

## MONITORING OF PCDDs, AND PCDFs EMISSIONS OF WASTE INCINERATORS IN WALLONIA: UNCERTAINTY EVALUATION

Bergmans B<sup>1</sup>, Idczak F<sup>1</sup>, Maetz P<sup>1</sup>, Nadin C<sup>1</sup>, Nicolas J.<sup>2</sup>, Petitjean S<sup>1</sup>

1. Environmental Monitoring Direction, Atmospheric Emissions Departement, Institut Scientifique de Service Public, rue du Chéra 200, 4000 Liège, Belgium
2. Environmental Sciences and Management Department, Research Group Environmental Monitoring, University of Liège, Avenue de Longwy 185, 6700 Arlon, Belgium

### Abstract

Since the end of 2000, a continuous sampling to monitor PCDDs and PCDFs emission was implemented on the 11 municipal waste incineration ovens in Walloon Region, to check the compliance with the EU emission limit value, 0.1 TEQ ng/Nm<sup>3</sup>. For this purpose, uncertainty estimation is one of the most crucial points for decision making. The sampling and analytical uncertainty was estimated by two different ways: 1. Identification and quantification of the major contributions through QA/QC data (type A evaluation) or by other sources (type B evaluation), 2. Direct assessment through specific duplicate measurements. Both ways were found to give results in good agreement, with an extended uncertainty of about 30 to 40%, depending on the congener, with a coverage factor  $k=2$ .

### Introduction

Wallonia in Belgium is typically one region where incineration remains needed to cope with waste. Since the transposition of the EU emission limit value of 0.1 TEQ ng/Nm<sup>3</sup> PCDDs/Fs at the end of 2000, a continuous sampling network to monitor PCDDs and PCDFs emission was implemented on the 11 municipal waste incinerators. For such a network, the uncertainty estimation is of key importance and shall include both sampling and analytical steps. From a practical point of view, the uncertainty estimation can be realized either via a bottom-up approach or via a top-down approach. As the well-known GUM<sup>1</sup> focuses on the bottom-up approach, for air quality measurement, an ISO standard, ISO 20988<sup>2</sup>, focussing on a direct approach for the uncertainty evaluation, is currently under publication. Input data for uncertainty assessment can be provided through QA/QC procedures or specific experimental design. The uncertainty arising mainly from the QC data is compared to the assessment made from paired measurements.

### Methods and Materials

The AMESA system samples all original phases for PCDDs and PCDFs on XAD-2 cartridges. Isokinetic sampling is maintained so that particulate collection remains representative of particles present in the stack flow. Relevant physical parameters on oven, stack and sampling system are stored on a memory card.

Sampling time used for this control network is 14 or 28 days, and the sampling volume approximately 50 to 200 Nm<sup>3</sup>.

A backflush of the probe during long shutdown periods of the plant was added in 2002. This system was implemented in order to avoid eventual contamination of the probe especially during the drying of the refractory bricks of the oven.

XAD-2 cartridges are spiked with EN-1948 <sup>13</sup>C PCDDs-PCDFs extract standards and extracted in toluene (24h, large volume Soxhlet extractor). The concentrated extract is subjected to a full automatic (Power Prep<sup>(c)</sup>) multistep clean-up (Silica-Alumina-Carbon), according to EN-1948. All <sup>13</sup>C spiking levels are adapted to the high sampled volume of flue gas.

The final extract (100 µl, in n-nonane) is analysed by HRGC-HRMS, using a MICROMASS Autospec ULTIMA (SIM Mode, RP 10000, 10% Valley) equipped with a HP-Agilent (GC 6890 Series) Chromatograph.

The 2378 congeners are separated by a 60m x 0.25mm x 0.25µm Df CP-Sil 8 CB-MS Low Bleed CHROMPACK-VARIAN (5% Phe-95% Me silicon gum) column. The injected volume is 1.5µl (Splitless, EPC Constant Flow Mode), using a HP-Agilent 7683 Series autosampler. Concentrations calculations are reported in compliance with EN 1948.

## Results

The main uncertainty contributions, as listed on the following simplified cause-effect diagram (figure 1), were quantified either by statistical evaluation of series of observation (type A evaluation) or by other evaluation of standing data or expert judgement (type B evaluation).

