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

Dr. Gerhard Kahr, Kottingbrunn, Austria
Ing. Thomas Steiner, Purkersdorf, Austria
Ing. Joep Verwoerd, Rotterdam, Netherlands

## 1 Summary

In 1993 a fixed bed activated carbon filter was installed at the hazardous waste incinerator (DTO 9) of Rotterdam by Austrian Energietechnik GmbH to reduce dioxin emissions below the legal limit of 0.1 ng/m$^3$.

During the start up of this filter system performance tests were done, using the dilution method according VDI 3499, a special application of EN 1948.

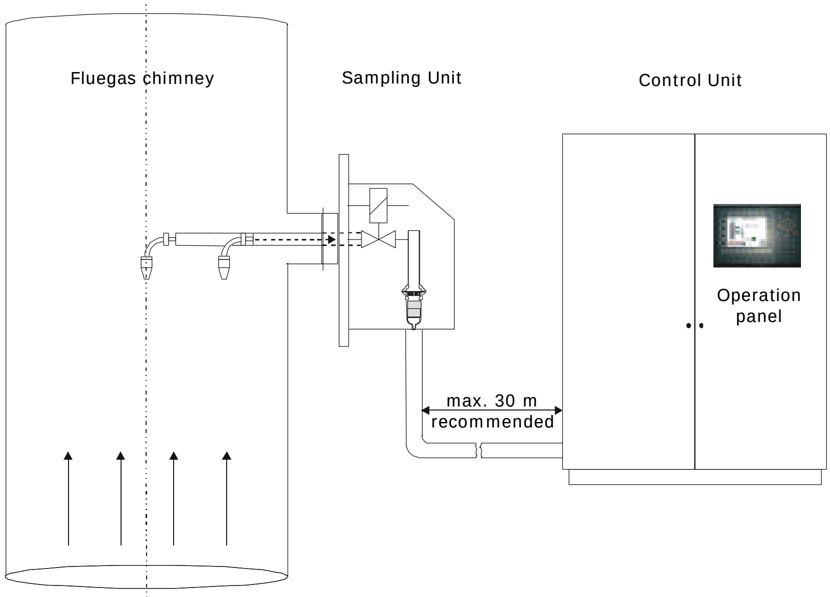
In August 2000 the DioxinMonitoringSystems® was installed at this hazardous waste incinerator to check periodically the performance of this filter system.

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 the 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




*Picture 1: DioxinMonitoringSystem® schema*

At stacks with inhomogen fluegas concentration, additional Sampling units can be installed to ensure representative sampling.

