

TEMPERATUR RANGE FOR CONTINUOUS MONITORING OF UNINTENTIONALLY PRODUCED POPs (PCDD/Fs, PCBs, HCB) USING AMESA® LONG TERM SAMPLING SYSTEM

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Introduction

Over the past 10 years it was discovered that especially during start-up and shut-down periods of (state of the art) incinerators the dioxin emissions in the flue-gas can increase compared to normal operation¹⁻⁴ up to factors of 1000 in raw gas and after bag-filters^{1 A}. Another study quantified that around 60 % of the yearly dioxin emissions of a plant are produced and emitted during one start-up². These findings revealed and demonstrated that dioxin and POPs emissions of incinerators cannot be reliably monitored by manual short term sampling since such spot measurements represent only 1 – 2 % of the yearly operating time of the plants during normal operating conditions. Hence it is obvious that short term measurements are not suitable for compliance measurements of the actual average PCDD/F emissions of a plant. Since continuous online monitoring of PCDD/F is not feasible for compliance measurements⁵, the continuous sampling with e.g. AMESA (Adsorption Method for Sampling of dioxins and furans) is the method of choice for supervision of incinerators and other thermal facilities. The increasing interest can be noted also by the fact that the European CEN/TC 264 WG 1 applied in March 2008 for a project to establish a standard for long-term sampling of PCDD/F and dioxin-like PCBs (as EN 1948-5). Additionally in the assessment of Directive 2000/76 EC⁶ the long-term sampling of PCDD/Fs and PCBs was included as a proposed amendment of considerable interest.

A specific area which requires continuous monitoring of PCDD/F and other unintentionally produced POPs (UPOPs) is the destruction of POPs⁶ stockpiles (PCBs, Pesticide stockpiles) and other waste streams with elevated halogen content (e.g. waste from organochlorine or organobromine industry, electronic waste etc.). POPs destruction projects will increase in the framework of the Stockholm Convention forcing the reduction and elimination of POPs in the next two decades (www.pops.int). These activities will request a strict emission monitoring⁶. It has already been demonstrated successfully that the AMESA system has the capability to monitor all U-POPs (PCDD/F, PCBs and HCB) listed under the Stockholm Convention under standard application (XAD-II, 30 °C, 4 weeks sampling duration)⁷. In most thermal plants the ambient temperatures around the stack are above 30 °C and in some cases an active cooling would be necessary. To minimize these cooling efforts it is interesting to evaluate if also by higher sampling temperatures good sampling efficiencies can be guaranteed.

The present paper describes results from tests with the sample cartridge temperature of up to 50 °C in a hazardous waste incineration plant during long-term sampling of 4 weeks and 2 weeks respectively. The results demonstrate that the AMESA system is capable of sampling PCBs and the full range of Stockholm Convention UPOPs with XAD2 temperatures up to +50 °C. This is a cartridge temperature which is relatively easy to maintain by the usage of a cooled probe up to flue-gas temperatures of 200 – 250 °C.

Materials and Methods

The tests were performed in a hazardous waste incinerator. The hazardous waste incinerator consists of a rotary kiln, a secondary combustion chamber (SCC), a boiler and flue gas cleaning. The AMESA sampling device is installed after the last cleaning step in the flue gas cleaning process, i.e. just before the stack. The flue gas cleaning consists of a semi-dry absorber, a fabric filter and a wet scrubber. Between the absorber and the fabric filter activated carbon is injected for dioxin removal.

^A The emissions during start-up could be significantly reduced by optimizing the start-up procedures (Gass et al 2003). This optimisation should be required for each incinerator.

The functional principle of the AMESA[®] system was described in earlier publications^{8,9}. 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. 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 and POPs emissions of a plant can be determined.

To determine the adsorption capacities or possible breakthroughs of the XAD-II cartridge the cartridge box of the AMESA system which included the XAD-II-cartridge was equipped with a door that contained an integrated climate control device, so that the temperature in the cartridge box could be kept constant between +20 and +50°C. To further assure that the desired temperature was achieved, the sampling probe was tempered with a temperature controlled circulating water flow. A second back-up cartridge was placed after the main cartridge to measure possible breakthroughs. This cartridge was placed in a water bath and kept below +20°C during all the tests. The temperatures of the probe, the cartridge, and the water bath were monitored continuously and stored as minute averages in a computer.

The cartridges were spiked with ¹³C-labeled PCB#60, PCB#127 and #159 and 1,2,3,4-Tetrachlorobenzene (TetraCBz) in addition to the PCDD/F sampling standards. The back-up cartridge was spiked with ¹³C-labelled PCB#47.

