

## Continuous Monitoring of Unintentionally Formed POPs Listed Under the Stockholm Convention (PCDDs/PCDFs, PCBs, HCB) Using AMESA<sup>®</sup> Long Term Sampling System

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### Introduction

Most discussions over last few years about monitoring of dioxin emissions of incineration facilities were focussed on the possibility of on-line monitoring, long-term sampling or manual sampling. Because of the fact, that manual sampling can give only insufficient information of the total dioxin emissions due to a spot measurement of several hours during one year, the general wish is to have an on-line monitoring, which is however not yet possible. Therefore long term sampling with AMESA<sup>®</sup> is the practical choice for continuous monitoring of PCDD/PCDF emission from waste incinerators and other industrial emission sources.

The Stockholm Convention on persistent organic pollutants (POPs) lists in addition to PCDD/PCDF also polychlorinated biphenyls (PCBs)<sup>A</sup> and hexachlorobenzene (HCB) as unintentionally formed POPs (UPOPs). This might result in an increased request for emission monitoring of UPOPs. Furthermore one aim of the Stockholm Convention is to reduce and eliminate POPs in the next two decades and will result in destruction of POPs stockpiles and POPs remediation projects. These activities will request a strict emission monitoring.

Therefore the question arose if these listed UPOPs and POPs can be monitored by the AMESA<sup>®</sup> system under the standard application (XAD2, 30 °C, 4 weeks sampling duration) or if a modification of the sampling system would be necessary. The present paper demonstrates that the AMESA system is capable to sample the whole range of POPs listed in the Stockholm Convention and can therefore be used for monitoring of UPOPs emission and for supervision of POPs remediation and destruction projects.

### Materials and Methods

#### Description of AMESA

The functional principle of the AMESA<sup>®</sup> system was described in several publications<sup>2, 3</sup>. In principle the used method complies with the cooled probe method of EN-1948 with the exception that the condensate flask is installed after the XAD-II cartridge and that therefore the condensate does not need to be collected and analysed. This is in accordance to US EPA method 23A. Additionally the plane filter for the dust collection is replaced by quartz wool included in the top of the XAD-II cartridge. The cartridge containing the adsorbed dioxins and



Figure 1: AMESA control cabinet



Cartridge box with XAD II cartridge

<sup>A</sup> In addition some PCBs are assigned TEQ values (WHO-TEQ). Therefore e.g. in Japan emission measurements of regulated emission sources require in addition to PCDD/PCDF also the monitoring of these PCB congeners.

furans is evaluated together with a data medium in an accredited laboratory. By means of this process, dioxins and furans are separated from the gas phase and the condensate in one adsorption step. With this method it is possible to collect the dioxin and furans up to 4 weeks on one XAD-II cartridge. Therefore the complete yearly dioxin emission of a plant can be determined.

### 2.2 Test of AMESA in municipal waste incinerator

To prove the comparability of PCDD/PCDF short term (6 to 16 h) sampling results to long-term (> 16 h) sampling results several short term (6 to 18 h) samplings were performed parallel to 4 three-days samplings. In a second measuring campaign at the same incinerator 4 weekly samplings were performed in parallel to 1 four-week sampling (fig. 2)<sup>4</sup>.

