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DETERMINATION OF POLYCHLORODIBENZO-*p*-DIOXINS AND POLYCHLORODIBENZOFURANS IN ENVIRONMENTAL SAMPLES BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY*

A. LIBERTI*, P. CICCIOLI, E. BRANCALEONI and A. CECINATO
Istituto sull'Inquinamento Atmosferioc del C.N.R. C.P. 10, 00016 Monterotondo Stazione (Rome) (Italy)
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SUMMARY

An analytical procedure has been developed for the simultaneous determination at ppt (10^{12}) level of tri-, tetra-, hexa-, hepta- and octachlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) in solid environmental samples and water condensate from urban incinerators.

The benzene extract was gas chromatographed on both fused silica capillary and packed columns, coupled with a high-resolution mass spectrometer equipped with a time-programmable power supply for selected ion detection. Specific detection of various PCDDs and PCDFs with the same chlorine atom content is accomplished by recording in the same time their three most characteristic ions. By sequentially switching the *m/e* values stored on seven programs of selected ion detection, it is possible to record in the same chromatographic run PCDDs and PCDFs having a content of chlorine atoms ranging from four to eight. The use of a relatively high mass spectral resolving power ($M/\Delta M = 5000$) permits an accurate determination of these compounds without use of sophisticated clean-up procedures.

INTRODUCTION

The recognized diffusion of polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) in the environment from several sources, mainly from urban waste incineration[1–3], requires a reliable analytical procedure for their determination. It is a difficult task because a total of 75 PCDD and 135 PCDF compounds are possible, ranging from mono- to octachlorinated species, most of wich are found in environmental samples. A wide range of biological[4] activity is attributed to these compounds, which mainly depends on the number and ring positions of the chlorine atoms. A great deal of analytical work has been devoted to quantitation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which is considered to be the most toxic species, and a variety of techniques have been developed[5–7]. The determination of all 22 tetrachlorodibenzo-*p*-dioxins isomers has been also carried out[8], and an analytical

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procedure has been studied for tetra-, hexa-, hepta- and octachlorodibenzo-*p*-dioxin isomers determination in particulate samples at the parts per trillion (10^{12}) levels[9].

The authors believe that the evaluation of environmental samples in terms of chlorinated species should cover the determination of both PCDDs and PCDFs; the latter are comparable in toxicity with the former, with a similar biological effect, and are always present in incineration residues. On account of the large number of isomers, the authors point out that the determination of these compounds in terms of the concentration of species containing the same number of chlorine atoms might be a convenient way of reporting analytical results. This paper describes an analytical procedure for the simultaneous determination of these classes of compounds in samples obtained from various emissions of urban waste incinerators.

EXPERIMENTAL

The determination of PCDDs and PCDFs in environmental samples requires three steps: sampling, sample extraction and its clean-up, and determination through gas chromatography–mass spectrometry (GC–MS).

There are no problems in the sampling of solid and liquid materials, but when the determination has to be carried on fumes emitted from incinerators, great attention must be paid to the isokinetic sampling of particulates and to an efficient trapping of the gaseous phase. This operation can be carried out by cold condensation of the water vapour and by trapping the effluent gases in ethylene glycol, at low temperature.

Extraction of the sample is a very important process, and a number of investigations have been carried out in order to evaluate its efficiency for particulate matter. Toluene extraction of acid-treated material in a Soxhlet apparatus for 35 h is reported[10] to give the highest recovery, though other authors indicate that by using xylene as a solvent a higher yield of chlorinated compounds is obtained[11]. Both results have been questioned as it has been shown that a pyrolytic reaction synthesis, similar to the one taking place in the incinerators among the precursors of these compounds[12], might occur during the extraction process[12]. To prevent this reaction a non-thermal procedure, such as ultrasonic treatment, solvent percolation or solvent leaching through the sample, has to be used.

As the mechanisms of the various processes have not yet been clarified, the extraction of solid samples was carried out in a Soxhlet apparatus for 72 h with benzene as eluent. The extract of 25 g of sample was concentrated to 1 ml under a high purity nitrogen flow, transferred to a silica column (2 g Merck kieselgel 60, 70–230 mesh) and eluted with 25 ml of *n*-pentane. The eluent was evaporated to dryness, and a suitable amount of benzene or tetramethylbenzene was added. In most cases, this procedure was found to be sufficient for an accurate GC–MS analysis.

