

RELATIVE CORRELATION OF JET-REMPI MONITORING WITH ADSORPTION TUBE SAMPLING FOLLOWED BY TDS-CIS-GC/MS

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Introduction

During earlier work¹⁻³ rapid and highly sensitive Jet-REMPI (resonance-enhanced multiphoton ionization) mass spectrometry was applied for monitoring the effluent from thermal treatment of a filter dust during a *de novo* test under laboratory conditions. The sample, from ESP-Field 2 of an iron ore sintering plant, was already loaded with dioxins (Σ PCDD/F = 132 ng/g), their precursors (PCBz, PCPh) and other products of incomplete combustion. Heating filter dust in a temperature window 200-350 °C under a flow of air results⁴ in further formation of these pollutants. As described elsewhere¹, on-line detection was mostly carried out using a non-selective ionization mode, to measure a wide range of compounds simultaneously. The changes of output suggest that the reaction products increase in chlorination level with time. Another explanation is that higher-chlorinated compounds appear later as a consequence of lower volatility and stronger adsorption. However, due to mass spectrometric interferences, the basis of any interpretation was ambiguous. To resolve this uncertainty experiments were repeated, and the gas phase was sequentially sampled on a series of Tenax absorption tubes, which were then thermally desorbed and GC/MS-analysed. Since test conditions were comparable to those, when the effluent was monitored with Jet-REMPI, it is plausible that the gaseous products are similar in quality in both cases. In this paper the resulting peaks' identifications are combined with earlier Jet-REMPI data with the purpose of investigating:

- How well do Jet-REMPI profiles, measured in a non-selective mode, reflect target compounds such as low chlorinated PCDF, PCBzF, PCBz and PCPhenols/PCNaphthalenes?
- If these target compounds are ill-represented, which are the other compounds present that could be mistaken for target compounds?

Materials and Methods

All graphs and tables use a conventional notation *Tests A*, referring to former Jet-REMPI effluent monitoring, and *Tests B* for this work, with off-gases sampled onto adsorption tubes. Equipment and procedures of *Tests A* were reported elsewhere¹⁻³. Briefly summarizing, a vertical glass reactor containing 5 g of the filter dust was heated to a desired temperature in a range 200-350 °C using a tubular oven, and air passing through the reactor carried the resulting products directly to the Jet-REMPI inlet for on-line monitoring. The description of REMPI principle and Jet-REMPI devise can be found in literature⁵⁻⁶. During *Tests B* the same sample was placed into a TA Instruments

thermogravimetric analyzer 951, allowing to monitor the weight loss of filter dust during thermal treatment. The effluent was sampled on Gerstel Tenax adsorbent tubes (Mülheim a/d Ruhr, Germany), which were desorbed thermally using a Gerstel TDS-2. Temperature conditions during sampling were identical to those during *Tests A*, as illustrated in Figure 1.

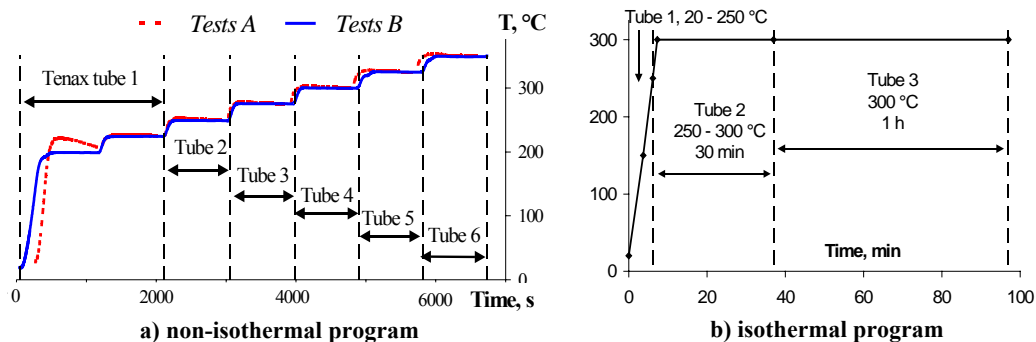


Figure 1. Temperature settings during *Tests A* and *B*

The TDS-2 was mounted onto a 6890 HP GC-5973 MSD (Agilent Technologies). The thermal desorption unit was heated from 35 °C to 300 °C at 60 °C/min with an initial time of 1 min and final time of 5 min, to desorb the analytes from the sample. Evolved compounds were swept towards the CIS (Cooled Injection System) at 100 ml/min and trapped at a temperature of -150 °C in an empty baffled liner. When desorption was completed the CIS was heated to 300 °C at 12 °C/s. All samples were injected in the splitless mode, with a 1 min splitless time. Separation was performed on a HP-5MS fused silica capillary column, 30 m x 0.25 mm I.D., 0.25 µm d_f . Carrier gas was helium, set at a constant pressure of 70 KPa. The oven was programmed from 35 °C (1 min) and raised to 300 °C at 5 °C/min, held for 2 min. For easy profile identification the MSD was used in the electron impact mode (70 eV), generating full scan spectra between 50 and 500 amu. Peak identification was performed using the Wiley 6th edition mass spectral data library.