After the sampling the cartridges were analysed by an accredited laboratory with GC/HRMS.

Results and Discussion

PCBs are one of the key POPs in stockpiles and additional they are one of the key POPs listed in the Stockholm Convention. For the tests the cartridges were spiked with sampling standards to evaluate the adsorption limits. The breakthrough tests showed that all PCBs were adsorbed in the first cartridge. The only PCB congener 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 (Table 1). The test revealed that care has to be taken with field blanks in incinerators where ambient air contents of PCBs are orders of magnitudes higher compared to the PCB concentrations in the off gas: Even for AMESA samples with volumes of more than 100 Nm³, the field blanks for the marker PCBs (including PCB #118!) can be in the range of the sampled PCBs. Therefore for short term sampling with volumes around 5 Nm³ the field blank values (and sometimes the laboratory blank values) can be expected in concentrations above the actual sampled PCBs from the off gas.

Table 1. WHO PCBs concentrations in the 1st and 2nd XAD-II cartridge in 2 and 4 weeks sampling at different temperatures of the 1st cartridge (n.d. = non-detectable, detection limit 0,05 ng, no laboratory blank was found).

Sampling period	4 weeks (+50 °C)		2 weeks (+50 °C)		2 weeks (+ 20 °C)	
	1 st cartridge (ng)	2 nd (ng)	1 st cartridge (ng)	2 nd (ng)	1 st cartridge (ng)	2 nd (ng)
PCB 81	0.288	n.d.	9.255	n.d.	2.272	n.d.
PCB 77	1.725	n.d.	2.314	n.d.	1.203	n.d.
PCB 126	1.725	n.d.	2.479	n.d.	0.936	n.d.
PCB 169	0.575	n.d.	0.165	n.d.	0.401	n.d.
PCB 123	0.288	n.d.	1.653	n.d.	0.535	n.d.
PCB 118	4.026	0.575	8.098	0.826	3.342	0.658
PCB 114	1.725	n.d.	4.297	n.d.	1.337	n.d.
PCB 105	2.013	n.d.	4.132	n.d.	1.470	n.d.
PCB 167	0.575	n.d.	1.487	n.d.	0.535	n.d.
PCB 156	1.438	n.d.	2.479	n.d.	1.203	n.d.
PCB 157	1.150	n.d.	1.653	n.d.	0.535	n.d.
PCB 189	0.863	n.d.	1.653	n.d.	0.802	n.d.

Additional proofs that the PCB #118 in the 2nd cartridge (table 1) was a field blank is the fact that the more volatile PCB's #81 and #77 with comparable concentrations as PCB #118 in the off gas were not detected in the 2nd cartridge. Further the more volatile sampling spike PCB #60 added to the first sampling cartridge was not detected in the second cartridge (considering the detection limits, approximately 1% of sampling spike would have been detected).

The adsorption limit of XAD-II was evaluated by additional analysis of the more volatile chlorobenzenes (Table 2; Figure 2). Surprisingly the HexaCBz, PentaCBz and even the TetraCBz were adsorbed at the two weeks measurement even at 50 °C for more than 99% in the first cartridge. Therefore for the 2 weeks standard sampling period of AMESA, even the chlorobenzenes can be sampled at our recommended upper temperature limit for XAD-II.

When prolonging the sampling duration to 4 weeks HexaCBz was still detected as more than 99% in the first cartridge. However approximately 14% of TetraCBz was detected in the back-up cartridge (kept below 20 °C) (Figure 2).

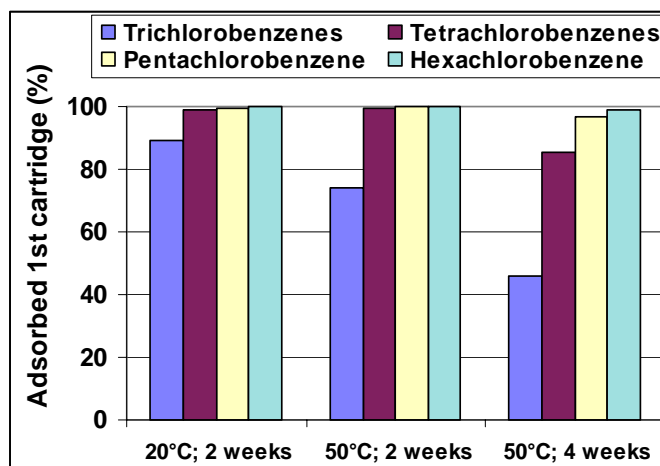


Figure 2: Chlorobenzenes (Trichlorobenzenes to Hexachlorobenzene) in the 1st XAD-II cartridge in 4 weeks sampling at 50 °C and 2 weeks sampling at 20 °C and 50 °C (Back-up cartridge below 20 °C)

Table 2: Boiling points (760 mm Hg) of some PCDDs, PCDFs^{10,11}, Pentachlorophenole (PCPh), Pentachlorobenzene (PCBz), Polyaromatic Hydrocarbons (PAHs), PCBs, Dichlorodiphenyltrichloroethane (DDT) and Hexachlorocyclohexane (HCH)^{8,9}.

