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Author Cavallaro, A.

Corporate Author

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SUMMARY OF RESULTS OF PCDD_s ANALYSES FROM INCINERATOR EFFLUENTS

A. Cavallaro (*) - L. Luciani (**) - G. Ceroni (**)
I. Rocchi (**) - G. Invernizzi (**) - A. Gorni (***)

Laboratorio Provinciale di Igiene e Profilassi
Reparto Chimico - via Juvara 22 - Milano

(*) Director
(**) Laboratory of TCDD analysis
(***) Laboratory of mass spectrometry

ABSTRACT

A carefully selected combination of the techniques of gas-chromatography and negative ion chemical ionization mass spectrometry permits reliable quantitative determination of specific chlorinated dioxins in environmental samples. PCDD_s and PCDF_s were shown to be present in the fly ash and flue gases of all six municipal incinerators which were specially analyzed for these compounds.

INTRODUCTION

- Presence of chlorinated compounds in incinerator emissions

The recent interest in the public press and elsewhere on identification and possible toxic effects of chlorinated dibenzo-p-dioxins, has been sparked by the growing recognition of their environmental hazard.

Early concern for these substances as environmental pollutants was related to their presence in emission of trace amounts of highly toxic organic pollutants as a consequence of the large scale combustion of municipal wastes for recovery of energy.

Also serious consideration must be given to the PCDF_s isomers, mainly to the 2,3,7,8-TCDF which has approximately the same degree of toxicity as 2,3,7,8-TCDD.

The predominance of dibenzofurans can be interpreted as being due to the widespread environmental presence of PCB_s, which could be preferential precursors of PCDF_s.

Thus, continuing our work on incinerators installed in various regions of Italy, we assessed airborne particulates and Fly ash released with gaseous emissions. These emissions constitute one of the generally more objectionable aspects of incinerators in urban locations even though little environmental impact data exist for this type of air pollution.

SAMPLING METHOD

- Fly ash and slags

Fly ash and slags were collected from the dust collectors and from moistening bunkers as described in previous report (1).

- Chimney Effluents

The sampling criterion under isokinetic conditions proposed by the Italian Thermotechnical Committee (2) was followed to exactly measure the dusty effluents from individual chimney. If samples have to be taken from chimneys with no smoke-cooling system, i.e. with extremely hot smoke (700-900°), the sampling probe should be modified as follows: the first section should be made from steel able to stand temperatures of up to 1200°C and coupled with a water-based cooling system making it possible to achieve flue gas temperature of about 150°C.

- Extraction and Purification Methods

Basically we followed the analytical method as described in previous report.

- GC-MS Analysis

HRGC glass capillary column (OV 17, 50 m, 0,25 mm I.D.) was coupled via a glass capillary interface leading into the ion source of a Finnigan 3200 and 4000 quadrupole MS operated in the Electron Impact (E.I.) mode (70 eV.) and methane negative ion chemical ionization (MNICI) mode.

The samples extracts were splitlessly and on-column injected using a Carlo Erba GC fractovap serie 4160 - Isomer identifications was based on co-injections with a selected number of PCDD isomers and using single ion detection.

IDENTIFICATION AND MEASUREMENT OF PCDD₅ AND PCDF₅ BY GC-MS AND GC-MASS
FRAGMENTOGRAPHY

As regards qualitative identification and quantification of PCDD₅ and PCDF₅, we undertook individual fragmentographic determination of the various isomers using both electron impact (E.I.) and methane negative ion chemical ionization (MNICI) mode.

Negative ion chemical ionization is frequently employed to increase the sensitivity and specificity of some analysis - this is particularly true of molecules that have a high electron capture cross section due to the presence of electrophilic groupings or atoms such as the halogens.

It should be stressed that identification of the various isomers was based not only on the MS data obtained for each compound, but also on the co-injection of a selected number of dioxin isomers available in our laboratories.

