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GENERAL PAPER

Setting up a decision rule from estimated uncertainty: emission limit value for PCDD and PCDF incineration plants in Wallonia, Belgium

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Abstract Complex analytical procedures are often required to prove the non-compliance with a specific legislation. In the case of a small overlap of the limit, integration of the method uncertainty in the decision-making process is essential. The decision rule proposed in Wallonia, Belgium, for the non-compliance of waste incineration plants with the EU limit value for PCDD and PCDF emissions is presented. The method uncertainty was estimated annually over 6 years from duplicate measurements using two top-down approaches. Depending on the congener, the standard uncertainty varies from 30 to 85%, with a good correlation between calculations. The analytical contribution was estimated using a bottom-up evaluation. The impact of the sampling step was deduced from the whole estimation and represents more than 80% of the total uncertainty budget. No optimisation is foreseen at this time because of practical field constraints. Based on the average fraction of each congener, the uncertainty associated with the measurement result has been established and shows a high stability over the years. Using this value, a guard band has been calculated and will be proposed to the regulatory body.

Keywords Uncertainty · Top-down · Bottom-up · Decision-making · Dioxin

Abbreviations

PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofurane
I-TEF	International Toxicity Equivalency Factor
I-TEQ	International Toxicity Equivalent
Nm^3	m^3 of gas in normal conditions of temperature and pressure (273.15 K and 101325 Pa)

Introduction

In the Walloon region of Belgium, approximately 60% of the total production of municipal solid waste is incinerated and the total amount of emitted combustion gas reaches up to 4 billions Nm^3 per year. According to the European directive EU 2000/76/CE [1], PCDD and PCDF emissions shall be monitored. A specific European standard EN 1948 [2] has been developed to cope with sampling and analytical technical aspects. Since the end of 2000, a sampling network has been implemented on the 11 municipal waste incineration ovens of Wallonia to check their compliance with the EU emission limit value of 0.1 ng I-TEQ/Nm^3. The control network uses a continuous isokinetic sampling system (AMESA®, Environnement SA, Becker Messtechnik). PCDD and PCDF are collected on XAD-2 cartridges, over a 14-day sampling duration and, after extraction/purification, analysed by high-resolution gas chromatography/

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high-resolution mass spectrometry (HRGC/HRMS) chromatography.

Decisions of the regulatory body are founded on the results of this network and can go up to the closing down of the oven in the case of non-compliance. Due to the strong impact that they can have, interpretations of the analytical results are, thus, of key importance. As uncertainty could have an impact on the final judgment of the decision-makers, it needs to be taken into account in the decision-making process, as recommended by ISO 17025 [3].

PCDD and PCDF emissions measurement includes both complex sampling and analytical steps which must be considered for uncertainty estimation. From a practical point of view, this evaluation can be realised either via a bottom-up approach or via a top-down approach. As the well-known GUM [4] focuses on the bottom-up approach, for air quality measurement, two recently published documents, the Nordtest Technical Report TR 604 [5] and the ISO 20988 standard [6] are focussing on a direct approach based among other methods on replicate measurements.

The second approach has been preferred to estimate the uncertainty of the entire process. Actually, a top-down calculation includes all sources and requires no evaluation of standing data or expert judgement (type B evaluation) and, thus, guarantees a high-quality estimation of the final uncertainty. The uncertainty of the method was estimated annually over 6 years to ensure the stability of the result over time. The result has also been calculated through either the Nordtest TR 604 range statistics or the ISO 20988 standard, as the calculation formula involved in these two reference documents are somewhat different.

Nevertheless, a bottom-up analysis is needed to identify the main contributions and is, therefore, necessary if one wants to reduce the uncertainty. The main sources of uncertainty have been listed on a cause–effect diagram. Contributions of the analytical steps of the method can be easily calculated. These sources could be quantified by the statistical evaluation of series of observations (type A evaluation) based on the available QA/QC data. The budget of the sampling step was then deduced from the whole estimation.

As a conclusion, the process followed in Wallonia for the evaluation of the compliance of municipal waste incineration plants with the PCDD and PCDF EU emission limit value is presented. In order to reduce the risk of a false-positive result, a guard band [7] has been calculated. Any value above the EU limit, but lying in this specific zone, will be considered as compliant. This decision rule will be proposed to the regulatory body. This method could be considered as more favourable for plant operators, but is necessary to avoid any possible contestation.