Compound	123-T₃CBz	1235-T₄CBz	P₅CBz	H₆CBz	245-T₃CP	PCP	HCH
boiling point (° C)	219	247	276	322	253	310	323.4
Compound	Naphthalene	Phenanthrene	Pyrene	Benz[a]pyrene	Biphenyl	PCBs	DDT
boiling point (° C)	217	340	404	495	256	350-550	260
PCDD	DD	23-D₂CDD	124-T₃CDD	2378-T₄CDD	123678-H₆CDD	H₇CDD	O₈CDD
boiling point (° C)	279	358	375	447	487	507	510
PCDF	DF	23-D₂CDF	238-T₃CDF	2378-T₄CDF	123678-H₆CDF	H₇CDF	O₈CDF
boiling point (° C)	287	375	408	438	488	507	537

Of additional interest was an investigation into whether rinsing of the sampling probe was required in the long-term sampling of dioxins. In the case of negligible losses it is then not necessary that the probe is rinsed after the sampling. In these tests therefore the sampling probe was rinsed twice after a sampling period of 2 weeks and the rinsing solution was analyzed separately from the cartridge. In both cases no dioxins/furans were detected in the washing solution of the sampling probe (Table 3). Therefore in this state of art facility with low dust (<2 mg) and soot content in the off-gas, less than 3% of the PCDD/Fs were adsorbed in the probe and the probe does not need to be rinsed. Experiences from facilities with high dust/soot content show that the concentrations in the probe can be above 10% and have to be included in the sampling¹².

Table 3. Losses in sampling probes after 2 weeks sampling

	Total TEQ (ng) in XAD-II cartridge	Total TEQ (ng) in rinsing solution of probe (detection limit < 0.004 ng/congener)
2 weeks sampling no. 1:	0,782	n.d.
2 weeks sampling no. 2	1,050	n.d.

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 UPOPs (PCDD/F, PCBs, HexaCBz) listed under the Stockholm Convention. Additionally it was demonstrated that even at the XAD II cartridge upper temperature used (50 °C) there are no significant losses of any UPOPs.

Furthermore the tests revealed that the AMESA[®] system is capable of adsorbing and hence monitoring even molecules with higher volatility (pentachlorobenzene and tetrachlorobenzene) and under standard conditions (30 °C) even the trichlorobenzenes can be sampled over several weeks.

Since all POPs listed in the Stockholm Convention are less volatile (Aldrine, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene) 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.

References

- 1a. Gass H.C, Lüders K and Wilken M. *Organohalogen Compounds* 2002; 56: 193-196.
- 1b. Gass H.C, Lüders K, Wilken M. *Organohalogen Compounds* 2003; 63: 25-28.
2. Wang L.C., His H.C., Chang J., Yang X, Chang-Chien G, Lee W, *Chemosphere* 2007, 67: 1346-1353.
3. Tejima H., Nishigaki M., Fujita Y., Matsumoto A., Takeda N. and Takaoka M. *Chemosphere* 2007; 66: 1123–1130.
4. Loethgren C.J. and van Bavel B. *Chemosphere* 2005: 61:405-412.
5. Weber R. *Organohalogen Compounds*. 2005; 67:321-325
6. Weber R. *Chemosphere* 2007; 67:109-117
7. Reinmann J., Kuch B., Weber R. *Organohalogen Compounds*, 2006, 68: 852-855.
8. Funcke W., Linnemann H., Phillipp Ch. *Chemosphere* 1993, 26: 2097-2101.
9. Becker E., Reinmann J., Rentschler W, Mayer J. *Organohalogen Compounds*, 2000, 49: 21-23.
10. Weast P.C, Astle M. J., Beyer W. H. (Eds.), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 1984.
11. Aldrich Katalog - Handbuch Feinchemikalien, Steinheim (Germany), 1995.
12. Mehl K.W., Huang A, Reinmann J., *Organohalogen Compounds*, 2003, 60: 497-500.