Quality assurance of the dioxin precipitation at a hazardous waste incinerator in the Netherlands using permanent dioxin monitoring

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1 Summary
In 1992 a fixed bed activated carbon filter was installed at the hazardous waste incinerator (STO 6) of Rotterdam by Austrian Energy GmbH to reduce dioxin emissions before they reach the legal limit of 0.1 ng/m³.

During the start-up of this filter system performance tests were done, using the diocin-monitoring system (DMS), a special application of EN 12457.

In August 2000 the DioxinMonitoringSystem® was installed at this hazardous waste incinerator to check the performance of the filter system periodically.

In this paper a control chart is introduced, using the data of the DioxinMonitoringSystem® which enables the operator to evaluate the I-TE emission values by statistical methods.

2 Description of DioxinMonitoringSystem®

The complete system for surveillance of 1 stack consists of the following equipment:

- one sampling unit with 2 probes
- one control unit
- filter units for delivery to the laboratory

3 Analytical method

At the plant the process engineer serves measurement's starting and stopping and exchange of the filter unit. The DioxinMonitoringSystem® is operated with 8 hours and 7 days sampling time and delivers the I-TE mean value of the measurement period.

The DioxinMonitoringSystem® performs the following routines automatically during sampling:

- automatic leak test (to avoid leakage) before start
- automatic cleaning routine for the probes before start (to reduce blank values)
- automatic control of the kathodic sampling
- automatic control of the I-TE sample
- automatic temperature control of mixing chamber and filter unit
- configurable standards (e.g. in case of plant shut down)
- automatic measurement reports

After stopping the measurement the engineer sends the filter unit with connected mixing chamber together with the measurement protocol in a transportation box to the laboratory, where the filter unit is extracted and cleaned according EN 1948 part 2 and evaluated by HTGC/HRMS according to EN 14181 part 1.

The engineer receives the results by E-mail from the laboratory, including:

- the I-TE values obtained at the laboratory
- the statistical evaluation of the obtained results

4 Results of the performance tests in 1992

In 1992 several performance tests (1) of the fixed bed activated carbon filter were done during start-up of the filter system.

| Date       | Laboratory No | Total       | Equivalent I-TE (dry) | Quality assurance of the dioxin precipitation at a hazardous waste incinerator in the Netherlands using permanent dioxin monitoring

5 Statistical data of the DioxinMonitoringSystem®

5.1 Uncertainty caused by the application of reference material

The "C"-Standard reference material is checked by the quality assurance system of the involved laboratory with a threshold level ≤ ± 10% relative.

Because of this threshold level the uncertainty can be estimated with lower than ± 5% relative independent on the concentration level.

5.2 Uncertainty caused by blank values

During the field tests the dioxin measurement working group of CEN (2) the blank values (based on I-TE on a suck volume of 20 l) were determined.

Because of the correlation of these blank values to the sucked flue gas volume, the impact is strong dependent on the sucked flue gas amount.

The DioxinMonitoringSystem® sucked approximately 6 m³ in an eight hours measurement period and approximately 130 m³ in a one-week measurement period.

Before each start the system performs a purge cycle to remove precipitated dust particles from the probes.

This results in an uncertainty of ± 10% for a 6 hour monitoring period

5.3 Uncertainty caused by the volume measurement

The uncertainty of the volume measurement is caused by the error of the gasometers, the error of the temperature and pressure correlation and the error caused by leakage in the sampling system.

The DioxinMonitoringSystem® uses two gasometers for the measurement of the sucked volume, before each start the system performs a test cycle. When the leak test fails the system does not start the measurement.

Summing up all errors the uncertainty of the volume measurement can be estimated with 5% relative.

5.4 Uncertainty because of deviation to representative particle sampling

The uncertainty is dependent on the character of the particles in the stack and the error of the velocity measurement. A detailed discussion of this impact is given in (2).

The fixed bed activated carbon filter has activated carbon grains inside with an average diameter of 120 µm, more than 95% of the dioxin content is adsorbed on particles of a diameter of 1 µm, outside the fixed bed, particles up to 500 µm can be transported to the stack, if released. This can happen as the effect for different filtering/removal of the activated carbon grains. Therefore the representative sampling of the particles has a high impact to the uncertainty.

The DioxinMonitoringSystem® measure the velocity at each probe position by a sensor sequence (velocimetry) in the sampling volume, which is a 1 cm³ cylinder and is defined as the checkvalue, which is 0.019 ng/m³.

5.5 Uncertainty caused by the probe position in the stack

The DioxinMonitoringSystem® uses fixed inserted probes. Therefore no uncertainty impact because of different probe positions can occur.

5.6 Uncertainty defined by the recovery standard

Before each measurement "C" recovery standard is applied to the filter unit, to have a check value for total removal during the sampling.

A detailed discussion of the uncertainty is given in (3).