Materials and methods

Description of the plant

Within the Walloon monitoring network, one incinerator oven is equipped with two separate stacks. Therefore, from this specific furnace, the PCDD and PCDF can easily be sampled and analysed in duplicate with the same equipment and procedures. The emission treatment lines of the plant include an activated carbon injection, an acid gas scrubber, a basic scrubber with lime injection and a baghouse filter. The abatement designs applied on the waste gas are identical, but each stack has its own separated line of treatment.

Sampling system

The AMESA® (Environnement SA, Becker Messtechnik) system samples all original phases for PCDD and PCDF on XAD-2 cartridges. Isokinetic sampling is maintained so that particulate collection remains representative of particles present in the stack flow. The sampling time used is 14 days and the sampling volume is usually between 50 and 200 Nm^3. A back-flush of the probe during long shutdown periods of the plant is used in order to avoid possible contamination, especially during the drying of the refractory bricks of the oven.

Analytical procedure

XAD-2 cartridges are spiked with ^{13}C PCDD/PCDF extract standards and extracted in toluene (24 h, large-volume Soxhlet extractors). The concentrated extract is subjected to a full automatic (Power Prep) multistep clean-up (silica-alumina-carbon). All ^{13}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 an HP-Agilent (GC 6890 Series) chromatograph. The 2,3,7,8-congeners are separated by a 60 m × 0.25 mm × 0.25 µm CP-Sil 8 CB Low Bleed/MS Chrompack/Varian column (5% Phenyl–95% Dimethylpolysiloxane). The injected volume is 1.5 µl (Splitless, EPC Flow Ramp Mode), using an HP-Agilent 7683 Series autosampler. All steps are in compliance with EN 1948.

Relative uncertainty estimation

The relative uncertainties of the method were calculated through the two following approaches:

Nordtest range statistics The uncertainty is derived from the mean relative range between the two results by Eq. 1, according to the Nordtest technical report TR 604 (§ 6.2 Range statistics):

$$u = \frac{1}{1.128n}\sum_{i=1}^{n}\frac{\left|x_{i,1} - x_{i,2}\right|}{\bar{x}_i} \quad (1)$$

where u is the uncertainty estimation, n the number of replicates, $x_{i,1}$ and $x_{i,2}$ are the results of both duplicates of the ith sampling and $\bar{x}_i$ is the mean value of the two replicates.

ISO 20988 standard The uncertainty is calculated using Eq. 2. This formula is derived from ISO 20988 (Experimental design A6, Paired measurements), but has been adapted to give a relative value instead of an absolute value. This adjustment is needed to obtain comparable results with those resulting from Eq. 1:

$$u = \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{x_{i,1}-x_{i,2}}{\bar{x}_i}\right]^2}{2n}} \quad (2)$$

The main uncertainty sources of the analytical step were calculated by a statistical evaluation of the results obtained by performing the following QA/QC tests:

- Extraction/purification: the sample is spiked with ^{13}C-labelled congeners before the extraction/purification to estimate the recovery. The uncertainty was estimated from the standard deviation of the mean recovery, $s/\sqrt{n}$, from a set of 30 data randomly chosen over 3 years.
- Analysis: a commercial quality control standard (EN 1948CVS from Wellington Laboratories) is routinely added within each analytical series. The recoveries are between 80 and 100%. The uncertainty (u_{GC}) was estimated from the standard deviation of the results over 1 year combined with the uncertainty of the standard (u_{std}), estimated through a rectangular distribution from the commercial specification of 5%.

The impact of the sampling step can be deduced from the previous calculations using Eq. 3:

$$u = \sqrt{u_{\text{sampling}}^2 + u_{\text{analysis}}^2} \quad (3)$$

Results and discussion

Relative uncertainty of the method

The uncertainty was estimated annually for each congener over 6 years using either Eq. 1 or Eq. 2. The uncertainty presents a good stability from one year to another and the standard deviation, s, is quite low (see Table 1).