## 3 Analytical method

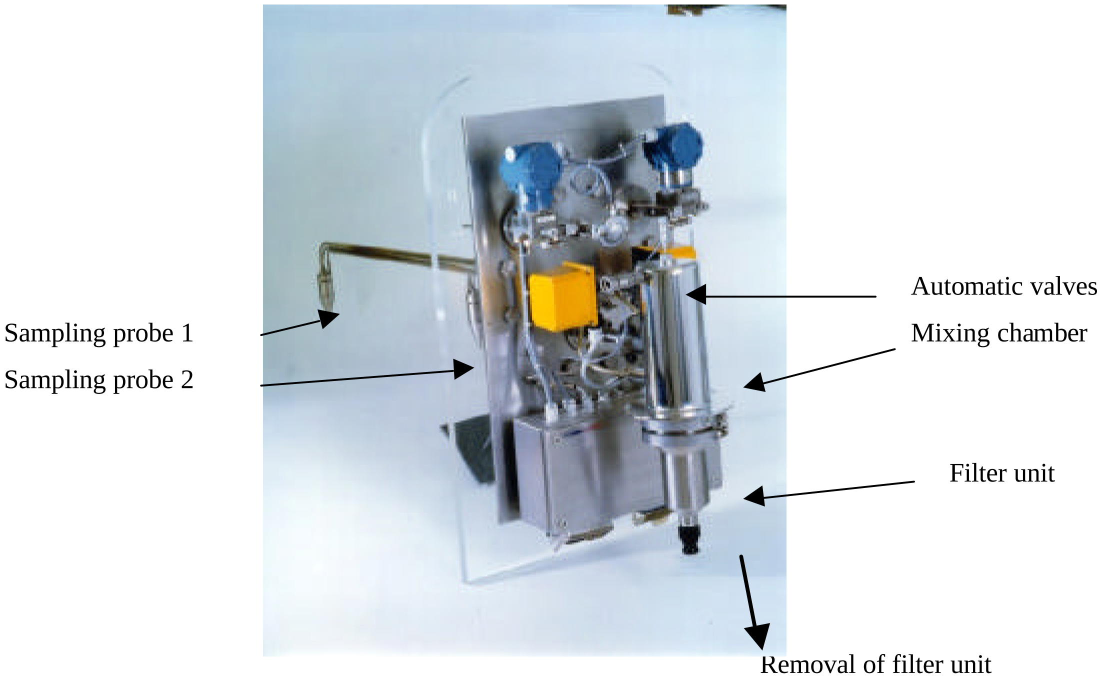
At the plant the process engineer serves measurement’s starting and stopping and exchange of the filter unit. The DioxinMonitoringSystem® is operated with 8 hours and 7 days sampling time and delivers the I-TE mean value of the measurement period.
The DioxinMonitoringSystem® performs the following routines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

- automatic leak test (to avoid leakage) before start
- automatic cleaning routine for the probes (to reduce blank values) before start
- automatic control of the isocinetic sampling
- automatic temperature control of mixing chamber and filter unit
- configurable stand by parameters (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 HRGC/HRMS according to EN 1948 part 3.

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

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




*Picture 2: Sampling unit*

The flue gas is sucked alternating by one of the two heated Sampling probes. Each of the sampling probes are designed as "Zero pressure probes" to ensure isocinetic sampling.
Two automatic valves, one for each probe permits the selection of one of the two stack positions. Behind the valves a thermostatic mixing chamber is situated, where the extracted flue gas is mixed with dried and dust free dilution air.

# 4 Results of the performance test in 1992

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

Table 1 shows the results of these performance tests.

| Performance test 1992 | Laboratory No | Toxicity equivalent I-TE (dry) |
|---|---|---|
| 4.9.1992 | 920357 | 0.014 |
| 10.9.1992 | 920361 | 0.032 |
| 22.9.1992 | 920379/1 | 0.021 |
| 23.9.1992 | 920379/2 | 0.043 |
| 25.9.1992 | 920386/1 | 0.016 |
| 29.9.1992 | 920386/2 | 0.012 |
| 30.9.1992 | 920386/3 | 0.010 |
| 1.10.1992 | 920386/4 | 0.008 |

| | | |
|---|---|---|
| Average value | | 0.0193 |
| Confidence limit (p = 0.95) | | 0.0080 |

# 5 Statistical data of the DioxinMonitoringSystem®

The uncertainty of the toxicity equivalent measurement depends on the many parameters, which are

| Uncertainty | Described in |
|---|---|
| Application of the standard reference material | chapter 5.1 |
| Blank values (measurement & lab) | chapter 5.2 |
| Volume measurement | chapter 5.3 |
| Deviation to representative particle sampling | chapter 5.4 |
| Probe position in the stack | chapter 5.5 |
| Defined by the recovery of internal standard | chapter 5.6 |
| Inhomogenity of the flyash | chapter 5.7 |

## 5.1 Uncertainty caused by the application of reference material

The $^{13}C$ Standard reference material is checked by the quality assurance system of the involved laboratory with a threshold level of ± 10 % relative.

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

## 5.2 Uncertainty caused by blank values

During the field tests of the dioxin measurement working group of CEN [2] the blank values (based on a sucked volume of 20 $m^3$) were determined. Because of the correlation of these blank values to the sucked flue gas volume, the impact is strongly dependent on the sucked flue gas amount.

