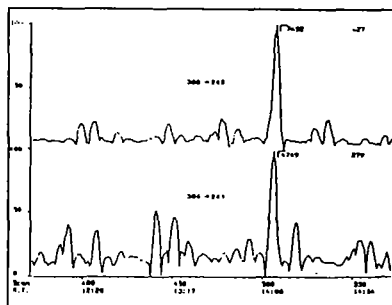


Figure 5: Analysis of 350 fg of TCDF by hybrid GC-MS-MS using COCl loss

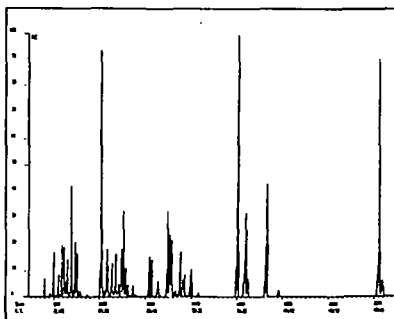


Figure 6: Hybrid GC-MS-MS analysis of heavily-contaminated smoke stack sample for PCDDs and PCDFs.

Figure 8 shows an MS-MS ion chromatogram of a composite smoke stack sample, this time showing a predominance of the hepta-chloro isomers.

Figure 9 shows an MS-MS mass chromatogram of a 1000 m³ air sample with TCDD and TCDF isomers at pg levels. Subsequent isomer quantitation of these samples has been performed using our standard software package, with both internal or external calibration. Results of this fall outside the scope of this paper and are to be reported elsewhere.

Conclusion

Overall sensitivity in PCDD and PCDF analysis is primarily a function of the selectivity of the analytical process. The wide variety of potentially interfering matrices encountered in everyday samples precludes the use of any one analytical method. This study illustrates an alternative approach, providing reasonable sensitivity in situations where traditional SIM is inadequate.

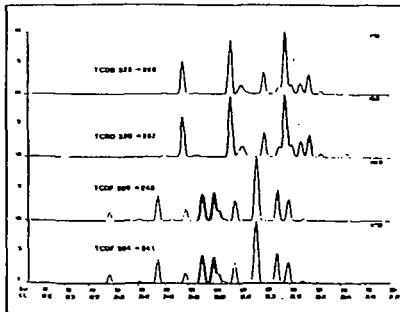


Figure 7: GC-MS-MS trace for TCDD and TCDF components in the same analysis shown in Figure 6

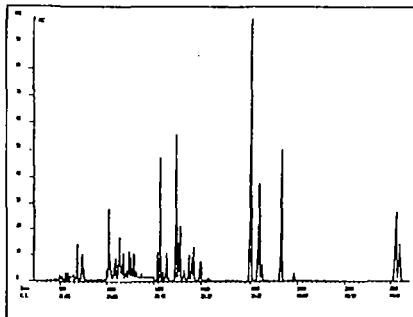


Figure 8: GC-MS-MS trace for the analysis of a composite smoke stack sample

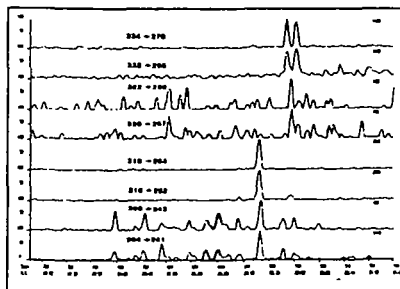


Figure 9: GC-MS-MS trace for the analysis of a 1000 m³ air sample