**Volume:** estimated by applying the law of propagation of uncertainties to equation (a). The classical working values of the AMESA and the maximum relative uncertainties as stated in EN 13284<sup>3</sup> were used for the calculation giving a value of 4.6%.

$$V_{gaz} = V_{meas} \frac{T_n (p_{meas} - p_{H_2O})}{P_n T_{meas}} \quad (a)$$

**O<sub>2</sub> content:** the uncertainty contribution was estimated at 5%, value taken from literature<sup>4</sup>.

**Representative sampling:** this contribution was estimated at 10% according to EN 1948-3<sup>5</sup>.

**Isokinetic sampling:** this contribution was calculated using equation (b)<sup>6</sup> in a worst case estimation: maximum isokinetic ratio, 115% (EN 13284), and maximum dust fraction 10% of the whole emission. The uncertainty is about 1.3%.

$$\varepsilon = 1 + \left( \frac{w}{v} - 1 \right) \left( 1 - \frac{1}{1 + 2P} \right) \quad (b)$$

with:  $\varepsilon$  = ratio between the measured and the actual concentrations,  $v$ : actual rate,  $w$ : sampling rate.

**Extraction/Purification:** the standard deviation of the mean recovery of a set of 10 to 20 results randomly chosen within one year results is varying from 3 to 5% depending on the substituted congener.

**Analysis:** a quality control standard is routinely analysis within an analytical series. The standard deviation of the control charts, is varying from 6 to 15%, with means from 82 to 102% over a one year period (n=30) at 4, 8 or 16 pg/µl level depending on the substituted congener.

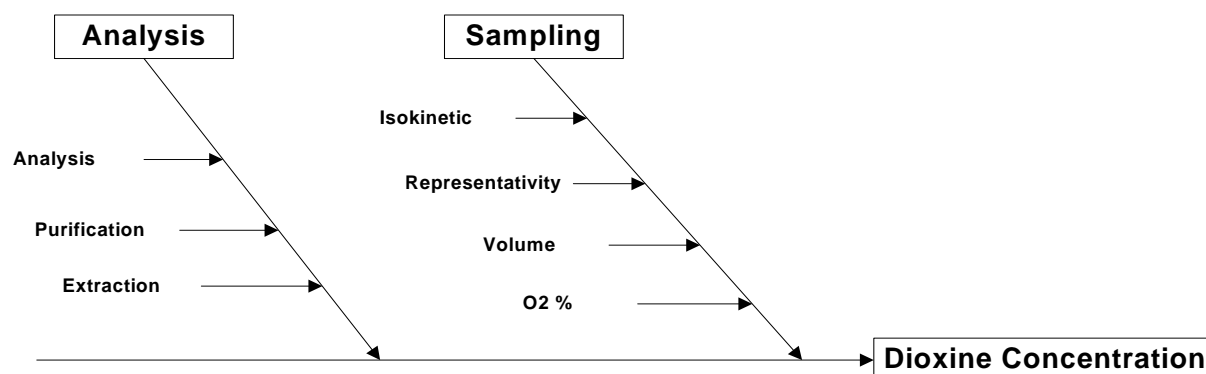


Figure 1: Simplified cause-effect diagram for the dioxin concentration uncertainty

The detailed results, combined and expanded uncertainties are given in table 1.