In the case of solutions where the concentration of PCDDs and PCDFs was so low that possible interfering compounds (such as polychlorobiphenyls (PCBs)) could render the quantitative determination very difficult, the sample eluted from the silica column was further purified on an aluminium oxide column (Woelm basic activity grade 1) by using 10 ml of a methylene chloride–*n*-hexane (2:98, v/v) solution. A 50:50 (v/v) solution of the same solvents was then employed to bring the PCDDs and PCDFs into solution.

Vapour samples collected in ethylene glycol were analysed after multiple extraction of this solution with methylene chloride[12].

The solution containing PCDDs and PCDFs was chromatographed on both capillary and packed columns.

A fused silica capillary column (25 m × 0.2 mm I.D.) coated with OV-1 was employed. This column gave 105,000 theoretical plates *vs.* pentadecane. The samples were analysed according to the following experimental conditions: 2 μl of sample dissolved in tetramethylbenzene were injected into the column via the so-called splitless injector. After 2 min at 25°C the splitter was opened and the temperature was rapidly raised to 190°C. After 5 min the temperature was programmed at 2°C/min to 240°C, and then 4°C/min to 270°C.

The packed column used (2 m × 1.5 mm I.D.) was filled with Supelcoport (Supelco, Bellefonte, PA, U.S.A.) 100–120 mesh coated with 1.5% SP 2250 plus 1.95% SP 2401. The analyses were carried out by raising the initial isothermal temperature (200°C for 4 min) at 2°C/min to 245°C.

A Dani gas chromatograph Model 3900 (Dani S.p.A., Monza, Italy), equipped with a double injector enabling the use of both capillary and packed columns, was combined with a VG 70-70 F (VG Analytical, Altrincham, Great Britain) double focusing mass spectrometer able to supply a maximum resolution of 25,000 at 10% valley.

The packed column was connected to the MS via a single-stage jet separator, whereas the capillary column was directly connected to the ion source. As the external diameter of the fused silica capillary column was less than 0.5 mm, the column end was placed in contact with the ion source inlet. This was achieved by passing the column through the glass coated metal capillary connecting the gas chromatograph to the mass spectrometer. The column was tightly fixed to the metal line by means of a 1/16 in. metal connection commonly employed in liquid chromatography. The columns were sealed with Graphlock connectors (Supelco) of the proper size. The flow-rates of the packed and capillary column were, respectively, 30 and 1 ml/min of UHP helium (Matheson, East Rutherford, NJ, U.S.A.) in order to optimize the sample transmission to the mass spectrometer without affecting the chromatographic efficiency.

For selected ion detection (SID), the instrument was operated at a resolution ranging from 3 to 5000, depending on the impurities present in the sample. In the optimal conditions the MS was able to discriminate (10% valley) ions differing by 0.05 a.m.u.

The electron energy was 70 eV, and the accelerating voltage of the electron multiplier was 2 kV. The SID unit consisted of eight channels, each of which enables the simultaneous recording of eight ions. For the specific detection of PCDDs and PCDFs the molecular ion and the other two most intense isotopic peaks, $(M + 2)^+$ and $(M + 4)^+$, were selected. Seven programs were stored into the SID unit using perfluorokerosene ions as reference masses.

Although the SID unit can be programmed for both the magnetic and acceleration voltage channel cycle, the latter was perferred in order to match the high sample input rate determined by the capillary column, and a residence time in each channel was 0.1 sec.

By a proper sequential switching of the *m/e* values stored on these programs, it

was possible to record PCDDs and PCDFs with a chlorine atom content ranging from 2 to 8 in the same chromatographic run.

Under the experimental conditions used, the program relative to dichlorinated species was found to be of little practical use. Because of the low concentration of di-CDDs and di-CDFs and the presence of interfering compounds with the same retention time, this program was never successfully applied to the quantitation of these compounds present in real samples.

In the other programs only the trace corresponding to the ions having mass $(M + 4)^+$ for tri-CDDs and tetra-CDDs was affected by the interferences originated by other ions. Although in some cases these interferences could be eliminated by increasing the resolution, the quantitative determination of various compounds can be carried out as well in terms of the ions with mass M^- and $(M + 2)^+$, not affected by the same interferences. This was confirmed by the constancy of the isotopic ratios measured on the M^+ and $(M + 2)^+$ traces.