Figures 1, 2, 3, 4 show the MNICI mass spectra of 2,3,7,8-TCDD and other TCDD isomers, such as 1,2,6,7 - 1,2,8,9 - 1,2,3,8 - 1,2,7,8 - 1,3,7,9 - 1,3,6,8 - 1,3,7,8 and 1,2,3,4-TCDD isomers.

As mentioned above tetrachlorodibenzodioxin is a molecule that could be confidently expected to have a high electron cross section because of the presence of four chlorine atoms.

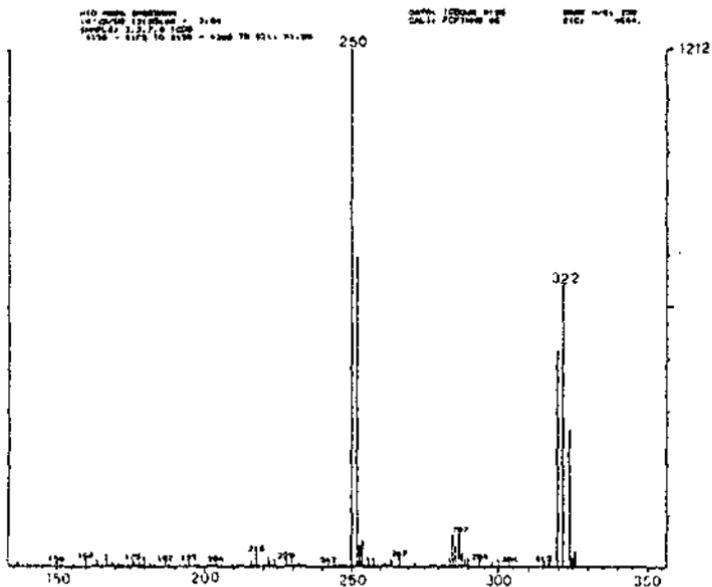
We have made some measurements, however, and found that the enhancement obtained by using MNICI instead of Electron Impact is less than a factor of two. This may be due to the fact that the E.I. spectrum is characterized by an intense molecular ion group which carries most of the ion current.

A further observation is that dioxin is often associated with compounds that also give strong spectra with MNICI and consequently there is little improvement in specificity if the GC-MS analysis is not preceded by efficient clean-up. It is therefore understandable that fragmentation obtained using negative ions is complementary to the data obtained using positive ions.

On the basis of the experiments carried out on samples of PCDD₅ and PCDF₅, we can state that, when using MNICI, peak area for a given concentration of sample increases from penta-CDDs through hepta-CDDs. A small decrease in sensitivity is observed for octa-CDD. Increased delocalization of the negative charge with additional chlorines can help to rationalize this trend.