As the PCDD/PCDF concentration of the plant is very low, some results are below the quantification limit of the analytical method. As statistical analysis can only take the quantified results into account, the number of results involved in each calculation varies from 11 to 26, depending on the congener and the year involved. For one

Table 1 Yearly uncertainty results obtained with data from the last 6 years using Eq. 2

Congener	Uncertainty							
	2002	2003	2004	2005	2006	2007	Mean	s
2378-TCDD	22%	47%	35%	43%	42%	30%	39%	9%
2378-TCDF	28%	45%	18%	39%	44%	41%	40%	11%
12378-PeCDD	28%	42%	26%	31%	36%	27%	35%	6%
12378-PeCDF	31%	44%	12%	35%	37%	32%	36%	11%
23478-PeCDF	30%	42%	21%	30%	28%	36%	35%	7%
123478-HxCDD	26%	33%	31%	26%	25%	20%	30%	5%
123678-HxCDD	30%	38%	36%	26%	34%	18%	34%	7%
123789-HxCDD	39%	41%	39%	32%	29%	25%	38%	6%
123478-HxCDF	32%	38%	35%	34%	22%	31%	35%	5%
123678-HxCDF	37%	39%	37%	31%	20%	30%	36%	7%
234678-HxCDF	48%	40%	46%	33%	20%	39%	42%	10%
123789-HxCDF	40%	38%	19%	27%	22%	33%	31%	9%
1234678-HpCDD	36%	39%	53%	32%	27%	34%	41%	9%
1234678-HpCDF	49%	41%	62%	47%	36%	54%	54%	9%
1234789-HpCDF	67%	50%	63%	51%	39%	56%	56%	10%
OCDD	44%	29%	42%	39%	36%	39%	40%	5%
OCDF	71%	57%	68%	59%	51%	68%	65%	8%

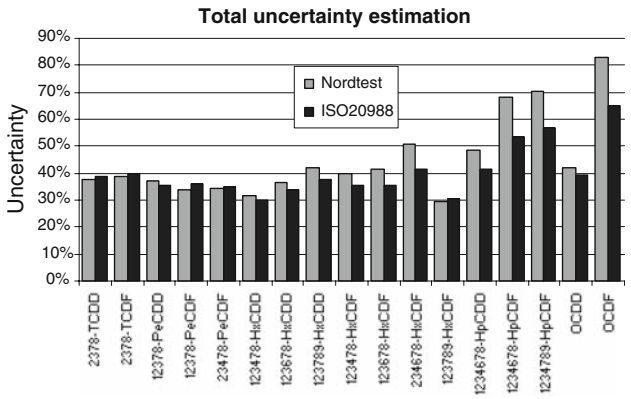

Fig. 1 Nordtest versus ISO 20988 results for the period 2002–2007

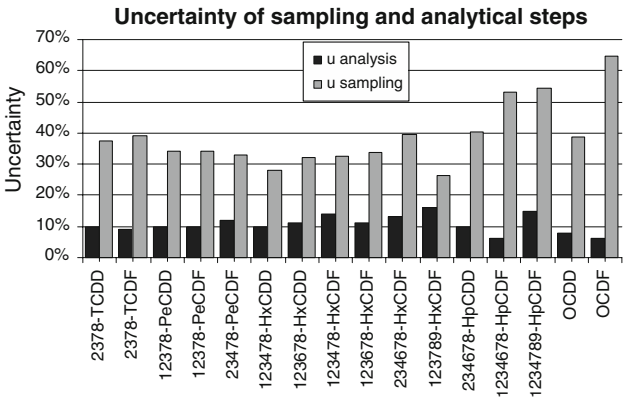

Fig. 3 Uncertainty of the sampling and analytical steps of the method

sampling period in 2003, a result four times higher was found for one line with respect to the other; this result was considered as an abnormal value and was removed.

Despite the fact that the formulas involved are different in the two reference documents, a good correlation is observed between the two calculations (see Fig. 1).

Improvement of the uncertainty

The estimated uncertainty obtained is quite high, but is not surprising due to the very low limit value and the complexity of the method. Before using this result in the decision-making process, it could be interesting to determine the main sources of uncertainty and check if some aspects of the method could be optimised. The main uncertainty contributions have, thus, been listed on a simplified cause–effect diagram (Fig. 2).

Both sampling and analytical steps contribute to the uncertainty. For the sampling step, different environmental parameters and field constraints which are not totally under control have, probably, a significant effect on the sampling step. Even for identified uncertainty sources, the budget is very difficult to be established and requires several type B evaluations, which can lead to an inaccurate estimation of the final uncertainty.

