

ANALYSIS OF POLYCHLORINATED DIBENZO-*p*-DIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) BY ON-LINE LC-GC-MS

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1. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two series of tricyclic almost planar aromatic compounds that exhibit similar physical, chemical and biological properties and have been the subject of much concern in recent years.

The chemical structures and numbering of these hazardous compounds are given in Figure 1.

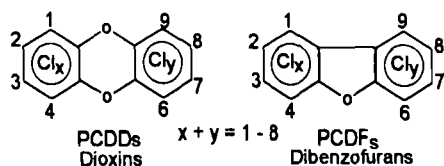


Figure 1. Formulas for PCDDs and PCDFs

PCDDs or PCDFs having different numbers of chlorines are called congeners, while those with the same number of chlorines are called isomers. There are 75 PCDD congeners, while there are 22 PCDD isomers having 4 chlorine atoms.

These compounds are of interest because of the high toxicity. The most toxic PCDD/PCDF compound is 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (2, 3, 7, 8-TCDD), which demonstrated an LD₅₀ of 0.6 µg per kg body weight for the Guinea pig. Extrapolation of this toxicity to humans would make 2, 3, 7, 8-TCDD one of the most toxic substances known. Other PCDDs/PCDFs have also demonstrated low LD₅₀ values in laboratory animal studies.

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Because of this, the confirmation and accurate quantitation of dioxins is a serious task which rests upon the analytical chemist.

Identification and quantification of PCDD/PCDFs in complex environmental matrices are very difficult because low levels of these compounds are present with a significant number of other organic components at much higher concentrations.

Generally, an extensive sample preparation is required for the analysis of PCDD/PCDFs using multistep clean-up procedures. Open column reversed phase high performance liquid chromatography have been used to provide class separation. The collected fractions are further on analyzed using capillary gaschromatography with mass spectrometric detection.

An off-line approach is undesirable due to poor sensitivity and loss and/or contamination of the sample during the intermediate fraction collection stage. However, by coupling HPLC and GC in one integrated instrument, fractions from the LC separation can be directly introduced into the GC column thereby improving sensitivity, reproducibility and detection limits. On-line LC-GC has been shown to be an excellent technique for the analysis of PCDD/PCDFs in samples coming from thermochemical treatment of Refuse Derived Fuel (RDF)¹⁾, and can be combined easily and directly with a Low Resolution Mass Spectrometer (LRMS).

This paper demonstrates that a Low Resolution Quadrupole Mass Spectrometer (LRMS) can be used instead of a High Resolution Mass Spectrometer (HRMS), when combined with LC-GC, because of his selectivity and separation power. The coupled techniques, LC and GC, allow the isolation of the fractions containing the PCDDs and PCDFs from the sample matrix, eliminating the interfering compounds and lowering, in this way, the detection limit and increasing the confidence in the identification by MS.

Besides, the on-line combination of these three techniques permits integration of the sample preparation step with the final analytical step and allows full automation of the whole procedure.

2. EXPERIMENTAL

2.1. INSTRUMENTATION

The analyses were performed using an ON-LINE HPLC/HRGC DUALCHROM 3000 and a Low Resolution Mass Spectrometer TRIO 1000, all of them from FISIONS INSTRUMENTS.

2.2. SAMPLE PREPARATION

A sample coming from combustion of Refuse Derived Fuel was extracted in a Soxhlet apparatus with toluene/methanol 4:1 for 24 hours. Before of ON-LINE LC-GC-MS analysis, the extract was concentrated to about 5 ml on a rotary evaporator and then to 1 ml with a nitrogen evaporation device.

2.3. LC ANALYSIS

A system of two columns 15 cm x 4 mm I.D. NUCLEOSIL 5 C₁₈ PAH (MACHEREY-NAGEL), connected in series, was used for the HPLC separation with pentane as eluent.

These columns contain an electron acceptor (EA) stationary phase.

2.4. TRANSFER AND GC/MS ANALYSIS

The transfer of fractions to the GC was made using the loop-type interface ¹⁾. A 5 m x 0.53 mm I.D. uncoated precolumn was connected to a 30 m x 0.32 DB-5 column using a glass press-fit connector. An early solvent vapour exit was positioned between the analytical column and a retaining precolumn, consisting of a 2 m piece of analytical column.

The loop-type interface was used as transfer technique for this method because the components of interest, PCDDs and PCDFs, are of low volatility and the fractions were of relative wide dimension (700 μ l). In this case, the loop-type interface permits easy transfer with almost complete elimination of the solvent through the solvent vapour exit, leaving only a small amount of solvent reaching the detector. To further reduce the amount of solvent to the detector, a 0.18 mm I.D. deactivated fused silica was placed at the end of a column inside the MS interface, so that the resistance of the column was increased and the amount of solvent entering into the MS, during the transfer, was reduced.