It does not, however, explain the three order of magnitude difference between

2,3,7,8



1,3,6,8

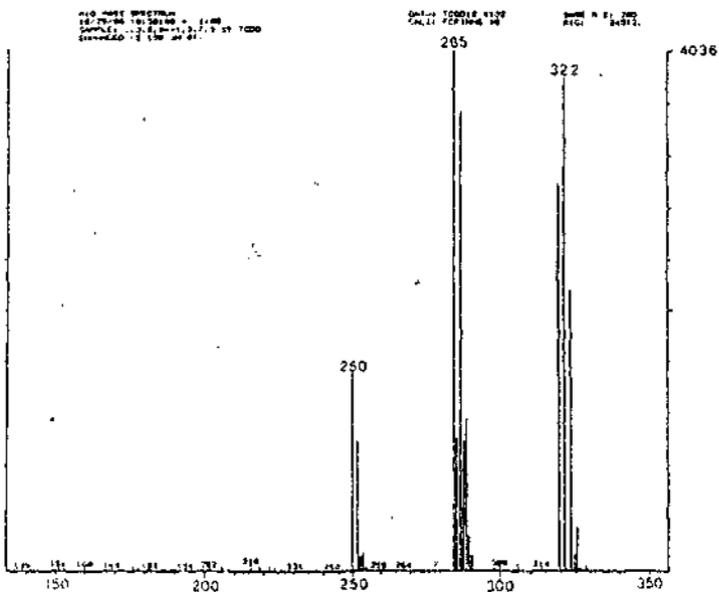