RESULTS AND DISCUSSION

The determination of PCDDs and PCDFs in environmental samples with the aim of obtaining sufficient data for the quantitation of species with the same number of chlorine atoms might be achieved by using either GC–low-resolution MS (LRMS) or GC–high-resolution MS (HRMS). The identification and quantification of the chlorinated species are strongly affected by the clean-up procedure as well as by the gas chromatographic conditions employed.

According to Nestrick *et al.*[8], an accurate determination of PCDDs by GC–LRMS can be carried out only when the sample has been purified on two different high-performance liquid chromatographic columns. This method is undoubtedly quite effective for the unambiguous determination of each of the various PCDDs isomers. The method is unable, however, to provide the simultaneous determination of PCDFs, which were not considered by these authors. On the other hand, the use of GC–LRMS requires an extensive clean-up of the sample and highly efficient capillary columns to eliminate interfering compounds (such as PCBs and pesticides). In practice we found that appreciable losses can be observed in the analysis of PCDFs when the sample is further chromatographed on the basic alumina column. Thus GC–HRMS seems to yield more reliable results.

GC coupled with HRMS (ranging from 3000 to 5000 depending on the impurities in the sample to be analyzed) offers the most rapid and accurate method for the simultaneous determination of these two classes of pollutants. Both capillary and packed columns can be used but it is important to evaluate the possibilities they afford. The simplest way is to use packed columns, as good resolution can be obtained if a suitable temperature program is employed.

The precision obtained with these columns is better than 7%, and external standards can be used for quantitative purposes with small errors. However, the analysis with packed columns requires a large amount of sample because the peak width is much wider than that obtained with capillary columns.

The maximum sensitivity is of the order of 50–100 pg, measured for octa-CDD and octa-CDF, which is not sufficient for the determination of these compounds in diluted samples.

The use of capillary columns can lead to the determination of a few picograms of these compounds. However, the precision of the GC–MS measurements becomes much smaller than that observed with packed columns, and a value of *ca.* 20% should be accepted as satisfactory because of the splitting effect connected with the use of the so-called split-less injector. The quantitative determination of PCDDs and PCDFs requires the use of internal standards and the knowledge of the factor response for each class of dioxins and furans. As no internal standards for each class of PCDDs and PCDFs were available, the sample was divided into two equal portions. One was directly analyzed and the other was spiked with known amounts of octa-, hexa-, and tetra-CDDs and octa-CDF and then analyzed. The peak area of the original solution was measured by using the proper response factors, and the concentration was calculated with respect to the internal standards added.

