Certification of a Long-Term Sampling System for PCDFs and PCDDs in the Flue Gas from Industrial Facilities

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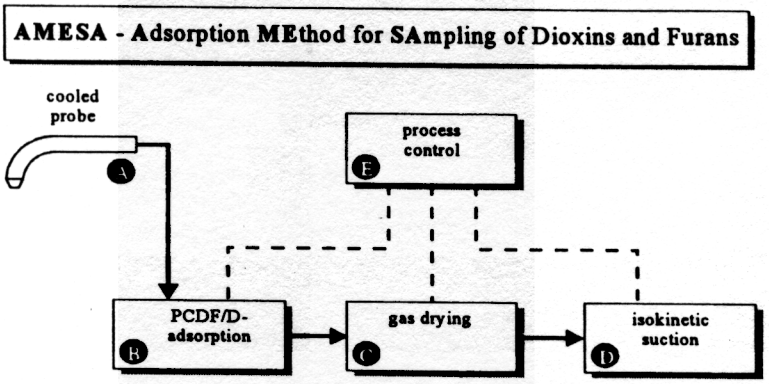
Abstract
A long term sampling system for PCDF/Ds, called: „AMESA" (Adsorption MEthod for SAmpling of dioxins) has been tested and undergoing a certification procedure according to the German guidelines for certification of systems for continuous supervision of special substances. The certification covered parameters such as disposability of the system, reproducibility of the results and comparability of the sampling method with German and European standard methods. Furthermore break throughs, blank values and sample storability were inverstigated. The results prove that AMESA is a state of the art sampling system for continuous supervision of dioxin/furan emissions.

Introduction
In 1993 and 1994 the companies bm and GfA developed a system, called AMESA, for long term supervision of dioxin emissions from industrial processes based on the adsorption method [1,2]. The AMESA system has been tested in coal fired plants, steel plants and municipal and industrial waste incinerators. Sampling periods were between 4 h and 4 weeks. Dioxin concentrations ranged between < 0.001 ng(ITE)/m^3 and > 5 ng(ITE)/m^3.
To reach the requirements of § 6 of the 17th ordinance to the German Federal Immission Control Law (17. Bundes-Immissionsschutz-Verordnung / 17. BImSchV) [3], AMESA had to be tested according to the guidelines for certification of systems for continuous supervision of special substances [4].

Experimental
The certification tests were carried out by the TÜV Rheinland Sicherheit und Umweltschutz GmbH, D-51105 Köln, in 1996/1997. Up to three identical AMESA systems were in use during the tests. A sketch of AMESA is shown in figure 1.

Fig. 1: Sketch of AMESA



A Cooled (< 50 °C) titanium probe for isokinetic extraction of a volume stream.

B Measurement stream and condensate are drawn through the cartridge filled with adsorber resin (quartz wool as a prefilter).

C Drying of the measurement stream by cooling (< 5 °C).

D Infinitely variable control of the isokinetical extraction. Control possible either by means of an analogue volume stream signal from the system or by means of a separate measuring instrument.

E User-friendly operation of **AMESA** by menue dialogue in process controller. Data input for plant specific parameters and operation by means of keyboard and LCD-monitor. Readout and printout of all data and parameters possible at any time. Analysis of the emission values by means of SRAM memory chip and analysis results.

The whole certification procedure was divided in a laboratory test phase and a field test phase. After the examination program in the TÜV-laboratory had been finished whithin about 3 months the field tests were performed in the MSWI in Amsterdam. Up to 3 AMESA systems were in parallel operation for a 6 month period. During this time more than 150 PCDF/D analyses have been carried out in flue gas, condensates, back up units, washings and blanks.
The results of the certification tests for the following selected parameters are presented here: Disposability of the AMESA systems during the test period, reproducibility of the results, comparison of the results gained using AMESA with those received by German and European standard methods, potential break throughs from 4 week samples, blank values, storage periods of AMESA samples [5].

Results and Discussion

Disposability: During the field tests the disposability of 3 AMESA systems was 97 %.

Reproducibility: The reproducibility $R_D = X/(S_D \times t_{95\%})$ was calculated for the sampling periods 6 to 16 h, 16 h to 2 weeks and 4 weeks (R_D: reproducibility from double measurments; X: average; S_D: standard deviation from double measurments; $t_{95\%}$: student factor at 95 % statistical confidence).
R_D was 6.8 for short term samples, 5.5 for samples lasting 16 h to 2 weeks and 3.9 for long-term samples. All R_D values were higher than required.

Comparability: The results from the AMESA samples were compared with those using the adsorption method, a method according to VDI-Guideline 3499, part 2 [6], and a method according to EN 1948 [7]. In the scope of quality assurance the results were cross checked by interlaboratory exchange of sample extracts. Parallel samplings using the different methods mentioned above showed comparable dioxin results.

Break throughs: The PCDF/D amounts detected in the condensate that had passed the XAD-2 adsorbent were 1 to 3 % related to the ITE value found in the adsorbent. The PCDF/D percentage in a back up XAD-2 cartridge did not exceed 1.2 %.

Blank values: The absolute PCDF/D blank values from 5 XAD-2 cartriges were between 0.0060 and 0.0122 ng (ITE)/cartrige. The average was 0.0078 ng (ITE)/cartrige. This means a relative blank value of ca. 1 to 1.5 % related to the EC 0.1 ng (ITE)/m^3 limit for 6 to 16 h samplings and < 0.1 % for samplings of 1 week and longer.

Storage Periods: A part of the samples from the beginning of the tests was stored in a dark room at 18° C and analysed after 3 months storage and 5 months storage, respectively. The PCDF/D amounts of the stored samples as well as the PCDF/D profiles were comparable with those from parallel samples which had been analysed immediately after sampling had been finished.

The discussed results prove that AMESA is a state of the art sampling system for dioxins in emissions. In February 1998 AMESA has been announced as capable for long-term supervision of PCDF/D emissions from plants that underlie the regulations of the German 17th Bundes-Immissions-Schutz-Verordnung (17th BImSchV) [8]. Using AMESA the EC threshold value of 0.1 ng (ITE) /m^3 e.g. for waste incinerating plants can be supervised quasi continuously within 12 PCDF/D samples per year. Exceeding the results from the certification tests AMESA has been running more than 4 years in several plants, mostly waste incinerators, and has shown its potential to optimize the plant operation with respect to dioxin emissions.

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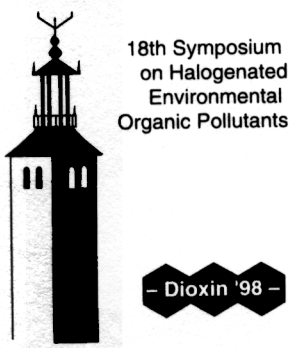
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