

## **Applications of Tandem Mass Spectrometry to Environmental Analysis: Ultratrace Determination of PCDD/PCDF, PCB, PAH, DDT and Related Compounds.**

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### **Introduction**

Tandem mass spectrometry combined with high resolution gas chromatography (GC-MS/MS) is a very powerful and versatile technique for environmental analysis. Because of its great selectivity, GC-MS/MS is able to reach ultratrace sensitivities for target analytes even in complex matrices such as those typical of environmental samples. Instrumental detection limits are always below 1 pg, and values in the range of a few tens of femtograms can be obtained in most cases. The requirements for successful GC-MS/MS analysis are the following: (i) the analyte should have an abundant molecular ion, (ii) it should be possible to dissociate the molecular ion with high efficiency and selectivity, that is the molecular ion should be completely converted into a single fragment ion, (iii) the fragmentation process should be specific for that analyte.

### **Materials and Methods**

GC-MS/MS analyses were run on two different mass spectrometers: a Finnigan TSQ-700 triple quadrupole instrument and a Finnigan GCQ ion-trap mass spectrometer. On the TSQ-700 dissociation of precursor ions was obtained by multiple collisions with argon at kinetic energies ranging from 5 to 60 eV. The ion-trap was operated in the resonant excitation mode at  $q=0.450$ , and dissociation of precursor ions was performed by collision with the helium buffer gas at excitation voltages of 1-2 V. Splitless injection and a Supelco MDN-5S low-bleeding capillary column (30m, 0.25mm ID, 0.25µm film thickness) were used on both instruments. All <sup>13</sup>C-labelled compounds were purchased from Cambridge Isotope Laboratories.

### **Results and Discussion**

The most common environmental application of GC-MS/MS is the analysis of PCDD/PCDF by selected ion monitoring of the COCl loss from the molecular ion (1). This is a very efficient and selective dissociation process and is highly specific for these analytes giving rise to very low detection limits. We have applied the GC-MS/MS method for PCDD/PCDF on a triple quadrupole instrument reaching a detection limit of 40 fg for 2378-TCDD. Our five-years long experience with thousands of samples has also demonstrated that the performances of MS/MS are totally similar to those of the high resolution (HRMS) method. In contrast with the literature (2, 3), we found that GC-MS/MS could easily meet the reproducibility, linearity and sensitivity requirements of the EPA 1613 and 8290 methods. The ion-trap instrument was also tested for MS/MS detection of PCDD/PCDF (4, 5), and the performances we obtained were comparable with those of the triple quadrupole, even though sensitivity was slightly reduced.

We have also investigated the use of GC-MS/MS for the analysis of PCB. In this case the dissociation process monitored was the loss of one or two Cl atoms from the molecular ions (6, 7). This fragmentation is quite efficient and selective, but the specificity is not very high since many

chloro-aromatic compounds may fragment by Cl loss. Nevertheless, we obtained an increased sensitivity and selectivity with MS/MS on the triple quadrupole mass spectrometer, especially for the most toxic co-planar PCB. Interferences observed during the analysis of real samples with the usual MS-SIM method could be completely eliminated by using GC-MS/MS, so that we were able to detect trace levels of PCB. Similar results could also be obtained on the ion-trap instrument that proved to be a suitable alternative to the triple quadrupole.

In the case of DDT and related compounds (DDD and DDE) MS/MS can not be applied since the molecular ion abundance is too low, therefore a different ionization technique must be employed. We found that chemical ionization (CI) by 'charge-exchange' with CS<sub>2</sub> formed an abundant molecular ion which could be readily dissociated by loss of CCl<sub>3</sub> with a yield approaching 100%. This fragmentation is also highly specific for the analyte, and a detection limit of 20 fg for DDT has been obtained with the GC-CI/MS/MS method we have developed. The method is also highly selective for DDT and related compounds with respect to PCB and phthalates which are known to be interfering compounds when the GC-ECD analysis is used.

The application of MS/MS to the analysis of PAH is more difficult because of the stability of the molecular ion of these substances. Careful optimization of experimental conditions is necessary in order to maximize the efficiency and selectivity of the dissociation processes that form fragment ions by loss of C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub> from PAH molecular ions. The GC-MS/MS detection limits are slightly below 1 pg, but a significant improvement of the selectivity with respect to the MS-SIM method has been observed during PAH determination in soil samples.

Our work has demonstrated that very low detection limits and high selectivity can always be obtained for different classes of environmentally relevant compounds by using GC-MS/MS, and this features make this technique suitable for ultratrace analysis of target analyte in difficult samples. Good linearity and reproducibility are readily achieved on the triple quadrupole instrument, so that robust methods can be easily developed and validated. In addition, the long-term stability of triple quadrupole instruments ensures that method performances are constant over a long period of time. The growing spread of low-cost MS/MS instrumentation based on the ion-trap design will surely increase the interest and the number of applications of GC-MS/MS to environmental analysis, especially for industrial laboratories where the use of certified methods is not necessary.

## References

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