For compounds for which no spiking can be performed, the final concentra-

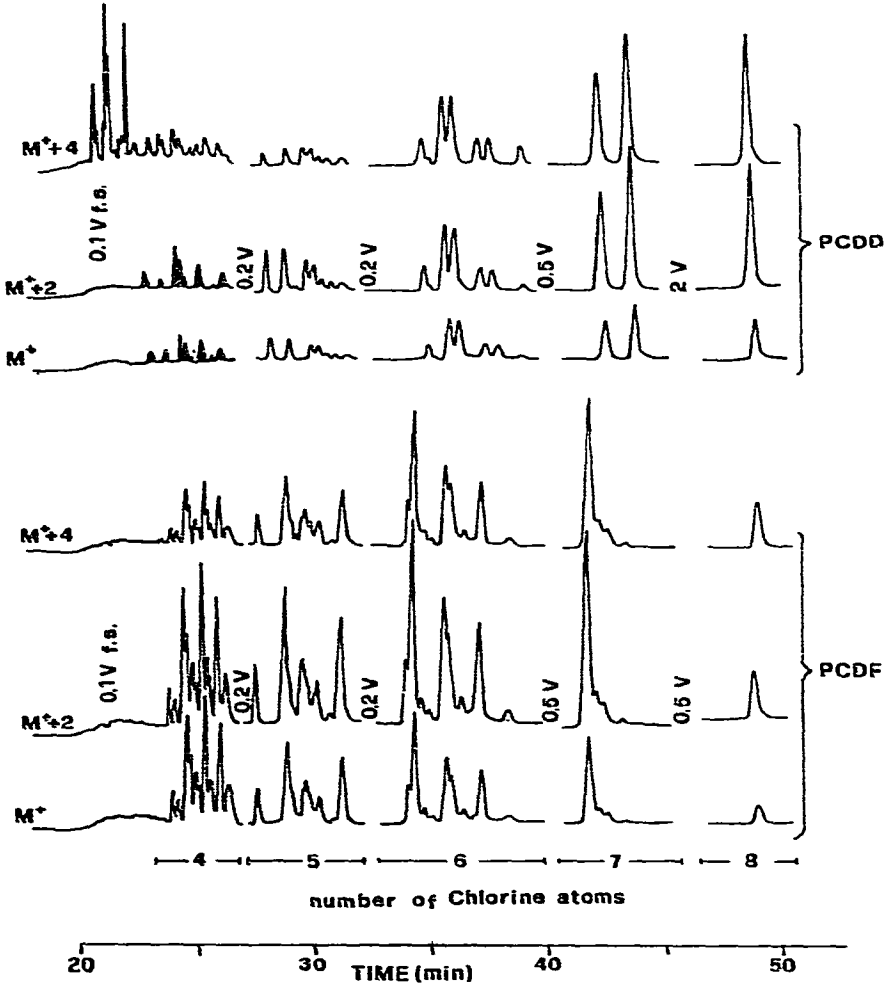

Fig. 1. Selected ion detection of PCDDs and PCDFs in a fly ash sample from an incinerator in an industrial area, obtained by capillary column GC–HRMS ($M/\Delta M$ = 5000).

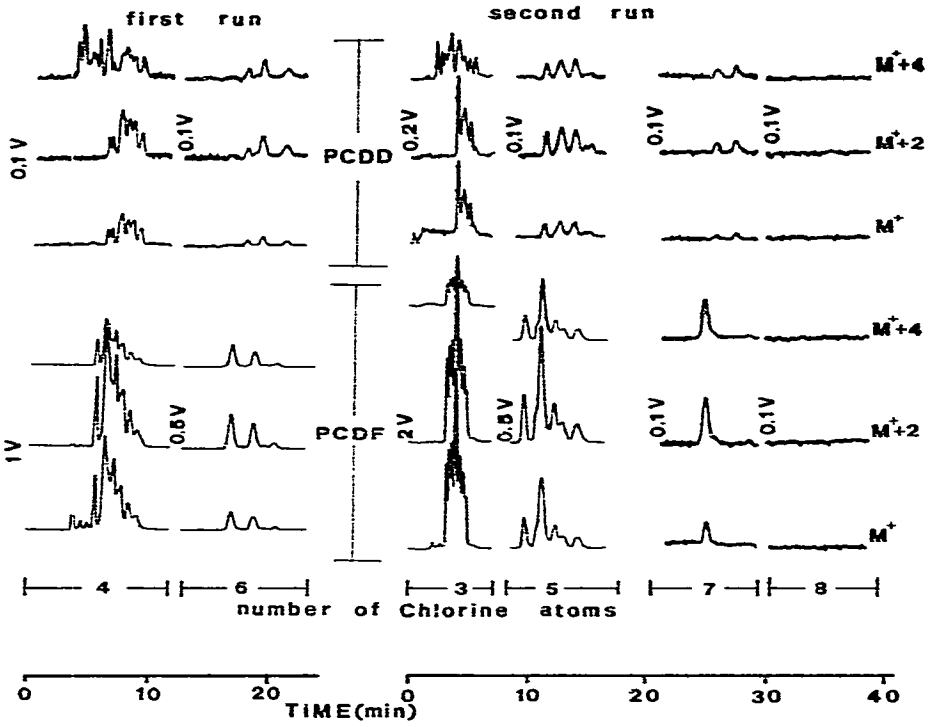

Fig. 2. Selected ion detection of PCDDs and PCDFs in vapours emitted from an urban incinerator, obtained by packed column GC–HRMS ($M/\Delta M$ = 3000).

tions were calculated by averaging the values measured with respect to the two internal standards with the closest mass values.

Fig. 1 shows the SID of PCDDs and PCDFs of a typical incinerator fly ash sample, which has been the object of an inter-laboratory experiment. The analysis was carried out on a capillary column. It is worth noting that CDFs with four, five or six chlorine atoms are more abundant than the CDD homologues, whereas octa-CDD is far more abundant than octa-CDF.

Samples of various emissions of different incinerators have been analyzed, and Fig. 2 shows the SID detection of PCDDs and PCDFs in the vapours emitted from an urban incincerator. The analysis was performed on a packed column in two different runs; the former was used to measure octa-, hepta-, penta- and tri-CDDs and -CDFs, the latter to determine hexa- and tetra-CDDs and -CDFs.