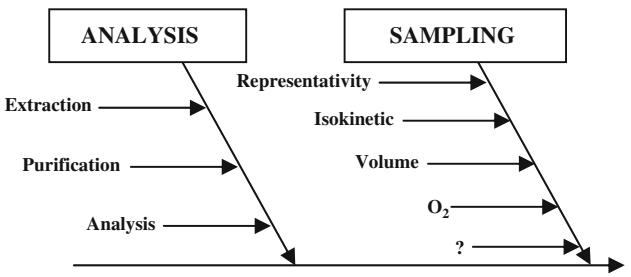

Fig. 2 Simplified cause–effect diagram

The main sources of uncertainty of the analytical step have been estimated using a bottom-up approach (see Table 2).

The impact of the analytical step has been deduced from this result using Eq. 3 and is presented in Fig. 3.

As expected, the sampling step has the most impact, taking up more than 80% of the total uncertainty budget. These assessments could be the starting point of future improvement of the method, but for the moment, the uncertainty value, as determine above by the top-down approach, will be used in the decision-making process.

Uncertainty of the measurement result

The average fraction of each congener of the plant, calculated on results obtained during the last 6 years and taking the I-TEF [8] into account, is presented in Table 2. Using the uncertainty of each congener, the previously calculated (Table 1) uncertainty of the method for a measurement performed on this plant could be determined (Table 3).

The uncertainty can be calculated using the same method for shorter periods of time. The variability of the results will probably increase for short periods, as the number of replicates decreases. The plant process could also shows variation over short periods. On the other hand, the period should not be too long for the purpose of the monitoring network. Yearly estimation has been calculated and shows a good stability over the 6 years considered (see Fig. 4). This period of time seems to be a good compromise and has been eventually selected.

Guard band for the decision-making process

In order to reduce the risk of false-positives to an acceptable level, a guard band should be used in the decision-making process. Any analytical result above the EU limit (specification zone), but lying in the "guard band zone"

Table 2 Bottom-up uncertainty estimation of the analytical step of the measurement method

Sources	Extraction/purification			GC analysis					Uncertainty
	Recovery (%)	s (%)	$s/\sqrt{n}$ (%)	Mean (mg/l)	s (mg/l)	s_r (%)	u_{std} (%)	u_{GC} (%)	u_c (%)
2378-TCDD	87	17	2	3.80	0.36	9	3	10	10
2378-TCDF	81	16	2	3.74	0.29	8	3	8	9
12378-PeCDD	86	15	2	7.78	0.69	9	3	9	10
12378-PeCDF	99	8	1	7.65	0.75	10	3	10	10
23478-PeCDF	84	16	2	7.76	0.85	11	3	11	12
123478-HxCDD	80	10	1	7.92	0.78	10	3	10	10
123678-HxCDD	77	10	1	7.93	0.84	11	3	11	11
123478-HxCDF	81	14	2	8.15	1.09	13	3	14	14
123678-HxCDF	77	15	2	7.99	0.84	11	3	11	11
234678-HxCDF	76	10	1	8.00	1.04	13	3	13	13
123789-HxCDF	112	16	2	7.09	1.07	15	3	15	16
1234678-HpCDD	84	14	2	14.36	1.31	9	3	10	10
1234678-HpCDF	76	14	2	15.16	0.80	5	3	6	6
1234789-HpCDF	114	14	2	13.08	1.92	15	3	15	15
OCDD	80	17	2	15.31	1.15	8	3	8	8
OCDF	83	18	2	15.31	0.82	5	3	6	6

Table 3 Dioxin emission fingerprint of the plant based on measurements performed over the last 6 years and the contribution of each congener to the uncertainty of the measurement result

Congener	I-TEF	Concentration (ng/Nm^3)	Toxicity (ng I-TEQ/Nm^3)	Relative toxicity (% I-TEQ)	u (congener) (%)	u (contribution) (%)
2378-TCDD	1	0.00108	0.00108	11	39	4
2378-TCDF	0.1	0.00080	0.00008	1	40	0
12378-PeCDD	0.5	0.00319	0.00159	16	35	5
12378-PeCDF	0.05	0.00103	0.00005	1	36	0
23478-PeCDF	0.5	0.01033	0.00517	51	35	18
123478-HxCDD	0.1	0.00161	0.00016	2	30	0
123678-HxCDD	0.1	0.00378	0.00038	4	34	1
123789-HxCDD	0.1	0.00190	0.00019	2	38	1
123478-HxCDF	0.1	0.00274	0.00027	3	35	1
123678-HxCDF	0.1	0.00338	0.00034	3	36	1
234678-HxCDF	0.1	0.00625	0.00063	6	42	3
123789-HxCDF	0.1	0.00025	0.00003	0	31	0
1234678-HpCDD	0.01	0.00787	0.00008	1	41	0
1234678-HpCDF	0.01	0.00893	0.00009	1	54	0
1234789-HpCDF	0.01	0.00195	0.00002	0	56	0
OCDD	0.001	0.00701	0.00001	0	40	0
OCDF	0.001	0.00510	0.00001	0	65	0
Total PCCD/PCDF	–	0.06721	0.01016	100	–	36