Fig. 1 - MNCI mass spectra of 2,3,7,8 - 1,3,6,8 TCDD isomers

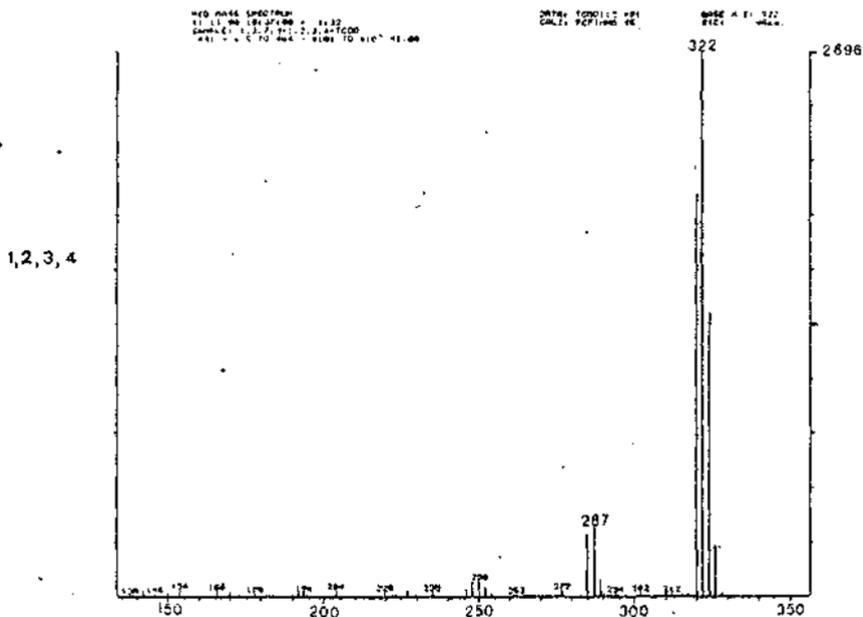
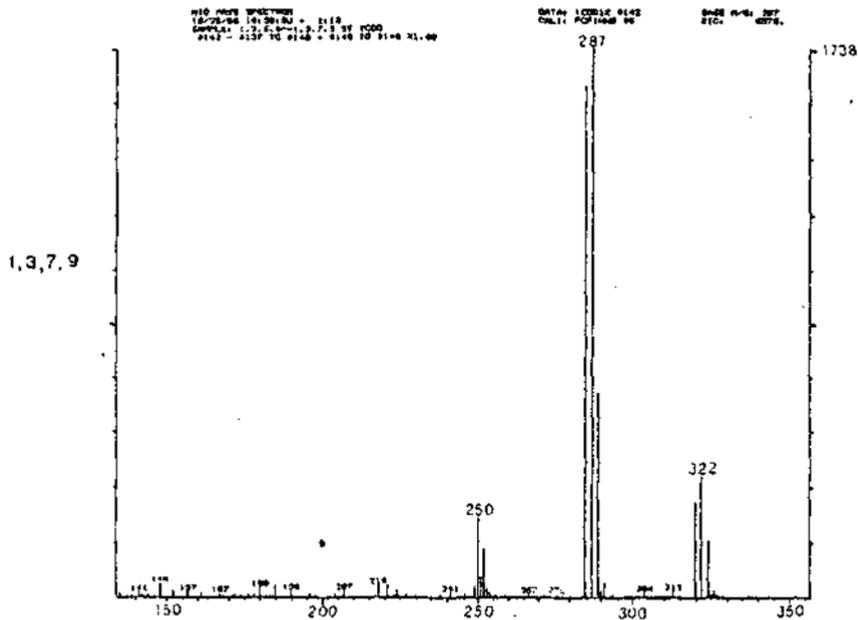
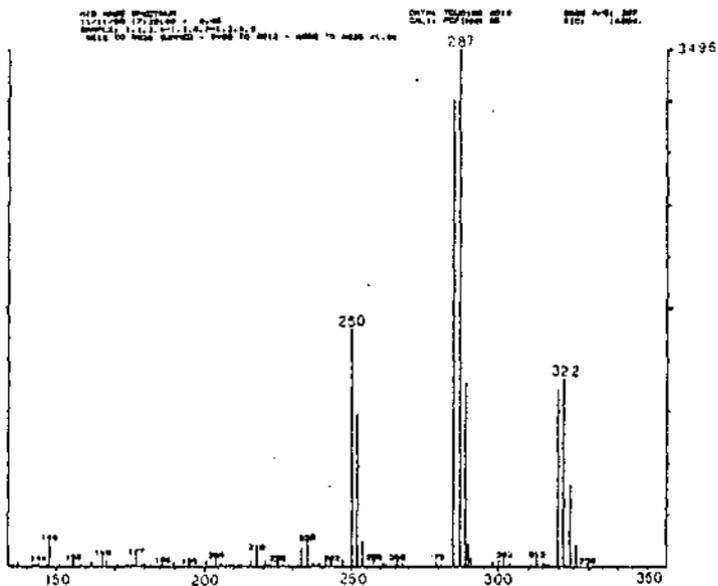


