

# VALIDATION AND OPTIMIZATION OF CONTINUOUS SAMPLING TO MONITOR PCDDs, AND PDDFs EMISSIONS OF WASTE INCINERATORS

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## *Introduction*

Wallonia in Belgium is typically one region where incineration remains needed to cope with waste. EU emission limit value of 0,1 TEQng/m<sup>3</sup> PCDD-PCDF was transposed in the Walloon Environmental law at the end of 2000. Regional authorities chose for extensive compliance control through implementation of an automatic continuous sampling system, for each of the 11 municipal waste incineration ovens of Wallonia. The firm Becker-Messtechnik won the procurement tender with its AMESA<sup>1</sup> equipment. For two years, ISSeP has supervised this equipment and analysed the samples.

## *Methods and Materials*

The AMESA system samples all original phases for PCDDs, 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. They are also accessible from ISSeP with an ordinary phone line. Main operations are similar to those for the manual method as in the EN-1948 standard. The differences are :

- The position of the probe never changes
- All analytes researched are collected on the XAD-2 resin (instead of on three phases for EN-1948)
- Resin cartridges are larger than those used with the manual method (larger Soxhlet are necessary)
- Validated by the German TUV on behalf of Becker-Messtechnik for sampling durations between 6 hours and 1 month (against 6-8 hours time bracket of EN-1948)

Sampling time used for this control network is 14 days, and the sampling volume approximately 50 to 200 Nm<sup>3</sup>. Results are available 2 weeks after sample collection and are posted on Environment Directorate's web site<sup>2</sup> at the authorities' request.

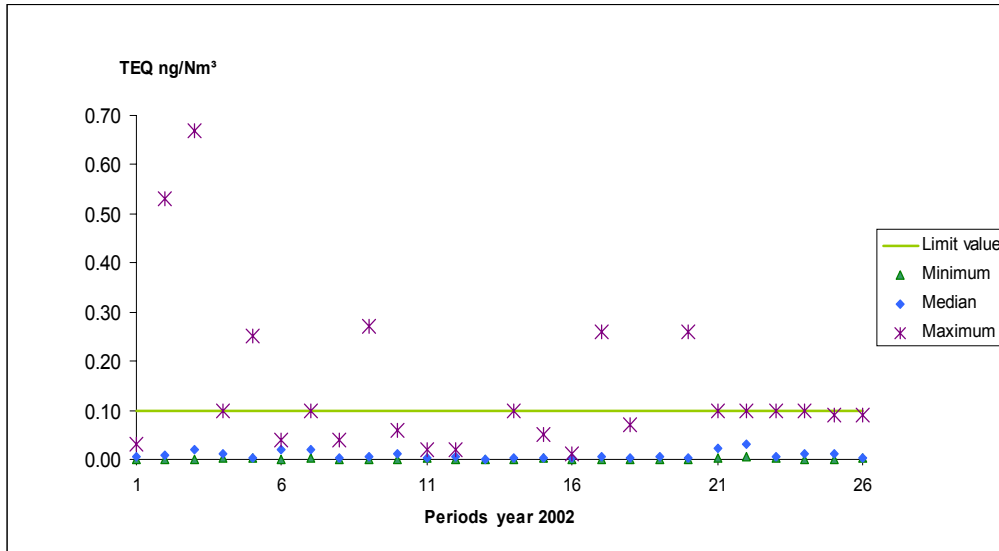
XAD-2 cartridges were spiked with EN-1948 <sup>13</sup>C PCDDs-PCDFs extract standards and extracted in toluene (24h, large volume Soxhlet extractor). The concentrated extract is subjected to a full automatic (Power Prep (c) ) multistep clean-up (Silica-Alumina-Carbon), according to EN-1948. All <sup>13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