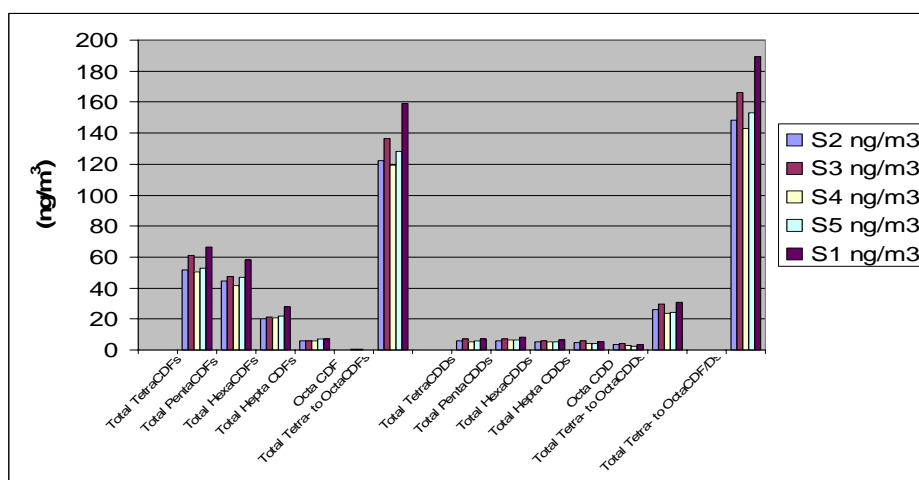


Figure 2: PCDD/PCDF concentrations in the flue gas of a combustion facility determined in one 4-week (S1) and four 1-week (S2 – S5)

In another measurement campaign a double XAD II cartridge was installed to check about possible breakthroughs. The results for polychlorinated benzenes (PCBz) and phenols (PCPh) are discussed below.

## Results and discussion

### Monitoring of PCDD/PCDF

After the installation of the AMESA systems in many different municipal waste incinerators, the application range was extended more and more to other kind of plants like e.g. hazardous waste incinerators, biomass combined heat and power plants, medical waste incinerators, cement plants, smelters, power plants, sulphuric acid plants and animal carcasses burning plants.

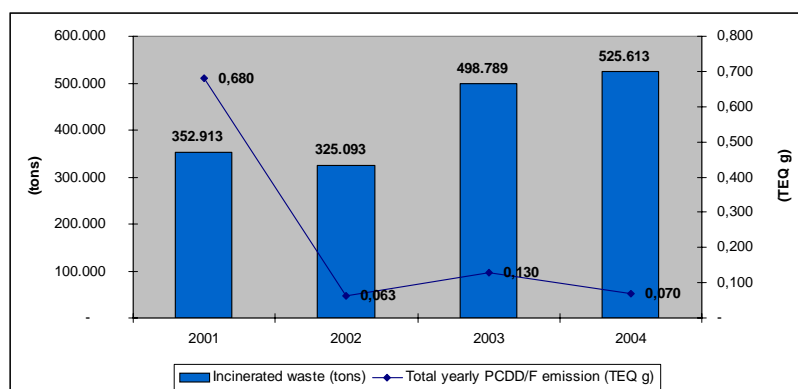


Figure 4: Total dioxin emissions and total burned waste in the Wallonia region of Belgium

## Formation, sources and source inventories

Therefore a lot of experiences could be collected and it could be shown also that the installations of such systems can help to reduce the total PCDD/PCDF emissions of the municipal waste incinerators of a complete region. Hereby the AMESA system can help the operators to understand better the impacts on the dioxin emissions created by the different operating conditions or operating problems like e.g. waste feeding or defect bypass sealing. Therefore the operators are able by using these experiences to optimise their plants, for which they are surely very interested because they are monitored permanently.

A good example for such a reduction is the Wallonia region of Belgium. After a network of 12 AMESA monitors was installed in this region, the total dioxin emissions of 4 waste incinerators were reduced by a factor of 10, whereby up to now the quantity of the total burned waste was increased by almost 50 % (fig. 4)<sup>5</sup>.

### *Sampling of PCBs, PAH, PCBz and PxCp*

The breakthrough tests showed, that all PCBs were adsorbed in the first cartridge and no PCB congeners were detected in the second back-up sampling cartridge. Furthermore, for hexachlorobenzene more than 99 % were adsorbed in the first XAD-II cartridge and 0.9 % was detected in the second back-up XAD-II cartridge (Table 1).

Table 1: PCBz and PCPh concentrations in the 1<sup>st</sup> XAD-II cartridge and percentages in the back-up XAD-II cartridge in 1 four-week and 4 one-week samples; PCBz/PCPh concentrations in the 1<sup>st</sup> adsorption cartridge are defined as 100 %<sup>4</sup>.

