Certification of a long-term sampling system for PCDFs and PCDDs in the flue gas from industrial facilities

Johannes Mayer a,*, Heinz Linne mann a, Ernst Becker b, Werner Rentschler b, Wolfgang Jocket c, Peter Wöhring c, Bernhard Gerchel c

a GFA Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH (GFA), D-40216 Düsseldorf, Germany
b bm Becker meßtechnik GmbH (bm), D-71364 Winnenden, Germany
c TÜV Rheinland Sachkunde und Umweltschutz GmbH (TÜV), D-51105 Köln, Germany

Abstract

AMESA (adsorption method for sampling of dioxins) is a fully automatic system for long-term monitoring of dioxin emissions from industrial processes based on the adsorption method. The system has been tested and undergoing certification procedures according to the German guidelines for certification of systems for continuous monitoring 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 through, blanks and sample storability were investigated. The results prove that AMESA is a state of the art sampling system for continuous monitoring of dioxin/PCDD emissions. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

In 1993 and 1994 the companies bm and GFA developed a system, called AMESA (adsorption method for sampling of dioxins), for long-term supervision of dioxin emissions from industrial processes based on the adsorption method (Funcke et al., 1993a,b). The AMESA system has been tested in a first step at coal fired plants, steel plants and municipal and industrial waste incinerators with dioxin concentrations between <0.001 ng (t-TEQ)/m³ and >5 ng (t-TEQ)/m³. Sampling periods were between 4 h and 4 weeks. A sketch of the AMESA system is shown in Fig. 1.

To reach the requirements of Section 6 of the 17th ordinance to the German Federal Ambient Air Control Law (17. Bundes-Immissionschutz-Verordnung/17. BImSchV) (BMU, 1990), AMESA had to be tested according to the guidelines for certification of systems for continuous monitoring of special substances (BMU, 1995).

A Cooled (<50°C) titanium probe for isokinetic extraction of a volume stream.
B Measured 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 isokinetic 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 menu dialogue in process controller. Data input for plant specific parameters and operation by means of keyboard and LCD monitor.

* Corresponding author.
Email address: jmayer@gfa-es.de (J. Mayer).
2. Experimental

The certification tests were carried out by the TÜV Rheinland Sicherheit und Umweltschutz GmbH, D-51105 Köln, in 1996/1997 (Wilbring and Gerchel, 1997). The whole certification procedure was divided into a laboratory test phase (approx. 3 months) in the TÜV-laboratory and a field test phase (approx. 6 months) at the MSWI in Amsterdam. Up to three identical AMESA systems were in use during the tests. The field test included the following subjects among others:

- Subjects of Field Test (Selection)
  - Testability of the system
  - Breakthrough
  - Reproducibility
  - Blank values
  - Comparability with EN 1948
  - Storability of the samples

3. Results and discussion

The results of the certification tests for the following selected parameters are presented here: Testability 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 breakthrough from 4 week samples, blanks, storage periods of AMESA samples (Wilbring and Gerchel, 1997).

**Reproducibility**

The reproducibility \( R_d = X / (S_d \times 100) \) was higher than required for samples lasting 16 h to 2 weeks and for long-term samples (Fig. 2).

**Comparability:**

A very good agreement between measurements according to Adsorption Method and to EN 1948 (European Committee for Standardization, 1997) could be confirmed (Fig. 3).

**Breakthrough:**

Only 1 to 3% of PCDD/F (I-TEQ) was found in the condensate and the amount in a back up XAD-2 cartridge did not exceed 1.2% I-TEQ (Table 1).