The DioxinMonitoringSystem® sucks approximately 6 $m^3$ in an eight hours measurement period and approximately 150 $m^3$ 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 an 8 hour monitoring period
- 1 % for a 1 week 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 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 leak test. When the leak test fails the system don't 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 within a range of 10 µm to 2 mm. At the operation temperature of 120°C, more than 90 % of the dioxin content is adsorbed on particles.
At a velocity of 0.2 m/sec (inside the fixed bed) particles up to 500 µm can be transported to the stack, if released. This can happen by leaks as well as during filling/removal of the activated carbon grains. Therefore the representative sampling of the particles has a high impact to the uncertainty.

The DioxinMonitoringSystem® measures the velocity at every probe position by zero pressure probes. Therefore the deviation to isokinetic sampling is limited to ± 1 m/sec which leads to an uncertainty of ± 7 % relative for 500 µm particles.

During a 1 week monitoring period, it is ensured that 300 mg to 600 mg particles are sampled. So there is only low impact to uncertainty.

This uncertainty is estimated as a function of the sampling volume with

± 12 % for 8 hour monitoring period
± 7 % for 1 week monitoring period

## 5.5 Uncertainty caused by the probe position in the stack

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

### 5.6 Uncertainty defined by the recovery standard

Before every measurement $^{13}C$ recovery standard is applied to the filter unit, to have a check value for losses during the sampling.

A detailed discussion of the resulting uncertainty is given in [3].

The obtained uncertainty is

- ± 9.2 % for 1 week monitoring period
- ± 3.2 % for a 8 hour monitoring period

### 5.7 Uncertainty caused by inhomogen dioxin concentration adsorbed on particles

As known from the chemical analysis of fly ash, the uncertainty of the analysis is dependent on the included mass. Nobody uses only 10 mg of fly ash for digestion to make a chemical analysis. As experienced analysts know, it is necessary to include at minimum 100 mg fly ash (for a grain size of 10 um) to have fair uncertainty.

In the case of long time sampling, the DioxinMonitoringSystem® samples 300 to 600 mg of fly ash, which gives an uncertainty of ± 10 %.

But for short time sampling, only 10 to 20 mg flyash are sampled, which gives an uncertainty of ± 25 %.

# 6 Statistical evaluation sheet of 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/$m^3$:

| Uncertainty | 1 week monitoring period | 8 hours monitoring period |
|---|---|---|
| Application of the standard reference material | 5 % | 5 % |
| Blank values (measurement & laboratory) | 1 % | 10 % |
| Volume measurement | 5 % | 5 % |
| Deviation to representative particle sampling | 7 % | 12 % |
| Probe position in the stack | 0 % | 0 % |
| Defined by the recovery of internal standard | 9.2 % | 3.2 % |
| Inhomogenity of fly ash particles | 10 % | 25 % |

| | | |
|---|---|---|
| u(I-TE of DTO 9) - 1 week monitoring | 16.9 % | |

| | | |
|---|---|---|
| u(I-TE of DTO 9) - 8 hour monitoring | | 30.5 % |

## 6.2 Check values

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

Check values for drift of dioxin emissions at level of 0.019 ng/m$^3$:

| monitoring period | hx | kx | hs | ks |
|---|---|---|---|---|
| 1 week | 0.009 ng/m$^3$ | 0.0030 ng/m$^3$ | 0.0037 ng/m$^3$ | 0.00033 ng/m$^3$ |
| 8 hour | 0.016 ng/m$^3$ | 0.0040 ng/m$^3$ | 0.0012 ng/m$^3$ | 0.00071ng/m$^3$ |

## 6.3 Dioxin emission evaluation sheet (example for 1 week monitoring period)

Table 2 shows a sample, which detects decreasing dioxin emissions with this statistical evaluation method using 1 week monitoring periods.