Fig. 2 - MNCI mass spectra of 1,3,7,9 - 1,2,3,4 TCDD isomers

1,2,8,9



1,2,6,7

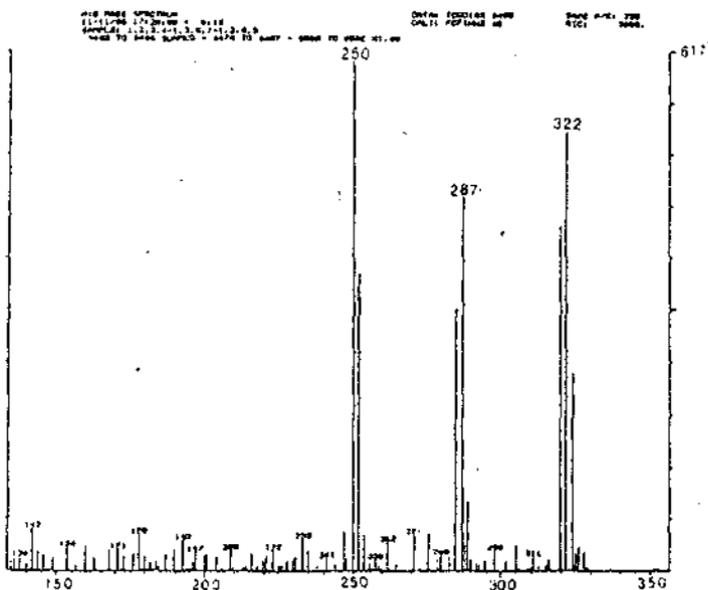


Fig. 3 - MNCI mass spectra of 1,2,8,9 - 1,2,6,7 TCDD isomers

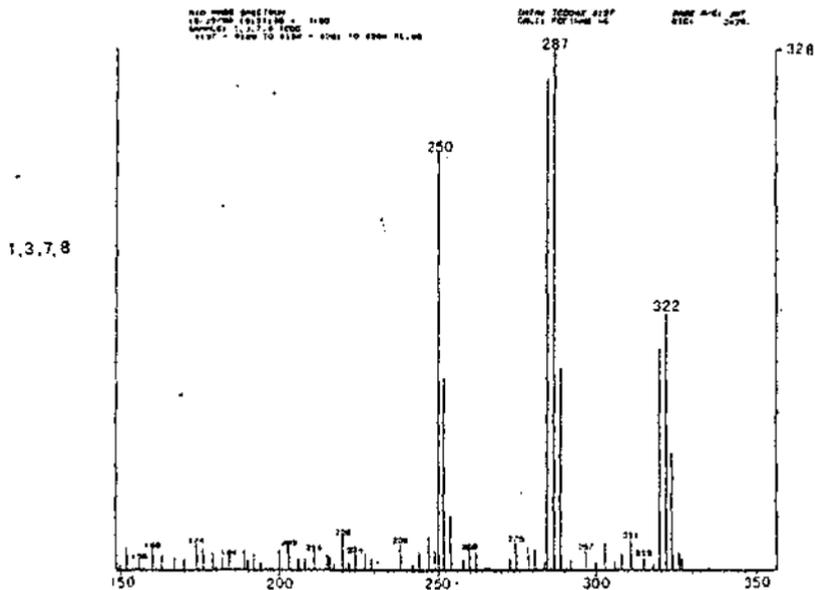
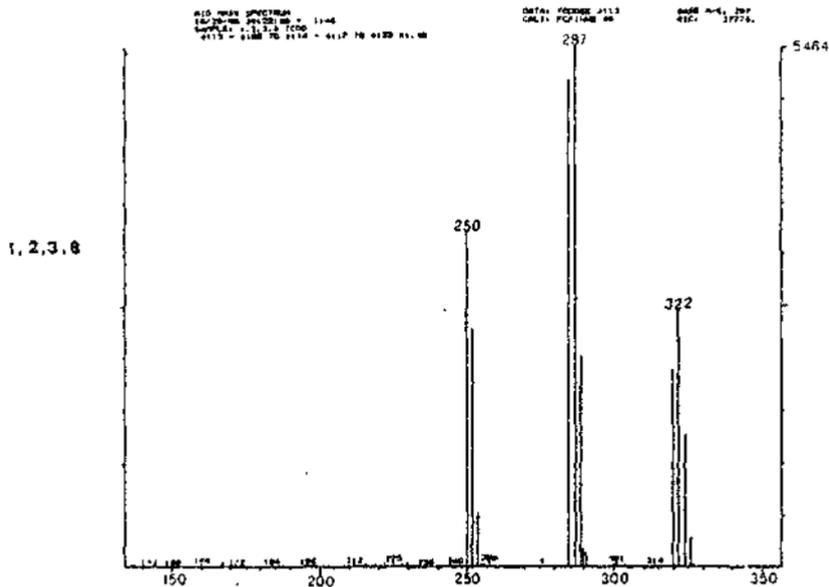


Fig. 4 - MNCI mass spectra of 1,2,3,8 - 1,3,7,8 TCDD isomers

the tetrachloro and heptachloro isomers, nor does it explain the decrease in sensitivity of octa-CDD relative to hepta-CDD.

Another particularly interesting point is that the two tetrachloro isomers studied, 1,2,3,4-TCDD and 2,3,7,8-TCDD differ in sensitivity by more than an order of magnitude.

In fact the sensitivity of the 1,2,3,4-TCDD isomer is comparable to that of the pentachloro isomers. This effect may in some way be linked to the symmetries of the various dioxin isomers.

The two more symmetrical isomers studied 2,3,7,8-TCDD and 1,2,3,4,6,7,8,9-octa-CDD, appear to have detection limits in the MNCI mode lower than the less symmetrical compound.

One possible way of relating these observations of the sensitivities of the various dioxin isomer under MNCI conditions is as follows. Initial ionization under MNCI conditions is thought to occur through resonance electron capture, resulting in an excited molecular anion. This ion can be relaxed to a stable electronic state via a number of processes which include spontaneous ejection of the extra electron, emission of light, fragmentation, or a collision with a reagent methane molecule. Unsymmetrical anions have available a greater number of non-degenerate energy levels than do the more symmetrical ones.

They can thus be expected to relax by light emission more rapidly to their ground states to produce stable anions which will then be detected in the mass spectrometer. More symmetrical isomers, which are forced to remain in the excited state for a longer period of time, are more prone to processes such as electron auto-ejection or dissociative electron capture (3).