<table>
<thead>
<tr>
<th>Table 1: Results of break through test</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td>Sample 1</td>
</tr>
<tr>
<td>Sample 2</td>
</tr>
<tr>
<td>Sample 3</td>
</tr>
<tr>
<td>Sample 4</td>
</tr>
<tr>
<td>Sample 5</td>
</tr>
<tr>
<td>Sample 6</td>
</tr>
<tr>
<td>Sample 7</td>
</tr>
<tr>
<td>Sample 8</td>
</tr>
<tr>
<td>Sample 9</td>
</tr>
</tbody>
</table>
Table 2
Results of blank test

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Average Blank Value (I-TEQ) (ng/canister)</th>
<th>Standard Deviation (I-TEQ) (ng/canister)</th>
<th>Typical Sample Volume (ml)</th>
<th>Concentration (I-TEQ) (ng/m³)</th>
<th>Proportional Blank Value related to Emission Limit (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short-term 6-h sample</td>
<td>0.0078</td>
<td>0.0027</td>
<td>5</td>
<td>0.00157</td>
<td>1.0</td>
</tr>
<tr>
<td>Daily sample (24-h)</td>
<td>0.0078</td>
<td>0.0027</td>
<td>10</td>
<td>0.00078</td>
<td>0.8</td>
</tr>
<tr>
<td>1-Week Sample</td>
<td>0.0078</td>
<td>0.0027</td>
<td>30</td>
<td>0.00011</td>
<td>0.1</td>
</tr>
<tr>
<td>4-Week Sample</td>
<td>0.0078</td>
<td>0.0027</td>
<td>140</td>
<td>0.00006</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Fig. 4. Results of storable test (mean values of 5 test series).

Blank values: Blank values were between 0.0060 and 0.0122 ng I-TEQ/canister. This means a relative blank value of approx. 1.0% related to the EC 0.1 ng I-TEQ/m³ limit for 6 h samplings and max. 0.1% for samplings of 1 week and longer (Table 2).

Storage Periods: The PCDF/D amounts of the stored samples (3 months and 5 months) as well as the PCDF/D profiles were comparable with those from parallel samples which had been analyzed immediately after sampling had been finished (Fig. 4).

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 capa-
ble for long-term monitoring of PCDF/D emissions from plants that underlie the regulations of the German 17th Bundes-Immissionsschutz-Verordnung (17th BImSchV) (BMU, 1998). Using AMESA the EC threshold value of 0.1 ng I-TEQ/m³ e.g. for waste incinerating plants can be supervised quasi continuous within 12 PCDF/D samples per year. Exceeding the results from the certification tests AMESA has been running more than 4 yr in several plants, mostly waste incinerators, and has shown its potential to optimize the plant operation with respect to dio-
oxin emissions.

References
Bundesministerium für Umwelt, 1990. Naturschutz und Rea-
kationskunde (BMU), Bundesgesetzblatt, Teil I, Nr. 64, 2545-2555 (in German).
Bundesministerium für Umwelt, 1992. Naturschutz und Rea-
kationskunde (BMU); Gemeinsames Ministerialblatt, 128 B (in German).
Bundesministerium für Umwelt, 1998. Naturschutz und Rea-
kationskunde (BMU); Gemeinsames Ministerialblatt, No. 1, 10 (in German).
Funcke, W., Littgenwein, H., Brokot, G., Göttge, K.-J., 1993. Prebenachweis von polychlorkierten Dibenzodioxinen (PCDD) und polychlorkierten Dibenzofurinen (PCDF) in Abgasen mit einem Adsorptionsverfahren, LISR report No. 119, Lande-
sammlung für Immisionsforschung, Nordrhein-Westfalen, Essen.
Funcke, W., Linnemann, H., Philipp, C., 1993b. Long-term sampling method for polychlorinated dibenzofurins (PCDF) and dibenzodioxins (PCDD) in flue gas of combus-
tion facilities. Chromatographia 26, 2997-2999.
Wihlring, P., Gierich, B., 1997. Bericht über die modellhafte Emissionsprüfung der 4 ausprobenbenannten richtung AME-
SA der Firma Becker GmbH und Gesellschaft für Arbeits-
sätze- und Umweltanalytik mbH, TUF report 91080107,B,
TUV Rheinland Soehne und Umweltschutz GmbH, Köln.