Sampling period	4 weeks Long term		Week A Weekly		Week B weekly		Week C weekly		Week D weekly	
	1 <sup>st</sup> cartridge (ug/m <sup>3</sup> )	2 <sup>nd</sup> cartr. (%)	1 <sup>st</sup> cartridge (ug/m <sup>3</sup> )	2 <sup>nd</sup> cartr. (%)	1 <sup>st</sup> cartridge (ug/m <sup>3</sup> )	2 <sup>nd</sup> cartr. (%)	1 <sup>st</sup> cartridge (ug/m <sup>3</sup> )	2 <sup>nd</sup> cartr. (%)	1 <sup>st</sup> cartridge (ug/m <sup>3</sup> )	2 <sup>nd</sup> cartr. (%)
PCBz										
P <sub>5</sub> CBz	0.7456	1.0	0.6563	4.4	0.6769	2.1	0.7318	0.7	0.8181	< 0.1
H <sub>6</sub> CBz	0.1320	0.9	0.1180	4.8	0.1070	1.6	0.1344	0.7	0.1370	< 0.2
Total Penta- and HexaCB	0.8776	0.9	0.7743	4.5	0.7839	2.1	0.8662	0.7	0.9551	< 0.1
PCPh										
2,4,6-T <sub>3</sub> CP	0.6377	0.6	0.4805	0.7	0.5709	0.7	0.4419	0.8	0.5595	0.4
2,3,6- T <sub>3</sub> CP	0.0433	1.9	0.0410	< 1.5	0.0345	< 1.7	0.0256	< 2.3	0.0554	< 1.1
2,4,5- T <sub>3</sub> CP	0.1501	1.1	0.1327	2.9	0.1111	1.5	0.0704	3.1	0.1604	1.0
2,3,5- T <sub>3</sub> CP	0.0926	1.3	0.0770	2.2	0.0621	1.8	0.0456	2.2	0.1055	0.7
3,4,5- T <sub>3</sub> CP	0.0215	< 5.6	0.0225	< 3.6	0.0166	< 3.6	0.0137	< 4.3	0.0238	< 0.4
2,3,4- T <sub>3</sub> CP	0.1517	1.4	0.1456	2.0	0.1090	2.5	0.0714	1.4	0.1656	
2,3,5,6/2,3,4,6- T <sub>4</sub> CP	1.3235	0.4	0.9379	0.8	0.9028	0.3	0.6481	0.6	1.6179	0.2
2,3,4,5- T <sub>4</sub> CP	0.1451	1.7	0.1248	3.1	0.0972	2.0	0.0602	3.0	0.1819	0.7
P <sub>5</sub> CP	0.3049	0.8	0.2278	1.4	0.2275	1.0	0.1286	1.6	0.3551	0.4
Total 10 PCP	2.8703	0.7	2.1898	1.2	2.1898	0.8	1.5055	1.0	3.2251	0.3

Similar results were found in the weekly tests. However in samples A and B slightly increased PCBz and PCP values were detected (up to 5 %). However the low breakthrough values in the 4 week measurement show that the analysed chlorobenzene and chlorophenol do not migrate through the cartridge within the 4 weeks time frame.

### **3.3. Monitoring of POPs by AMESA system based on volatility considerations**

The adsorption of organic compounds correlates with the volatility of a molecule. The boiling point is a good property to compare the volatility of organic molecules and therefore estimate their adsorption properties. The

commonly analysed T<sub>4</sub>CDD/T<sub>4</sub>CDF to O<sub>8</sub>CDD/O<sub>8</sub>CDF (containing the toxic 2,3,7,8-substituted congeners with boiling points above 400 °C (table 2)<sup>6, 7</sup>. The relevant PCBs (T<sub>4</sub>CBs to D<sub>10</sub>CB, containing the congeners with assigned WHO TEQ values) have comparable boiling points (table 2). Therefore they show similar adsorption behaviour as the PCDD/PCDF which explains the quantitative adsorption in the first XAD cartridge.

The higher chlorinated benzenes and phenols have lower boiling points between ca. 240 °C to 322 °C (table 2). Still their vapour pressure is sufficiently low that they are practically quantitatively adsorbed in the first XAD cartridge and less than 1 % of these compounds are detected in the back-up cartridge (table 1).

The POPs listed in the Stockholm Convention (Aldrine, Chlordane, DDT, Dieldrine, Endrine, Heptachlor, Mirex, Toxaphen) are less volatile<sup>B</sup> compared to pentachlorobenzene and the trichlorophenols. Therefore these compounds have an even better adsorption potential and can therefore also be monitored with the AMESA system.