RESULTS AND CONCLUSIONS

As reported in previous reports gaseous emissions commonly referred to as flue gas of the incineration process contain PCDD_s and PCDF_s. The data relating to tetra-CDF_s are particularly important since in many samples we found them to be present in higher concentrations than tetra-CDD_s, thus confirming our previous statement. The presence of 2,3,7,8-CDF should not be underestimated given its high degree of toxicity, particularly since the concentrations of tetra-CDF_s found both in chimney effluents and in fly ash coming from particle collectors, are generally higher than those of tetra-CDD_s. The results of the analyses carried out to determine PCDD_s and PCDF_s in relation to six solid-urban-waste incinerators, are reported in Table 1.

TABLE 1
Quantitative determination of PCDDs and PCDFs in fly ash, airborne particulate, flue gas condensate

INCINERATOR	SAMPLE	4-CDD	5-CDD	6-CDD	7-CDD	8-CDD	4-CDF	8-CDF
1	Fly ash (ppb)	*	*	*	*	*	*	*
	Airborne particulate released with emissions (ng/Nm ³ U)	1,1	2,7	11,5	1,03	3,0	N.D.	2,2
	Flue gas condensate (ng/Nm ³ U)	19,6	27,9	178,2	159,6	63,9	N.D.	59,3
2	Fly ash (ppb)	0,25	1,7	294,0	8,9	295,0	0,46	15,8
	Airborne particulate released with emissions (ng/Nm ³ U)	172,2	172,3	12015,0	575,0	7312,0	75,0	2883,0
	Flue gas condensate (ng/Nm ³ U)	17,0	107,0	26620,0	828,0	1179,0	108,6	4390,0
3	Fly ash (ppb)	N.D.	0,92	1,8	3,1	1,5	0,8	3,3
	Airborne particulate released with emissions (ng/Nm ³ U)	0,037	0,3	6,7	0,2	1,7	2,57	0,08
	Flue gas condensate (ng/Nm ³ U)	19,0	40,0	6542,0	124,0	776,0	429,0	1010,0
4	Fly ash (ppb)	46,4	65,4	2496,0	87,9	841,5	61,7	255,0
	Airborne particulate released with emissions (ng/Nm ³ U)	10,9	2,8	0,54	3,2	39,0	3,7	0,06
	Flue gas condensate (ng/Nm ³ U)	60,0	33,0	1390,0	167,0	2703,0	1814,0	1760,0
5	Fly ash (ppb)	0,7	0,05	0,021	0,007	0,1	1,18	0,0015
	Airborne particulate released with emissions (ng/Nm ³ U)	0,34	2,4	196,0	9,9	173,0	75,3	3,2
	Flue gas condensate (ng/Nm ³ U)	9,6	21,0	328,0	46,0	244,0	305,0	89,0
6	Fly ash (ppb)	N.D.	N.D.	N.D.	0,0012	5,86	N.D.	1,93
	Airborne particulate released with emissions (ng/Nm ³ U)	N.D.	0,010	0,28	N.D.	0,51	N.D.	N.D.
	Flue gas condensate (ng/Nm ³ U)	19,0	11,0	480,0	6,0	71,0	27,0	24,0

* = not available

N.D. = not detected

This table does not list the data relating to the slags since the concentrations of the contaminants were extremely low. Specifically, tetra and penta CDD_s were always present in concentrations of less than 0.004 ppb, hexa and hepta-CDD_s did not exceed 0.006 ppb in any sample, while octa-CDD did not exceed 0.008 ppb.

Octa-CDF was not present at the detectable limit of 0.008 ppb. The results described above do not move away from literature data (4), and they enable us to confirm our previous conclusions, i.e. the contaminants in question are mainly found in the gaseous phase. The high temperatures and the stripping effect by the overheated aqueous vapor seem they are reducing the adsorbent effect of the particles, especially if the latter has no carbon residues.

Different incinerator design, adequate combustion temperatures (1000-1100°C), longer incineration times and greater smoke movement would undoubtedly result in a considerable reduction in these contaminants, while inclusion of a suitable post-combustion chamber would destroy all residual traces. The study of the formation and topimal destruction conditions of chlorinated organic contaminants in incineration processes will be the subject of a CNR (Italian National Research Council) research program using a pilot plant (5).

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