CONTINUOUS MONITORING OF UNINTENTIONALLY PRODUCED POPS LISTED UNDER THE STOCKHOLM CONVENTION (PCDDS/PCDFS, PCBS, HCB) USING AMESA® LONG TERM SAMPLING SYSTEM

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Abstract: *After recognising more than 25 years ago, that combustion and incineration facilities are sources for polychlorinated dioxin (PCDD) and furans (PCDF), there were developed different methods to sample and to determine the dioxin concentrations in flue gas emissions.*
Because all the methods were manual sampling methods, the maximum sampling times were limited to several hours. Such spot measurements do not give reliable informations about the total PCDD/PCDF and other POPs emissions of a plant and do not help to decrease the mistrust of the residents living near to such plants. Since continuous online monitoring of PCDD/PCDF is not feasible for compliance measurements, the continuos sampling is the method of choice for supervision of facilities. The long-term sampling of PCDD/PCDF emissions over the whole year gives comprehensive information on the total emission of a facility and details of the emission of the chosen time periods.
Therefore long term sampling with AMESA 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)[1] lists in addition to PCDD/PCDF also polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) as unintentionally produced POPs (UP-POPs). This might result in an increased request for emission monitoring of PCDD/PCDF and other UP-POPs. Furthermore one aim of the Stockholm Convention is to continuously reduce and where feasible to eliminate UP-POPs in the next two decades. Furthermore the convention aims in destruction of POPs stockpiles and POPs remediation projects. These activities will request a strict emission monitoring including PCDD/PCDF, PCBs and other UP-POPs. Therefore the question arose if all listed UP-POPs can be monitored by the AMESA system under the standard application (XAD2, 30 °C, 4 weeks sampling duration) or if a modification of the sampling system would be necessary.
This presentation describes the test conditions and the results which where found during tests in waste incineration plants. For sampling term up to 4 weeks PCBs were adsorbed quantitatively by the AMESA system under the standard application. Also the lower volatile hexachlorobenzene and pentachlorobenzene was adsorbed by more than 99%. The results show that the AMESA sampling system can be used for long term monitoring of the full range of UP-POPs listed under the Stockholm Convention and can therefore be used for monitoring of UP-POPs emission from facilities and can be used for supervision of air emissions from POPs remediation and destruction projects.

Key Words: Dioxins, PCBs, POPs, Stockholm Convention, Continuous Monitoring

1. INTRODUCTION

The functional principle of the AMESA® system was described in several publications[2, 3]. 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 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.

Fig. 1 AMESA controller


Fig. 2 AMESA control cabinet


Fig. 3 XAD II cartridge box

2. APPLICATION AND TEST OF AMESA IN MUNICIPAL AND HAZARDOUS WASTE INCINERATORS

In several measurement campaigns it was already improved the comparability of PCDD/PCDF short term (6 to 16 h) sampling results to long-term (> 16 h) sampling results. Therefore several short term (6 to 18 h) samplings were performed parallel to 4 three-days samplings and in a second measuring campaign at the same incinerator 4 weekly samplings were performed in parallel to 1 four-week sampling[4].

After these first positive results and the successful passing of the instrument in a German Type Performance Test, the instrument was getting a kind of standard in Europe and in Belgium specifically where a complete network of approx. 50 systems was installed.
In other measurement campaigns a double XAD II cartridge was installed to check for possible breakthroughs during long terms sampling. Especially the question of possible breakthroughs by higher XAD II cartridge temperatures was of interest and therefore checked by several sampling campaigns. In these campaigns the 1st cartridge was heated up to + 50 °C and the 2nd cartridge was kept cool below +20 °C. The results for polychlorinated benzenes (PCBz) and phenols (PCPh) are discussed below.

3. RESULTS AND DISCUSSIONS

3.1. Monitoring of PCDD/PCDF

Since 1996 the AMESA systems were installed in many different municipal waste incinerators. 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 country.
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 air emissions of 4 waste incinerators were reduced by a factor of 20, though the quantity of the total burned waste was increased by almost 50 % (fig. 4)[5].
It could be demonstrated that the AMESA system can help the operators to better understand the impacts on the dioxin emissions created by the different operating conditions or operating problems like e.g. waste feeding, start-up and shut-down periods or defect bypass sealing. By using these experiences the operators are able to optimize their plants with respect to PCDD/F emissions. Since they are monitored continuously, focus and interest are put upon them.
In the last years the application range was extended more and more to other kind of plants like e.g. biomass combined heat and power plants, medical waste incinerators, cement plants, smelters, coal power plants, animal carcasses burning facilities and sulphuric acid plants. Furthermore most of the large hazardous waste incinerators in Belgium, France, Finland and Sweden have installed AMESA for continuous UP-POPs monitoring.
Therefore the experiences increase for a wide range of plants and operating conditions including most of the facilities listed under the Stockholm Convention.