Fig. 3 shows the SID of PCDDs and PCDFs present in the extract of a sludge obtained in the abatement of the emissions of an incinerator.

The analytical data relative to emissions of various incinerators are summarized in Table I, and they show that in most emissions PCDFs are present in greater concentrations than PCDDs.

CONCLUSIONS

The combination of selective GC with HRMS used in SID has been found a

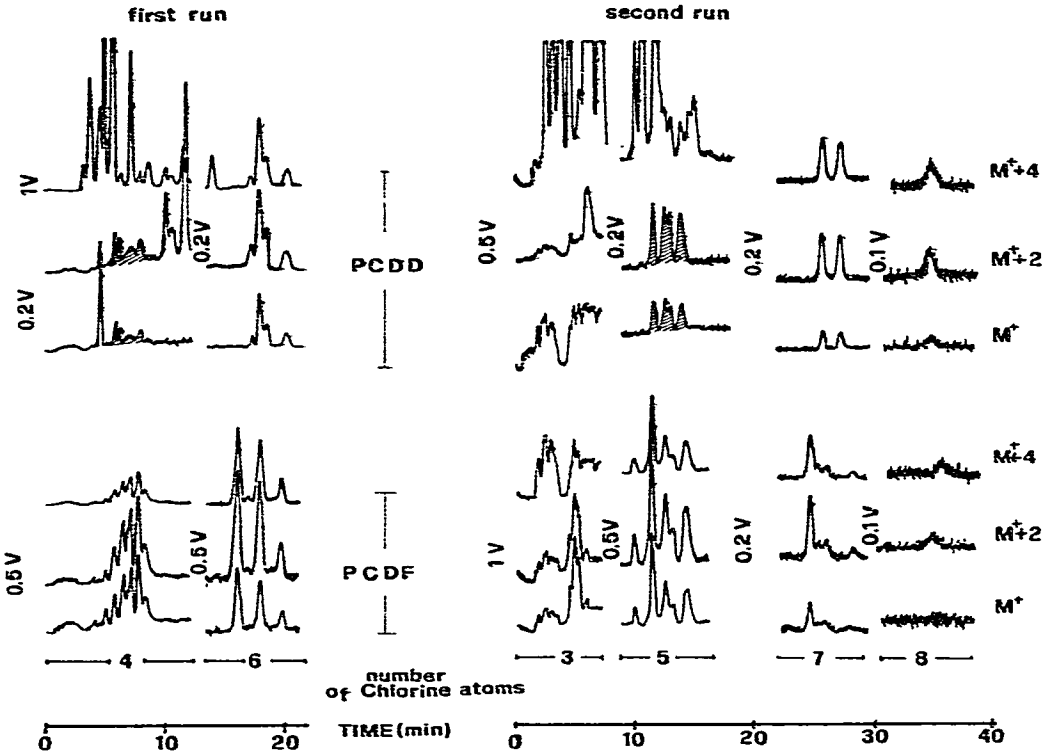

Fig. 3. Selected ion detection of PCDDs and PCDFs extracted from an incinerator sludge, obtained by packed column GC–HRMS ($M/\Delta M$ = 3000).

reliable procedure for determining PCDDs and PCDFs in complex matrices, such as those constituting the emissions produced by urban waste incinerators.

In many cases PCDFs with four or six chlorine atoms in the molecule have been found to be relatively abundant, and the simultaneous determination of these

TABLE I

CONCENTRATIONS OF PCDDs AND PCDFs FROM VARIOUS URBAN INCINERATOR EMISSIONS

Emission	*PCDFs*						*PCDDs*					
	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8
Fly ash Milan (ng/g)	n.e.	10.9	29.4	37	50.5	15	n.e.	2.7	7.4	21	47.1	92
Fly ash Florence (ng/g)	(60)	285	415	910	715	125	(10)	85	165	595	835	520
Fly ash Rome (ng/g)	n.e.	576	216	57	13	(1.5)	n.e.	49	33	14	6	(2.7)
Fumes Rome (ng/nm^3)	1218	994	373	135	16	n.e.	44	46	38	18	9	n.e.
Sludge Messina (ng/g)	n.e.	247-	358	93	34	3	n.e.	54	108	54	31	5

two species can help to answer the question of how these compounds are formed in the incineration processes.

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