

DIOXIN LIKE COMPOUNDS FROM MWI EMISSIONS: ASSESSMENT OF POLYCHLORINATED NAPHTHALENES PRESENCE

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Abstract

In an attempt to evaluate the presence of polychloronapthalenes (PCN) and the possible relationship with the polychlorodibenzo-*p*-dioxins (PCDD) and polychlorodibenzofurans (PCDF), emissions from Municipal Waste Incineration (MWI) were analyzed. The analysis of PCDD/PCDF and PCN were carried out by High Resolution Gas Chromatography coupled with High Resolution Mass Spectrometry in mode Selected Ion Monitoring (HRGC/HRMS-SIM).

Introduction

In the last 20 years, polychlorodibenzo-*p*-dioxins (PCDD), polychlorodibenzofurans (PCDF) and polychlorobiphenyls (PCB) have been the subject of many environmental studies because their bioaccumulative properties and demonstrated toxicity, extensively documented in the literature. As a consequence, countries all over the world set limit for these compounds in food, air, soils application, etc...

Recently, the PCN have attracted the interest of the laboratories. These compounds constitute other serie of halogenated compounds that include a mixture of 75 bicyclic aromatic compounds. The interest for these compounds¹⁻⁶⁾ is due to the similar properties with the PCB and PCDD/PCDF, and their demonstrated toxicity, which indicates that the PCN could be considered as a dioxin-like compounds. In fact, it is reported that PCN seem to be about as active as enzyme inducers (AHH) as certain coplanar PCB, and their toxicity can be expressed as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) toxic equivalents⁷⁾. Although, the PCN have been manufactured as industrial chemical (dielectric fluids, flame retardants, fungicides, etc...) since the beginning of the century, also other sources of PCN have been described, for exemple, as a contaminant in PCB formulations or industrial processes such as municipal waste incineration and ambient air. Also, pollution incidents were noticed in groundwater wells near Barcelona (Spain)⁸⁾. The aim of this work is to assess the fate of PCN and the posible relationship with PCDD/PCDF in emissions from Municipal Waste Incinerator.

Dioxin '97, Indianapolis, Indiana, USA

Experimental Methods

Stack Gas Samples were collected using a filter, condenser, adsorbent (XAD-2) sampling system. All pollutants were removed from solid matrices by Soxhlet extraction using toluene for 48 h. At the same time liquid-liquid extraction with dichloromethane was performed to extract these compounds from condensed water of the emissions samples. Next, extracts were concentrated prior to cleanup process. The cleanup process was based on liquid-solid adsorption chromatography using silica, florisil and alumina as an adsorbents, in a glass column at atmospheric pressure⁹⁾.

The HRGC/HRMS-SIM conditions were:

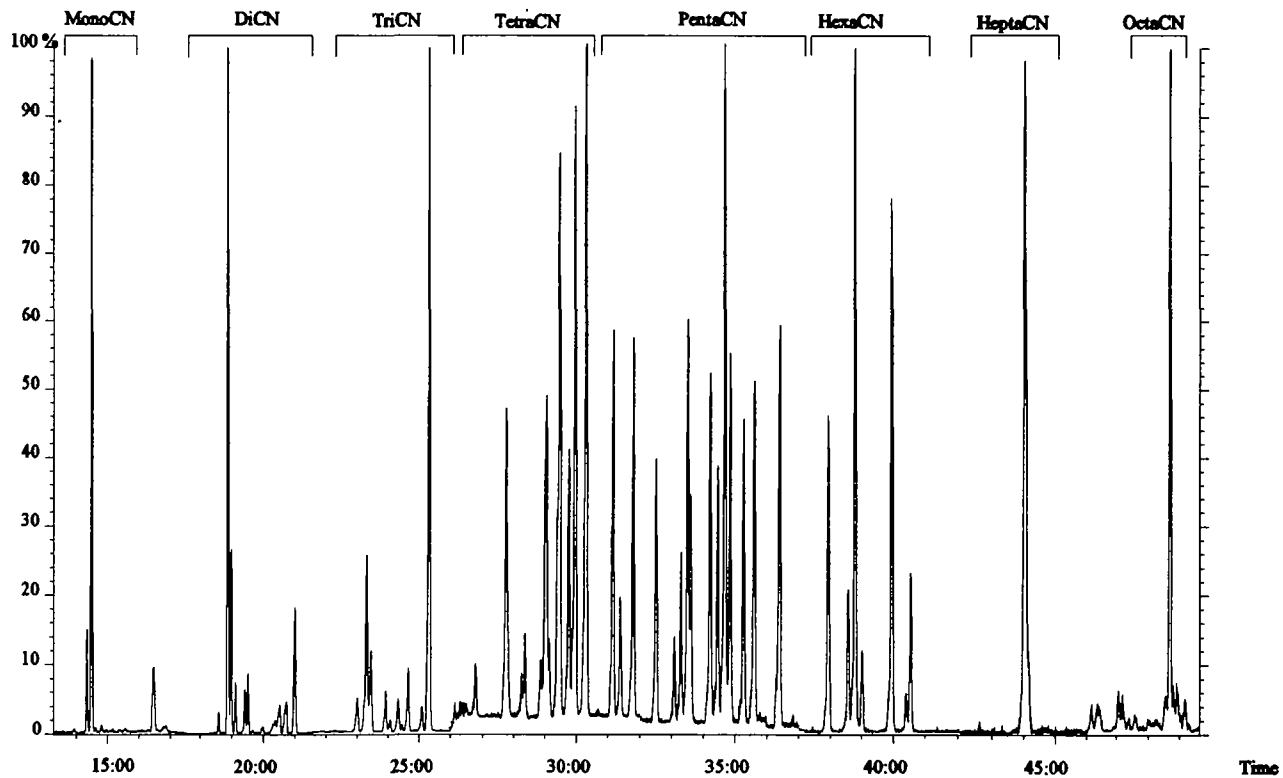
Gas Chromatography:	CE 8000 Series
Mass Spectrometer:	Autospec Ultima (Fisons Instruments)
Column:	J&W DB-5, 60 m length, 0.25 mm inter diameter and 0.25 μ m of film
Temperature:	PCN: 60 °C (1 min) to 150 °C (1min) at 20 °C/min, then at 4 °C/min to 285 °C and held isothermally for 12 min at 285 °C PCDD/PCDF: 140 °C (1min) to 200 °C (1min) at 20 °C/min, then at 3°C/min to 300°C and held isothermally for 20 min at 300 °C
Injection:	Splitless, 1-2 μ L, at 280 °C
Carrier Gas:	Helium (v: 35 cm/s; T: 100 °C)
Analyser Mode:	SIM voltage
Ionization Mode:	EI+, at 37 eV