The obtained uncertainty is:

- ± 0.9% for a 1 week monitoring period
- ± 3.2% for a 8 hour monitoring period

5.7 Uncertainty caused by inhomogen dioxin concentration adsorbed on particles

A check value for the dioxin concentration adsorbed on particles can be calculated as follows:

\[
\frac{\text{Concentration adsorbed on particles}}{\text{Concentration on particles}} \times 100\%\]

6 Statistical evaluation sheet for dioxin emission data

6.1 Uncertainty calculation of obtained toxicity equivalent

Summing up all uncertainties for the check value of 0.019 ng I-TE/m³:

<table>
<thead>
<tr>
<th>Source of Uncertainty</th>
<th>Contribution</th>
<th>% of Check Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume measurement</td>
<td>± 5%</td>
<td>± 0.0091</td>
</tr>
<tr>
<td>Blank values (meas)</td>
<td>± 5%</td>
<td>± 0.0096</td>
</tr>
<tr>
<td>Blank values (lab)</td>
<td>± 10%</td>
<td>± 0.0190</td>
</tr>
<tr>
<td>Volume measurement</td>
<td>± 5%</td>
<td>± 0.0095</td>
</tr>
<tr>
<td>Probe position (stack)</td>
<td>± 5%</td>
<td>± 0.0097</td>
</tr>
<tr>
<td>Probeposition (in flow)</td>
<td>± 5%</td>
<td>± 0.0099</td>
</tr>
<tr>
<td>Probeposition (in flow)</td>
<td>± 5%</td>
<td>± 0.0100</td>
</tr>
<tr>
<td>Probeposition (in flow)</td>
<td>± 5%</td>
<td>± 0.0102</td>
</tr>
</tbody>
</table>

6.2 Check values

Using the uncertainty evaluation of chapter 6.1 the check value can be calculated as follows:

Check values for dioxin emissions at level of 0.019 ng/m³:

<table>
<thead>
<tr>
<th>Monitoring period</th>
<th>Check value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 week</td>
<td>0.0090 ± 0.0030</td>
</tr>
<tr>
<td>8 hour</td>
<td>0.0160 ± 0.0040</td>
</tr>
</tbody>
</table>

6.3 Dioxin emission evaluation sheets

Table 3: 1 week monitoring

<table>
<thead>
<tr>
<th>Sample</th>
<th>I-TE (ng/m³)</th>
<th>I-TE of DTO 9</th>
<th>I-TE of DTO 9</th>
<th>I-TE of DTO 9</th>
<th>I-TE of DTO 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>week 1</td>
<td>0.019 ± 0.0092</td>
<td>0.014 ± 0.0085</td>
<td>0.012 ± 0.0070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>week 2</td>
<td>0.021 ± 0.0097</td>
<td>0.018 ± 0.0093</td>
<td>0.014 ± 0.0076</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: 8 hour monitoring

<table>
<thead>
<tr>
<th>Sample</th>
<th>I-TE (ng/m³)</th>
<th>I-TE of DTO 9</th>
<th>I-TE of DTO 9</th>
<th>I-TE of DTO 9</th>
<th>I-TE of DTO 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>week 1</td>
<td>0.019 ± 0.0090</td>
<td>0.014 ± 0.0085</td>
<td>0.012 ± 0.0070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>week 2</td>
<td>0.021 ± 0.0097</td>
<td>0.018 ± 0.0093</td>
<td>0.014 ± 0.0076</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7 Discussion

The example for statistical evaluation (Table 3 and 4) showed that the use of the DioxinMonitoringSystem® in a fixed bed activated carbon filter system could detect increasing as well as decreasing dioxin emissions in a very sensitive way.

The comparison of table 3 and 4 showed, that in week sampling time decreases increasing, dioxin emissions much more sensitive and easier than 4 hour sampling.

Especially at plants with inhomogeneous particle distribution (mixture of activated carbon and fly ash) it is essential to sample at least 300 mg of particles to reduce the combined standard uncertainty of the dioxin measurement to 10%. The required amount of material is 10 mg.

Therefore at plants with low particle concentration it is necessary to increase than 8 hours sampling time.

The comparison of table 3 and 4 showed, that the decreasing dioxin emissions much more sensitive and earlier than 4 hour sampling.

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8 References


9 Details of the lead author

The lead author, Mr. Kahr, has promoted at the Technical University of Vienna at the Institute of Energy Chemistry. In November 1988 he started in the GSF research institute (laboratory manager creating the dioxin-monitoring system) and in 1998 he transferred to the Gada Institute as head of the Environmental Analytical Laboratory. He is responsible for the development of the dioxin-monitoring system and its application in several hazardous waste incinerators in the Netherlands.

In 1999 he founded together with Mr. Steiner the company Dioxin Monitoring GmbH, which is used in monitoring technology to dioxin emissions.