# Statistical evaluation of dioxin filters efficiency using a fixed installed dioxin emissions monitoring and statistical control charts

Gerhard Kahr 1, Thomas Steiner 1, Joep Verwoerd 2, Sun-Ho Lee 3

1 DioxinMonitoringSystems, A-2542 Kottingbrunn, Austria

2 AVR Rijnmond, NL 3197 KK Rotterdam, Netherlands

3 We One Intertech Corp., #307 Sehyun B/D, 832-7 Yoksamdong, Kangnarnku, Korea

#### Introduction

In 1993 a fixed bed activated carbon filter was installed at the hazardous waste incinerator (DTO 9) of Rotterdam to reduce dioxin emissions below the legal limit of  $0.1 \text{ ng/m}^3$ . During the start up of this filter system numerous performance tests were done.<sup>1</sup>

In August 2000 a permanent installed dioxin monitoring and evaluation device was installed at this hazardous waste incinerator to check and to evaluate periodically (once a month) the performance of this filter system.

In this paper the control chart is explained, using the data of this dioxin monitoring system, which enables the operator to evaluate the dioxin emission values by statistical methods.

## **Methods and Materials**

The complete system of equipment used for this investigation consists of the following equipment:

- one sampling unit
- one control and evaluation unit



Picture 1: DioxinMonitoringSystem<sup>®</sup> schema

The sampling unit was mounted at the stack of the hazardous waste incinerator DTO 9. The Control and evaluation unit was installed nearby the mounted sampling unit.

Dioxin emission measurements at concentrations of the legal limit  $(0.1 \text{ ng/m}^3)$  were done with 8-hour monitoring period to enable measurement periods conform to the European standard EN 1948-part 1.

Dioxin emission measurements at very low concentrations (below  $0.01 \text{ ng/m}^3$ ) were done with 1 week monitoring period to have the advantage of very low detection limits. Using 1-week monitoring time detection limits of  $0.001 \text{ ng/m}^3$  could be achieved.

Once a month the process engineer of the plant performed the dioxin monitoring using the fixed installed monitoring system, which did the monitoring fully automatically. Details are described in <sup>3</sup>.

After stopping the measurement the engineer sent the filter unit together with the measurement protocol and corresponding parameters in a transportation box to the laboratory, where the filter unit was extracted and cleaned according European standards.

1 week later the process engineer received the results by E-mail from the laboratory. The evaluation of the results was done according the introduced control chart.



Sampling probe 1 Sampling probe 2

Picture 2: Sampling unit

## **Results of the performance test in 1992**

In 1992 several performance tests of the fixed bed activated carbon filter were done during the start up of the filter system.<sup>1</sup>

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

## Statistical evaluation of the performance data

Using the uncertainty evaluation of  $^{2}$  the check values can be calculated as follows:

Table 2: Check values for drift of dioxin emissions at level of  $0.019 \text{ ng/m}^3$ 

monitoring period	h <sub>x</sub>	k <sub>x</sub>	h <sub>s</sub>	k <sub>s</sub>
1 week	0.014 ng/m <sup>3</sup>	0.0024 ng/m <sup>3</sup>	0.0083 ng/m <sup>3</sup>	0.0022 ng/m <sup>3</sup>
8 hour	0.023 ng/m <sup>3</sup>	0.0040 ng/m <sup>3</sup>	0.0234 ng/m <sup>3</sup>	0.0063 ng/m <sup>3</sup>

## Control chart for increasing (decreasing) dioxin emissions

Table 3: Control chart to evaluate the trend of dioxin emissions (all values ng  $I-TE/m^3$ )

surveilled period	c(I-TE)	sum of pos. t	sum of neg t	calculated trend
1	0.034	0.0000	0.0000	
2	0.025	0.0036	0.0000	
3	0.007	0.0000	0.0096	
4	0.011	0.0000	0.0152	
5	0.007	0.0000	0.0248	decreasing emissions
6	0.043	0.0216	0.0000	
7	0.102	0.1022	0.0000	increasing emissions
8	0.074	0.1548	0.0000	increasing emissions

The statistical proof for decreasing dioxin emissions is done, in case the sum of negative t exceeds  $0.023 \text{ ng/m}^3$  (in case of 8-hour monitoring period) or exceeds  $0.014 \text{ ng/m}^3$  (in case of 1-week monitoring period). The statistical proof for increasing dioxin emissions is done, in case the sum of positive t exceeds  $0.023 \text{ ng/m}^3$  (in case of 8-hour monitoring period) or exceeds  $0.014 \text{ ng/m}^3$  (in case of 1-week monitoring period).

## Control chart for scattering dioxin emissions

Table 4: Control chart to evaluate obtained dioxin emissions for scattering (all values ng I-TE/m<sup>3</sup>)

surveilled period	c(I-TE)	dt	sp	calculated scattering
1	0.034	0.015	0	no increase of scattering
2	0.025	0.006	0.00004	no increase of scattering
3	0.007	- 0.012	0.00020	no increase of scattering
4	0.011	- 0.008	0.00021	no increase of scattering
5	0.007	- 0.012	0.00022	no increase of scattering
6	0.043	0.024	0.00087	no increase of scattering
7	0.102	0.083	0.00261	no increase of scattering
8	0.074	0.055	0.00300	no increase of scattering

The statistical proof for the increase of scattering is done, in case sp exceeds 0.0083 in case of 1-week measurement period.

## Discussion

The statistical evaluation showed that the use of the described dioxin monitoring system with 1-week monitoring period as well with 8-hours monitoring period can detect increasing as well as decreasing dioxin emissions in a very sensitive way.

Especially at low dioxin concentrations (below  $0.01 \text{ ng/m}^3$ ), only 1-week measurement periods enables the statistical evaluation of the obtained results.

The explanation is quite simple. At plants with inhomogen particle distribution in the flue gas (mixture of activated carbon and fly ash) and very low dust concentration (below  $1 \text{ mg/m}^3$ ) it is necessary to include as much particles as possible to be representative.

With 1-weeks measurement time 20 times more particles are sampled, which increases the representativness of the whole measurement. This is the main advantage of 1-weeks measurement time, instead of 8 hour measurement period.

Therefore at plants with low particle concentration it is an advantage 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 very well.

#### References

- 1. Kahr G., Eberl K., Report of performance measurement
- 2. Kahr G., Steiner T., Proceedings of the conference CEM 2001, Netherlands
- 3. Kahr G., Steiner T., VDI report of CEN Workshop 2001, Measurement of dioxin emissions, Düsseldorf