Results and Discussion

Analysis of PCN and PCDD/PCDF were accomplished by HRGC/HRMS in SIM mode. The two most abundant isotopes from the molecular ion region (M and M+2) and their isotopic ratio were used for confirmative purposes for each level of chlorination. In addition, chromatographic windows for each group of PCN, from monochlorinated to octachlorinated (table 1), and PCDD/PCDF homologues, from tetrachlorinated to octachlorinated, were defined. Quantification of PCDD/PCDF was based on the isotopic dilution method. Quantification of PCN consist in the use of the ¹³Cl-2,3,7,8- TCDD and ¹³Cl-1,2,3,4,7,8-HxCDD as an internal standard, assuming that each isomer of the same group had the same recovery and response factor than the available individual standard. Relative response factors (RRF) were obtained by a mixture of a PCN standards: 1 monochloronaphthalene (1), 2 monochloronaphthalene (2), 1,4 dichloronaphthalene (3), 2,3,6,7 tetrachloronaphthalene (4), 1,2,3,6,7 pentachloronaphthalene (5), 1,2,3,5,6,7 hexachloronaphthalene (6), 1,2,3,4,5,6,7 heptachloronaphthalene (7) and octachloronaphthalene (8). Individual congeners were from Aldrich (1,2) (Germany), Promochem (4,5,6,7) (Germany) and AccuStandard Inc. (3,8) (New Haven, CT, USA). As a analytical recovery standar and sampling ¹³C-1,2,3,4 TCDD and ³⁷Cl 2,3,7,8 TCDD respectively were employed (from CHEMSYN Science Laboratories, Lennexa, USA).

In MWI emissions, all isomers of PCN were found, and 1,2,3,4,6,7/1,2,3,5,6,7-HxCN (66/67) and 1,2,3,4,5,6,7-HpCN (73) were assigned. Figure 1 shows HRGC/HRMS chromatogram composites of the different homologue groups from monochloronaphthalenes to octachloronaphthalenes. Levels of PCDD/PCDF were lower than 0.1 ng -I-TEQ/Nm³. The values of the PCN emitted ranged from 2 to 8 ng/Nm³.

Figure 1. HRGC (J&W DB-5) /HRMS-SIM analysis of MWI emission extract.



Dioxin '97, Indianapolis, Indiana, USA

Table 1. Ions monitored in HRGC/HRMS-SIM analysis of PCN.

COMPOUNDS	M	M+2	Isotopic Ratio	Time Interval (min)
Monochloronaphthalenes	162.0236	164.0208	3.37	10:00-17:00
Dichloronaphthalenes	195.9847	197.9818	1.55	17:00-21:30
Trichloronaphthalenes	229.9457	231.9428	1.04	21:30-26:10
Tetrachloronaphthalenes	263.9067	265.9038	0.78	26:10-32:00
Pentachloronaphthalenes	299.8648	301.8619	1.55	32:00-37:00
Hexachloronaphthalenes	333.8258	335.8229	1.24	37:00-42:00
Heptachloronaphthalenes	367.7869	369.7839	1.04	42:00-47:00
Octachloronaphthalenes	401.7479	403.7450	0.89	47:00-52:00

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