Differences			Similarities between <i>Tests A</i> and <i>B</i>
Parameter	<i>Tests A</i> - REMPI	<i>Tests B</i> - Tenax	
Amount of sample	5.0 g	0.2 g	2 nd field ESP filter dust from iron ore sintering
Position of reactor	Vertical	Horizontal	
Volume of reactor	300 ml	55 ml	Carrier gas: air
Sampling	Directly to Jet-REMPI	Tenax adsorbent	Flow rate: 3 l/h
Separation	no	GC	Temperature
Ionization	REMPI	Electron impact	Duration

Table 1. Comparison of experimental conditions

The target compounds selected are low chlorinated PCDF (ions 168, 202, 236, 270 and 304 amu), PCBz (78, 112, 146, 180, 216 amu), PCPhenols together with PCNaphthalenes (both: 128, 162,

196, 232 and 266 amu) and benzofurans PCBzF (118, 152, 186 amu). Dibenzo-*p*-dioxins from *Tests B* are non-detected using low resolution GC/MS, and are not discussed further.

A reference sample was generated by combustion of 1,2-dichlorobenzene. The resulting products of incomplete combustion were adsorbed on Tenax and thermally desorbed afterwards. The 1,2-dichlorobenzene (Fluka, Germany) was injected (1 µl) in a 20 cm quartz tube, held in a tubular oven (Carbolite, UK) at 800 °C. The combustion gases were reacting for 1 min, after which a valve was opened for 5 min releasing gases onto the Tenax tube using an air flow of 200 ml/min. By this approach sufficient concentrations of target compounds were generated, allowing accurate library identification. Using retention time correlation, the identification of compounds released during the *Tests B* could be confirmed.

Results and Discussion

The effluent resulting from thermal treatment of filter dust is a very complex mixture of aliphatics and aromatics, often featuring heteroatoms (N, S, O, Cl and Br). All target ions listed above were identified using the extracted ion chromatograms (EIC). Peaks were declassified as non-identifiable if the match quality between the spectrum and its library reference spectrum was less than 78 %.

The contribution of peak areas, corresponding to the (chloro)aromatic compounds of interest when considering a particular target ion, is summarized in Table 2. Since the data is non-calibrated, there may be bias regarding the relative abundance of different compounds. Nevertheless, this approach allows comparisons, as well as first estimations.

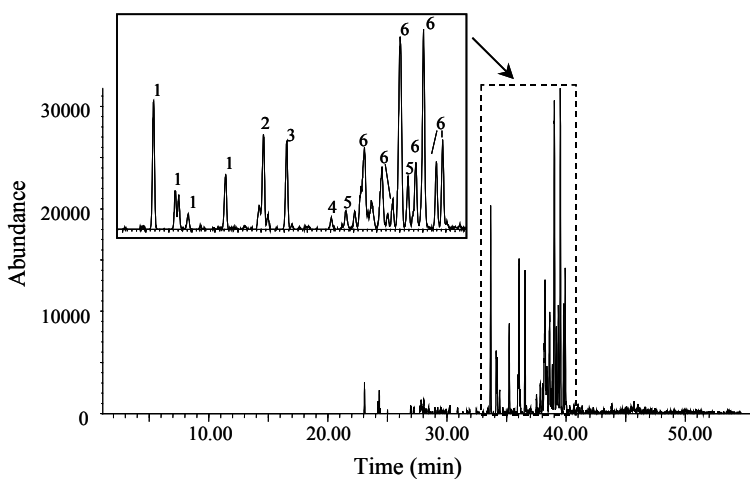
	Tenax tube 1 25-225 °C	Tube 2 step 250 °C	Tube 3 step 275 °C	Tube 4 step 300 °C	Tube 5 step 325 °C	Tube 6 step 350 °C
DF (168 amu)	21	25	16	10	0	0
Sum MCDF (202 amu)	0	0	16	35	46	47
Sum DCDF (236 amu)	0	0	0	53	57	68
Sum TrCDF (270 amu)	0	0	0	48	58	53
Sum TCDF (304 amu)	0	0	0	26	63	60
MCBz (112 amu)	0	12	45	90	90	84
Sum DCBz (146 amu)	100	96	95	98	94	100
Sum TrCBz (180 amu)	17	50	82	92	90	92
Sum TCBz (216 amu)	42	85	100	100	100	98
Naphthalene (128 amu)	53	0	0	0	0	0
Sum MCN (162 amu)	0	13	30	32	0	0
Sum DCN (196 amu)	0	0	64	79	85	79
Sum TrCN (232 amu)	0	0	46	90	94	89
Sum TCN (266 amu)	0	0	0	85	94	91
Phenol (94 amu)	50,5	61,4	61,0	23,4	0	0
Sum MCPH (128 amu)	0	8,6	0	0	2,7	1,6
Sum DCPh (162 amu)	0	0	3,3	0	2,8	3,5
Sum TrCPh (196 amu)	0	16,0	9,3	0	1,6	3,7
Sum TCPh (232 amu)	0	0	0	0	5,9	8,7