Table 2: Boiling points (760 mm Hg) of some PCDDs, PCDFs<sup>6, 7</sup> PCPh, PCBz, PAHs, PCBs, DDT and HCH<sup>8, 9</sup>.

<b>Compound</b>	<b>123-T<sub>3</sub>CBz</b>	<b>1235-T<sub>4</sub>CBz</b>	<b>P<sub>5</sub>CBz</b>	<b>H<sub>6</sub>CBz</b>	<b>245-T<sub>3</sub>CP</b>	<b>PCP</b>	<b>HCH</b>
boiling point (° C)	219	247	276	322	253	310	323.4
<b>Compound</b>	<b>Naphtalene</b>	<b>Phenantrene</b>	<b>Pyrene</b>	<b>Benz[a]pyrene</b>	<b>Biphenyl</b>	<b>PCBs</b>	<b>DDT</b>
boiling point (° C)	217	340	404	495	256	350-550	260
<b>PCDD</b>	<b>DD</b>	<b>23-D<sub>2</sub>CDD</b>	<b>124-T<sub>3</sub>CDD</b>	<b>2378-T<sub>4</sub>CDD</b>	<b>123678-H<sub>6</sub>CDD</b>	<b>H<sub>7</sub>CDD</b>	<b>O<sub>8</sub>CDD</b>
boiling point (° C)	279	358	375	447	487	507	510
<b>PCDF</b>	<b>DF</b>	<b>23-D<sub>2</sub>CDF</b>	<b>238-T<sub>3</sub>CDF</b>	<b>2378-T<sub>4</sub>CDF</b>	<b>123678-H<sub>6</sub>CDF</b>	<b>H<sub>7</sub>CDF</b>	<b>O<sub>8</sub>CDF</b>
boiling point (° C)	287	375	408	438	488	507	537

#### 4 Conclusions

The results of the present sampling tests show that the AMESA<sup>®</sup> sampling system can be used for long term monitoring of the full range of U-POPs (PCDD/PCDF, PCBs, HCB) listed under the Stockholm Convention. Furthermore the test revealed that the AMESA<sup>®</sup> system is capable to adsorb and hence monitor even molecules with higher volatility (pentachlorobenzene, tri- to pentachlorophenol). Since all POPs listed in Stockholm Convention are less volatile (Aldrine, Chlordane, DDT, Dieldrine, Endrine, Heptachlor, Mirex, Toxaphen) the AMESA<sup>®</sup> system has the potential to sample the full range of POPs. This indicates that the AMESA<sup>®</sup> system can be applied for monitoring and supervision of air emissions of POPs remediation projects and POPs destruction processes.

#### References

- 1) Stockholm Convention <http://www.pops.int/>
- 2) W. Funcke, H. Linnemann, Ch. Phillipp; Long-term-Sampling Method for Polychlorinated Dibenzofurans (PCDF's) and Dibenzo (p) dioxins (PCDD's) in Flue Gas of Combustion Facilities, *Chemosphere*, **1993**, 26, 2097-2101
- 3) Ernst Becker, Jürgen Reinmann, Werner Rentschler, Johannes Mayer, Continuous Monitoring of the Dioxin/-Furan Emission of all Waste Incinerators in Belgium, *Organohalogen Compounds*, **2000**, Vol. 49S
- 4) W. Funcke, H. Linnemann, Messen von PCDD, PCDF, sowie organischen Substanzen mit vergleichbarer Flüchtigkeit und Polarität in Abgasen von Feuerungsanlagen bei Anwendung des „Adsorptionsverfahrens“. GfA Report, January 1994.
- 5) <http://environnement.wallonie.be/data/air/dioxines/menu/menu.htm>
- 6) B. F. Rordorf, *Thermochimica Acta*, 112 (1987) 117.
- 7) B. F. Rordorf, *Chemosphere*, 18 (1989) 783.
- 8) P.C Weast, M. J. Astle, W. H. Beyer (Eds.), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 1984.
- 9) Aldrich Katalog - Handbuch Feinchemikalien, Steinheim (Germany), 1995.

<sup>B</sup> DDT with the highest vapour pressure has a boiling point of 260 °C. For the other POPs with lower vapour pressure no boiling points can be assigned since these compounds degrade before reaching the temperature window for evaporation.