will be considered as an acceptable result. Only results lying in the "rejection zone" will be considered as non-compliant (Fig. 5). This approach could be considered as more favourable for plant operators, but is necessary to avoid any possible contestation.

This guard band can be calculated using a one-sided tail Student's t-distribution. A level of risk of 5% ($\alpha = 95\%$) has been chosen. As previously assumed, only yearly estimation of the uncertainty will be considered. The number of degrees of freedom is, thus, equal to 5, as data

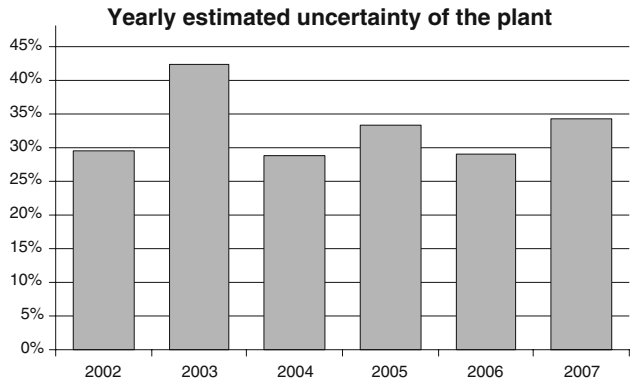

Fig. 4 Yearly estimated uncertainty of the plant

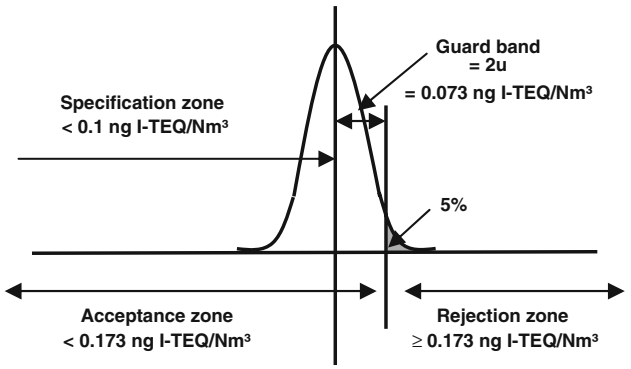

Fig. 5 Guard band for the decision-making process

are only available for the last 6 years (2002–2007). The *k*-value is, then, 2.015 and, using the uncertainty previously estimated, a guard band of $36\% \times 2.015 = 73\%$ can be calculated.

Conclusion

The method uncertainty over the 6 years considered is quite stable. This is the consequence of a combination of the two following points. First, the assessment is carried out over one year of results, so it is really under reproducibility conditions. Then, the uncertainties are calculated via a top-down approach, which is surely including all possible contributions.

Depending on the considered congener, the uncertainty lies between 30 and 85%, with a good correlation between results obtained using either the Nordtest report range statistics or the ISO 20988 standard formula.

The sampling step has the most impact, taking up over 80% of the total budget. The main source is probably the sampling representativity, and its strong impact could be the consequence of two main reasons. First is the fact that, for practical field constraints, a fixed sampling point is used in the automatic sampling procedure instead of the recommended grid sampling. Then, there is probably an effect of the efficiency of the two separated gas treatment lines, even if they are absolutely identical.

The number of duplicate measurements involved in each calculation (>90) is sufficient to obtain a representative assessment. A guard band of 73% based on the estimated uncertainty and the average fraction of each congener measured in the plant has been calculated. The risk of false-positives for a sample giving a result lying in the "rejection zone" is reduced to below 5%.

As the fingerprint for all municipal waste incinerators are quite similar, this value can be considered as a good approximation of the uncertainty of the whole monitoring network. The use of this guard band in the decision-making process will, thus, be proposed to the regulatory body in Wallonia, Belgium.

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