3. RESULTS AND DISCUSSION

In a previous work ¹⁾ the analyses of the Refuse Derived Fuel (RDF) were done as in this work with LC-GC, but using ECD as detector; Figure 2 shows a chromatogram of the dioxin fraction obtained in this way. The same fraction was analyzed using MS as detector and this is shown in Figure 3.

Figure 3 shows also a plot of ion abundances of characteristic m/z values for the pentachlorinated dibenzofurans (P_5 CDF) and pentachlorinated dibenzo-*p*-dioxins (P_5 CDD).

Peak A is observed to have the correct theoretical ratios 61:100:65 for the m/z 338:340:342 ions characteristic of PeCDF as shown by its mass spectrum (Figure 4).

No PeCDD are observed in this fraction.

The described application illustrates the power of on-line LC-GC-MS to perform analysis of trace levels of PCDD/PCDFs in complex mixtures, such as environmental samples, using a low resolution mass spectrometer.

These results indicate that this one-step HPLC separation for analysis of PCDD/PCDFs is very effective.

Besides, the applicability of quadrupole systems to complex sample analysis instead of magnetic systems has the advantage of the own lower cost and ease to use.

4. REFERENCES

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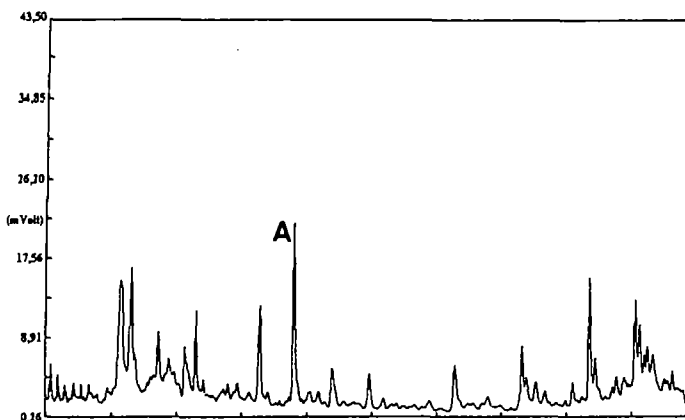


Figure 2. GC-ECD analysis of dioxin fraction transferred from HPLC

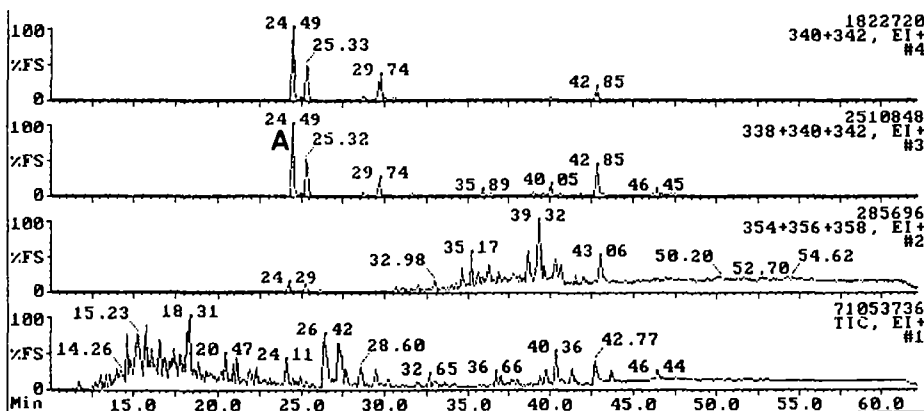


Figure 3. Total ion current (TIC) trace with plot of characteristic ions of PeCDF and PeCDD

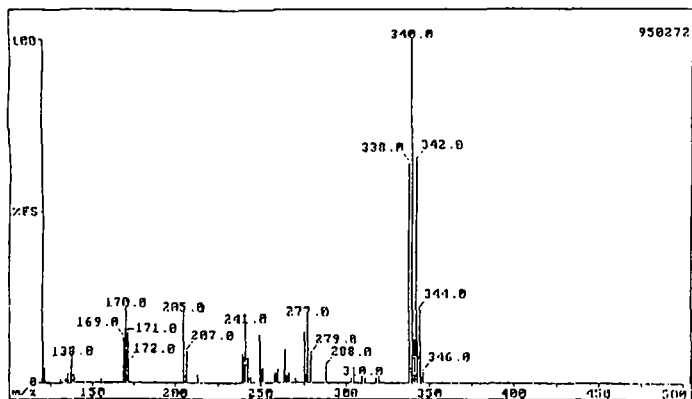


Figure 4. Mass spectrum of a P5CDF in a sample from combustion of Refuse Derived Fuel