**Statistics:** (valid at level 0.019 ng I-TE/m³)

| periode | 8 hours | 1 week | **Control values for CUSUM chart** | |
|---|---|---|---|---|
| u (srm) | 5.0% | 5.0% | | 1 week |
| u (blanc) | 10.0% | 1.0% | hx | 48.0% |
| u (Volume) | 5.0% | 5.0% | kx | 8.4% |
| u (repres) | 12.0% | 7.0% | | |
| u (position) | 0.0% | 0.0% | **Control values for CUSUM chart** | |
| u (recovery) | 3.2% | 9.2% | | 1 week |
| u (inhom) | 25.0% | 10.0% | hs | 19.6% |
| **u(I-TE of D** | **30.5%** | **16.9%** | ks | 5.3% |

**Check values:**

| Parameter: | hx | | hs | |
|---|---|---|---|---|
| hx(1) | 0.009 | ng/m³ | 0.0037316 | ng/m³ |

**Dioxin emission evaluation:**

| date | c(check) | c(actual) | Sum(pos)t | Sum(neg)t | s(t) | pos. drift | neg. drift |
|---|---|---|---|---|---|---|---|
| week 1 | 0.019 | 0.016 | 0.00000 | 0.00000 | 0 | | |
| week 3 | 0.019 | 0.018 | 0.00000 | 0.00000 | 0.000002 | | |
| week 5 | 0.019 | 0.021 | 0.00040 | 0.00000 | 6.5E-06 | | |
| week 7 | 0.019 | 0.032 | 0.01179 | 0.00000 | 0.000067 | pos. drift | |
| week 9 | 0.019 | 0.021 | 0.01219 | 0.00000 | 0.000128 | pos. drift | |
| week 11 | 0.019 | 0.016 | 0.00758 | 0.00140 | 0.00014 | | |
| week 13 | 0.019 | 0.011 | 0.00000 | 0.00779 | 0.000153 | | |
| week 15 | 0.019 | 0.012 | 0.00000 | 0.01319 | 0.000153 | | neg. drift |
| week 17 | 0.019 | 0.015 | 0.00000 | 0.01558 | 0.000158 | | neg. drift |
| week 19 | 0.019 | 0.017 | 0.00000 | 0.01598 | 0.00016 | | neg. drift |
| week 21 | 0.019 | 0.013 | 0.00000 | 0.02037 | 0.000168 | | neg. drift |
| week 23 | 0.019 | 0.011 | 0.00000 | 0.02677 | 0.00017 | | neg. drift |
| week 25 | 0.019 | 0.008 | 0.00000 | 0.03616 | 0.000174 | | neg. drift |

Table 3: sample for decreasing dioxin emission

The statistical proof is done, in case the value Sum (neg.) t exceeds the check value hx, which is 0.009 ng/m$^3$.

## 6.4 Dioxin emission evaluation sheet (example for repeated 8 hour measurements)

Table 3 shows the same evaluation as done in chapter 6.3, but with repeated 8-hour measurements.

**Statistics:** (valid at level 0.019 ng I-TE/m³)

| periode | 8 hours | 1 week | **Control values for CUSUM chart** | |
|---|---|---|---|---|
| u (srm) | 5.0% | 5.0% | | 8 hour |
| u (blanc) | 10.0% | 1.0% | hx | 86.8% |
| u (Volume) | 5.0% | 5.0% | kx | 15.3% |
| u (repres) | 12.0% | 7.0% | | |
| u (position) | 0.0% | 0.0% | **Control values for CUSUM chart** | |
| u (recovery) | 3.2% | 9.2% | | 8 hour |
| u (inhom) | 25.0% | 10.0% | hs | 64.1% |
| **u(I-TE of D** | **30.5%** | **16.9%** | ks | 17.2% |