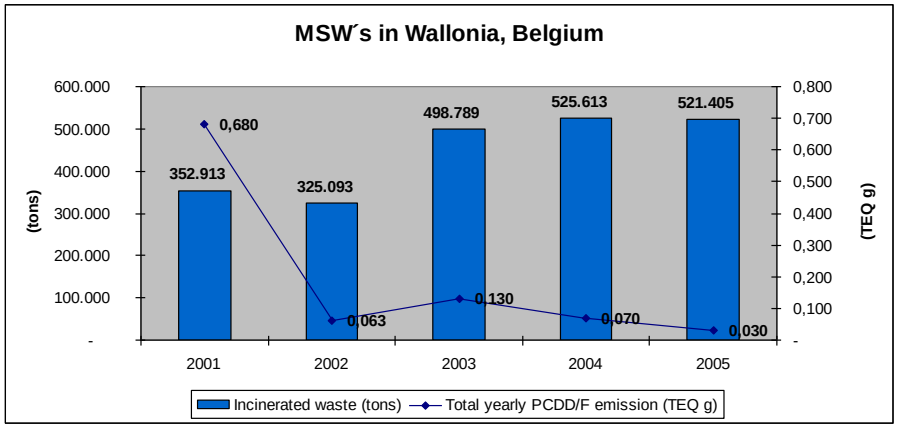

Fig. 4 Total dioxin emissions and total burned waste in the Wallonia region of Belgium

3.2. Sampling of PCBs, PAH, PCBz and PxCP

The breakthrough tests showed, that all PCBs were adsorbed in the first cartridge. The only PCB congeners detected in the second back-up sampling cartridge was the field blank of PCB #118 which is a prominent congener in technical mixtures and therefore present in the ambient air of hazardous waste incinerators).

Also hexachlorobenzene and pentachlorobenzene were adsorbed to more than 99.5% in the first XAD-II cartridge for the full temperature range of AMESA applications (normally between 20 °C and 50°C) (Table 1). Even the more volatile tetrachlorobenzenes were detected to more than 99 % in the first cartridge(Table 2).

Table 1. WHO PCBs concentrations in the 1st and 2nd XAD-II cartridge in 2 weeks sampling at different temperatures of the 1st cartridge.

Sampling period	2 weeks Long term (+50 °C)		2 weeks (+ 20 °C)	
	1st cartridge (ng/m3)	2nd (ng/m3)	1st cartridge (ng/m3)	2nd (ng/m3)
PCB 81	0,056	n.n.	0,017	n.n.
PCB 77	0,014	n.n.	0,009	n.n.
PCB 126	0,015	n.n.	0,007	n.n.
PCB 169	0,001	n.n.	0,003	n.n.
PCB 123	0,010	n.n.	0,004	n.n.
PCB 118	0,049	0,005	0,025	n.n.
PCB 114	0,026	n.n.	0,010	n.n.
PCB 105	0,025	n.n.	0,011	n.n.
PCB 167	0,009	n.n.	0,004	n.n.
PCB 156	0,015	n.n.	0,009	n.n.
PCB 157	0,010	n.n.	0,004	n.n.
PCB 189	0,010	n.n.	0,006	n.n.

Table 2: Chlorobenzenes (HexaCB, PentaCB and TetraCBz in the 1st XAD-II cartridge in 2 weeks sampling at 20 °C and 50 °C.

	(%) adsorbed in 1st cartridge (+50 °C)	(%) adsorbed in1st cartridge (+20 °C)
Sum Tetrachlorobenzene	99.35	99.00
Pentachlorbenzene	99.96	99.65
Hexachlorobenzene	99.93	99.80

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_4CDD/T_4CDF to O_8CDD/O_8CDF (containing the toxic 2,3,7,8-substituted congeners with boiling points above 400 °C (table 3)[6, 7]. The relevant PCBs (T_4CBs to D_{10}CB, containing the congeners with assigned WHO TEQ values) have comparable boiling points (table 3). Therefore they show similar adsorption behaviour as the PCDD/PCDF which explains the quantitative adsorption in the first XAD cartridge.
The higher chlorinated benzenes have lower boiling points between ca. 240 °C to 322 °C (table 3). 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 2).

Table 3: Boiling points (760 mm Hg) of some PCDDs, PCDFs [6, 7] PCPh, PCBz, PAHs, PCBs, DDT and HCH[8, 9].

Compound	**123-T_3CBz**	**1235-T_4CBz**	**P_5CBz**	**H_6CBz**	**245-T_3CP**	**PCP**	**HCH**
boiling point (° C)	219	247	276	322	253	310	323.4
Compound	**Naphtalene**	**Phenantrene**	**Pyrene**	**Benz[a]pyrene**	**Biphenyl**	**PCBs**	**DDT**
boiling point (° C)	217	340	404	495	256	350-550	260
PCDD	**DD**	**23-D_2CDD**	**124-T_3CDD**	**2378-T_4CDD**	**123678-H_6CDD**	**H_7CDD**	**O_8CDD**
boiling point (° C)	279	358	375	447	487	507	510
PCDF	**DF**	**23-D_2CDF**	**238-T_3CDF**	**2378-T_4CDF**	**123678-H_6CDF**	**H_7CDF**	**O_8CDF**
boiling point (° C)	287	375	408	438	488	507	537

4. CONCLUSION

The results of the present sampling tests show that the AMESA® sampling system can be used for long term monitoring of the full range of UP-POPs (PCDD/PCDF, PCBs, HexaCB) listed under the Stockholm Convention and even for the lower volatile pentachlorobenzene and tetrachlorobenzene.
Additionally it was demonstrated that even at the XAD II cartridge upper temperature use (+50 °C) there are no relevant losses of any UP-POPs.
Furthermore the test revealed that the AMESA® system is capable to adsorb and hence monitor even molecules with higher volatility (pentachlorobenzene and tetrachlorobenzene). Since all POPs listed in Stockholm Convention are less volatile (Aldrine, Chlordane, DDT, Dieldrine, Endrine, Heptachlor, Mirex, Toxaphen) the AMESA® system has the potential to sample the full range of POPs. This indicates that the AMESA® system can be applied for monitoring and supervision of air emissions of POPs remediation projects and POPs destruction processes.

5. REFERENCES

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