Table 2. Contribution of the area (%) of selected compounds to the total area of a target ion

Polychlorinated benzenes clearly prevail over other species at the same amu-value, so that Jet-REMPI profiles at ion 112, 146, 180 and 216 amu largely reflect the evolution of PCBz, even when considered at the non-resonant wavelength of 258.9 nm. *Tests B* are unsuitable for detecting benzene, which is too volatile to be retained by the adsorption system.

PCNaphthalenes definitely predominate over PCPhenols: for m/z 196, e.g., DCNaphthalenes contribute 80-85 % to the EIC total area, when TrCPhenols - as little as 0-4 % (Table 2). In the range of 300-350 °C di- to tetra-chlorinated naphthalenes, represented by 8-10 isomers, are the major compounds seen at 196, 232 and 266 amu respectively.

PCDF are well detectable in the effluent from the *Tests B*. Only non-chlorinated dibenzofuran is found below 275 °C. At 275 °C there are two monochlorinated isomers, and at higher temperatures the yield of PCDFs (P=1-4) significantly increases. Pyrene is a typical product of incomplete combustion. Therefore, its chlorinated derivatives were expected to create major MS interferences with PCDFs. However, they were not found within the detection limit of the TDS-GC/MS system.



1 - non-identifiable; 2 - TrCDF; 3 - 6,7-dibromo-1-naphthol; 4 - dichloroanthracene; 5 - PeCB; 6 - TCDF

Figure 2. Extracted ion chromatogram (303.70 - 304.70 amu) and details between 33-40 min of TDS-GC/MS of Tenax tube # 6 sampled at 350 °C (stepwise test)

At m/z 236, 270 and 304 amu, the sum of isomers of di-, tri- and tetrachlorinated dibenzofurans roughly represent 60 % of the EIC area (Fig. 2), confirming that the Jet-REMPI profiles reflect rather well the evolution of low chlorinated PCDF with temperature and time. The isotope ratios of m/z 270, 272 and 274 in mass spectra from one of the *Tests A* measured at 258.9 nm, support this conclusion (Figure 3, left, a). The curves are well synchronized over most of the test. At a number of time points, e.g. the cross-section at about 4000 s (b) the measured relative intensities of isotope peaks are very close to the theoretical values for a three chlorine atoms containing compound indicating the presence of trichlorodibenzofuran. The large ratio deviation between 50-60 min implies that the Jet-REMPI mass spectra reflect a mixture of compounds. Figure 3 (right part)

illustrates the isotope ratio of dichlorinated benzene. The same type of graph for dichlorinated naphthalene from the non-isothermal *Test A* is presented on Figure 4.

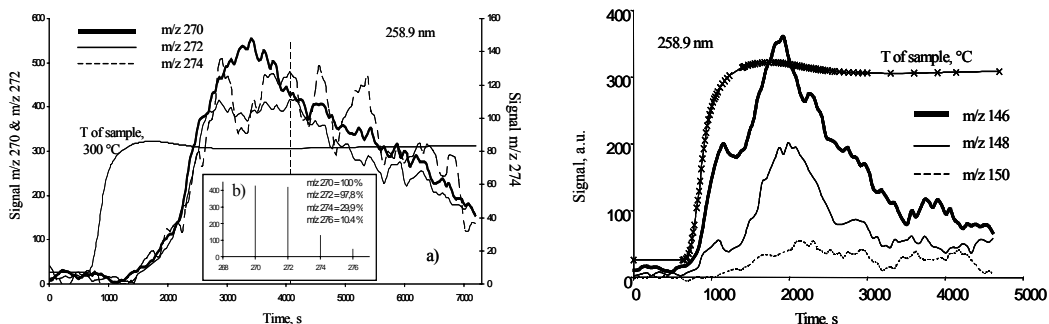


Figure 3. Jet-REMPI mass spectra from an isothermal test at 300 °C: isotope ratio between m/z 270, 272, 274 (left) and m/z 146, 148, 150 (right)