Source	Volume	O <sub>2</sub> content	Representative Sampling	Isokinetic Sampling	Extraction	Analysis	u	U
	%	%	%	%	%	%	%	%
Type	B	B	B	B	A	A		
<b>2378-TCDD</b>	4.6	5	10	1.3	4	10	16	<b>32</b>
<b>2378-TCDF</b>	4.6	5	10	1.3	4	8	15	<b>30</b>
<b>12378-PeCDD</b>	4.6	5	10	1.3	4	9	16	<b>32</b>
<b>12378-PeCDF</b>	4.6	5	10	1.3	3	10	16	<b>32</b>
<b>23478-PeCDF</b>	4.6	5	10	1.3	4	11	17	<b>34</b>
<b>123478-HxCDD</b>	4.6	5	10	1.3	3	10	16	<b>32</b>
<b>123678-HxCDD</b>	4.6	5	10	1.3	3	11	17	<b>33</b>
<b>123478-HxCDF</b>	4.6	5	10	1.3	3	14	19	<b>37</b>
<b>123678-HxCDF</b>	4.6	5	10	1.3	4	11	17	<b>34</b>
<b>234678-HxCDF</b>	4.6	5	10	1.3	3	13	18	<b>37</b>
<b>123789-HxCDF</b>	4.6	5	10	1.3	4	15	20	<b>40</b>
<b>1234678-HpCDD</b>	4.6	5	10	1.3	4	10	16	<b>32</b>
<b>1234678-HpCDF</b>	4.6	5	10	1.3	4	6	14	<b>28</b>
<b>1234789-HpCDF</b>	4.6	5	10	1.3	4	15	20	<b>39</b>
<b>OCDD</b>	4.6	5	10	1.3	5	8	15	<b>31</b>
<b>OCDF</b>	4.6	5	10	1.3	5	6	14	<b>29</b>

Table 1: Uncertainty results

#### Paired measurements

A series of paired measurements, 14 days cartridge, was performed on an incinerator (Table 2). The total concentration is varying from about 6 to more than 150 TEQ pg/Nm<sup>3</sup> and the range of the duplicate results from 6 to about 50%. The uncertainty, calculated using (c), was found about 20%.

$$u = \sqrt{\frac{\sum_{j=1}^N (A_{j,1} - A_{j,2})^2}{2 \cdot N}} \quad (c)$$

Trial	AMESA 1	AMESA 2	Mean	Range	Relative Range	
	(TEQ pg/Nm <sup>3</sup> dry)				%	
1	153	145	149	8	5	
2	37	23	30	14	47	
3	57	48	53	9	17	
4	14	13	14	1	7	
5	10	6	8	4	50	
6	24	22	23	2	9	
					u	21%
					<b>U (k=2)</b>	<b>42%</b>

Table 2: Results of the paired measurements.

## Discussion

Whichever the considered congener, the extended uncertainty can be estimated between 30 and 40%. The calculated values are in good agreement with the estimations presented in EN1948-3<sup>5</sup>, Annex B, especially for volume or recovery. The main uncertainty contributions are arising from the representative sampling and the analytical step.

Excepted trials 2 and 5, the repeatability of measurements is lying under 20% (table 2), in good agreement with the precision result found during the validation procedure of the AMESA<sup>(c)</sup> by the German TUV, about 10% for concentration in a range about 100 pg/Nm<sup>3</sup>. Higher results, 50%, were obtained for the second and the fifth trials. For the latter one, it must be stressed that the level of concentration was much lower. This could explain the bad repeatability observed. For the second trial (table 2), any reason could be given to explain the observed repeatability. Despite the uncertainty estimation through paired measurements is based on a small data aggregate, the calculated value, 42%, is close to the uncertainties calculated from QA/QC data.

These preliminary results show that the uncertainty could easily be assessed either through exploitation of QA/QC data or via some specific experiments, both at a reasonable cost. Nevertheless, additional results are needed to be more confident in the assessment.

## Acknowledgments

The authors wish to thanks A. Galloy and P. Duchateau from ISSeP analytical laboratory for technical help. ISSeP and the authors are also indebted to the Walloon Environment Directorate and the MWI which funds the monitoring network.

## References

---

<sup>1</sup> Guide for Uncertainty Measurement, ISO, 1995

<sup>2</sup> ISO 20988, Air Quality – Guidelines for estimating measurement uncertainty, under publication

<sup>3</sup> EN 13284-1, Stationary source emissions – Determination of low range mass concentration of dust – Part 1 : Manual gravimetric method, 2002

<sup>4</sup> M. Lewandowski & M. Woodfield, Proceedings of the 6<sup>th</sup> International Conference on Emission Monitoring, Eds. P. Dilara, D. Cipriano, S.P.I.04.098, 2004

<sup>5</sup> EN 1948, Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 3 : Identification and quantification of PCDDs/PCDFs, 2006

<sup>6</sup> Davies C.N., Brit. J. Apply. Phys. (J. Phys. D) 1, 921-932 (1968)