**Check values:**

| Parameter: | hx | hs |
|---|---|---|
| hx(1) | 0.016 ng/m³ | 0.0121823 ng/m³ |

**Dioxin emission evaluation:**

| date | c(check) | c(actual) | Sum(pos)t | Sum(neg)t | s(t) | pos. drift | neg. drift |
|---|---|---|---|---|---|---|---|
| week 1 | 0.019 | 0.016 | 0.00000 | 0.00000 | 0 | | |
| week 3 | 0.019 | 0.018 | 0.00000 | 0.00000 | 0.000002 | | |
| week 5 | 0.019 | 0.021 | 0.00000 | 0.00000 | 6.5E-06 | | |
| week 7 | 0.019 | 0.032 | 0.01010 | 0.00000 | 0.000067 | | |
| week 9 | 0.019 | 0.021 | 0.00920 | 0.00000 | 0.000128 | | |
| week 11 | 0.019 | 0.016 | 0.00330 | 0.00010 | 0.00014 | | |
| week 13 | 0.019 | 0.011 | 0.00000 | 0.00520 | 0.000153 | | |
| week 15 | 0.019 | 0.012 | 0.00000 | 0.00930 | 0.000153 | | |
| week 17 | 0.019 | 0.015 | 0.00000 | 0.01040 | 0.000158 | | |
| week 19 | 0.019 | 0.017 | 0.00000 | 0.00950 | 0.00016 | | |
| week 21 | 0.019 | 0.013 | 0.00000 | 0.01260 | 0.000168 | | |
| week 23 | 0.019 | 0.011 | 0.00000 | 0.01770 | 0.00017 | | neg. drift |
| week 25 | 0.019 | 0.008 | 0.00000 | 0.02580 | 0.000174 | | neg. drift |

Because of the higher uncertainty of the 8-hour measurement (compared to 1 week) the check value hx increases to 0.016 ng/m$^3$, which makes the statistical evaluation less sensitive.

In this example the decreasing dioxin emissions are detected 10 weeks later by statistical evaluation.

## 7 Discussion

The examples for statistical evaluation (Table 2 and Table3) showed that the use of the DioxinMonitoringSystem® with 1-week monitoring period could detect increasing as well as decreasing dioxin emissions in a very sensitive way.

The comparison of table 2 and 3 showed, that 1 week sampling time detects decreasing (increasing) dioxin emissions much more sensitive and earlier than 8 hour sampling time.

Especially in plants with inhomogen 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 values and to have 2 probes and more for sampling.

Therefore at plants with low particle concentration it is necessary to increase the sampling time to 1 week, to use the obtained dioxin emission data for statistical evaluation (trend calculation or drift calculation of dioxin emissions).

The application at the stack of the hazardous waste incinerator of Rotterdam showed that this statistical evaluation can be used as "Quality assurance control chart" to detect increasing (decreasing) performance of the installed fixed bed activated carbon filter.

## 8 References

| | | |
|---|---|---|
| [1] | Kahr, Eberl, | Report of performance measurement |
| [2] | CEN workgroup Dioxin measurement | Field test reports |
| [3] | Kahr, Steiner | CEN Workshop 2001, Measuring Dioxin Emissions |

## 9 Details of the lead author

Dr. Dipl. Ing. Gerhard Kahr
A-2542 Kottingbrunn
Anzengruberstr. 30
Tel. +43 664 30 42 046

The lead author has promoted at the Technical University of Vienna at the Institute of inorganic chemistry. In November 1986, Mr. Kahr started in the SGP research facilities as Laboratory manager introducing the Dioxin measurement technology. 1992 he prepared accreditation according EN 45000 for the monitoring method DioxinMonitoringSystem and gets accredited. In 1997 Mr. Kahr prepared as responsible Technician the project "Ambient Air Monitoring for metropolitan areas of Indonesia", which included the ambient air monitoring network for ten (10) main cities of Indonesia. 1999 he founded together with Mr. Steiner the company DioxinMonitoringSystem GnbR which is focussed in monitoring technology for dioxin emissions.