In certain temperature ranges a peak area of target compounds is either too small, compared to the total EIC area, or non-detected, as e.g., DiCNaphthalenes below 275 °C (Table 2). In case the target compound is unimportant, all other peaks were identified (Table 3). Aliphatics, containing from 11 to 30 carbon atoms, are the major compounds found at the low end of the studied temperature range (≤ 225 °C). Aromatic compounds are typically non-chlorinated under such conditions. Since the low temperature compounds substantially differ from those appearing at the higher temperatures, the former are considered to be desorption products, originally trapped on filter dust.

Ion	Tenax tube 1 25-225 °C	Tenax tube 2 step 250 °C	Tenax tube 3 step 275 °C	Tenax tube 4 step 300 °C	Tenax tube 5 step 325 °C	Tenax tube 6 step 350 °C
168	Alkanes	n. id.	diff.	n. id.	n. id.	n. id.
202	n. id.	n. id.	diff.	Cl-aromatics	MCDF	MCDF
236	n. id.	n. id.	n. id.	DCDF	DCDF	DCDF
270	n. id.	n. id.	diff.	TrCDF	TrCDF	TrCDF
304	n. id.	n. id.	n. id.	diff.	TCDF	TCDF
112	Alkanes	n. id.	MCBz	MCBz	MCBz	MCBz
146	DCBz	DCBz	DCBz	DCBz	DCBz	DCBz
180	n. id.	TrCBz	TrCBz	TrCBz	TrCBz	TrCBz
216	TCBz	TCBz	TCBz	TCBz	TCBz	TCBz
94	Phenol	Phenol	Phenol	n. id.	Cl-aromatics	n. id.
128	Naphthalene	Benzoic acid	Benzoic acid	diff.	n. id.	n. id.
162	n. id.	diff.	Cl-aromatics	PCNaphs	Cl-aromatics	PCNaph
196	Alkanes	diff.	DCNaph	DCNaph	DCNaph	DCNaph
232	n. id.	n. id.	TrCNaph	TrCNaph	TrCNaph	TrCNaph
266	n. id.	diff.	n. id.	TCNaph	TCNaph	TCNaph

Legend:

n. id. → non-identified peaks (with match quality < 78 %);

diff. → “different”, means that no single class of compounds reaches 40 % of the total area

Cl-aromatics → sum of all chlorinated aromatic compounds together

PCNaph → sum of naphthalenes with different degrees of chlorination

*Table 3. Dominating compound or class of compounds
(≥ 40 % of total extracted ion chromatogram area)*

Some compounds, such as phenol, benzaldehyde, acetophenone and decanal are quite prominent in *Tests B*, but are also listed as potential Tenax artifacts⁷ resulting from absorbent degradation.

Figure 4 illustrates how findings from TDS-GC/MS analysis of Tenax tubes containing qualitatively the same organic load as the one monitored on-line in other series of tests contribute to the interpretation of the Jet-REMPI non-selective profiles.

It can be concluded that in order to monitor on-line aromatic products from a dioxin formation process dealing with a real complex filter dust sample, it is not an adequate strategy to choose for non wavelength-selective ionization conditions. On the other hand, the additional research purposed to provide certain identifications of the organic load in the effluent proves that the earlier made tentative identifications¹⁻³ are correct for PCBz and PCNaphs (P=2-4), and partly fair for PCDFs.

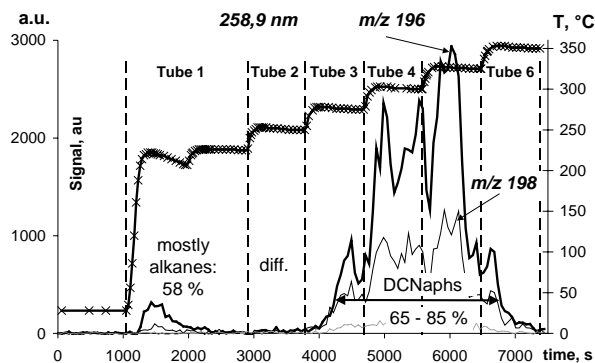


Figure 4. Implication of identifications from Tests B to interpretation of Jet-REMPI profiles

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