**Plot 1. Results with the AMESA sampling system, year 2002**



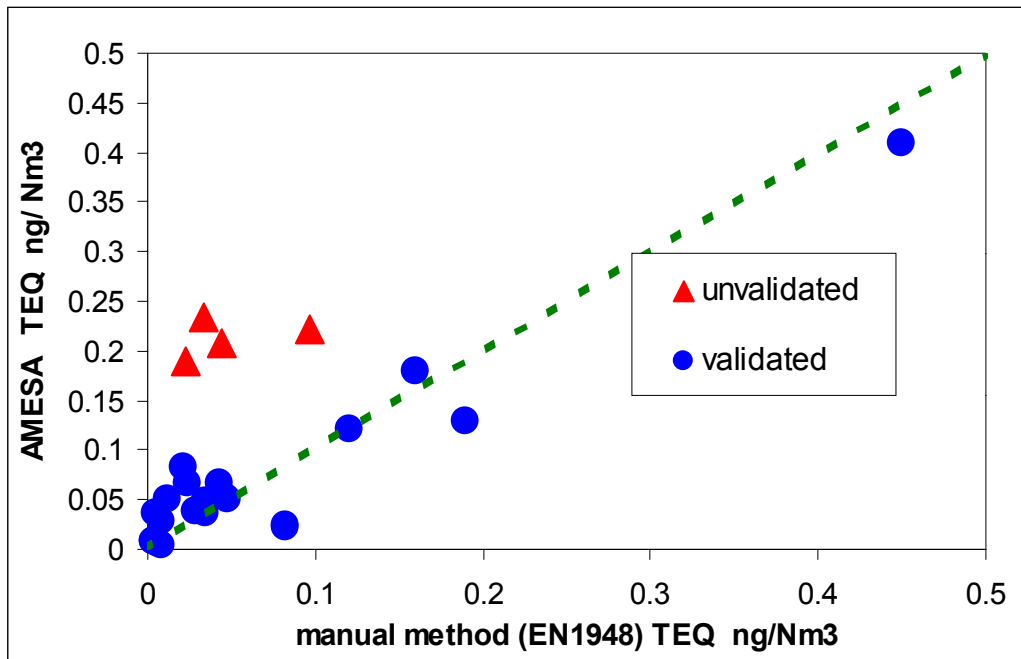
For each period maximum, medium and minimum of results of all eleven ovens are plotted. The maximum for each period is several times clearly above the limit value. The medium of results remains far below the limit value.

Table 1. Results, infringements and causes in 2001 and 2002

| Numbers of   | Year 2001 | Year 2002 |
|--|-----------|-----------|
| Results (cartridges)   | 227       | 179       |
| Infringements of Limit Value                                 | 31        | 8         |
| Infringements for which a reason was identified              | 23        | 8         |
| Older ovens shut down since then                             | 5         |           |
| Damage around filters  | 7         |           |
| Broken joint   | 1         |           |
| Recurrent difficulties of load feeding on one oven           | 3         | 6         |
| Memory effect of installation after significant infringement | 7         |           |

Since the enforcement of the Limit Value has to be done according to the European standard, checks of the AMESA results were done (with parallel AMESA and manual sampling during 8 hours). The sampled volume with the manual method is around 8 to 15 Nm<sup>3</sup> and the volume with the AMESA system 2 to 3 Nm<sup>3</sup>. ISSeP did this at least once a year for each oven.

**Plot 2. AMESA results versus simultaneous manual method (EN1948)**



Results for 4 out of the 26 checks of the AMESA system versus were invalidated. Criteria for this invalidation are internal variability given by EN-1948. The consequence is that authorities disregard the result of the preceding period and does not take possible corresponding infringement of Limit Value into account.

### *Discussion*

Evolutions of results since the launching of the programme show the benefits brought. Continuous monitoring with fast availability and publicity of results triggered efforts of operators. They managed their process and prevented breakdowns of their abatement system so that remaining problems are very limited.

Discrepancies cannot be actually attributed to a sampling effect, or to sampling effect only, since that effect could not be isolated from the possible one in the extraction and analysis steps at these very low concentrations encountered.

The 8 hour checks involve sampled volumes 8 to 15 Nm<sup>3</sup> (manual method) and 2 to 3 Nm<sup>3</sup> (AMESA) versus 50 to 200 Nm<sup>3</sup> for an AMESA fourteen day period, conditions for analysis with these simultaneous sampling are most unfavourable compared to the continuous sampling system.

Actually samples for 14 days periods are unquestionably more representative than sampling durations of 6 or 8h as usual with the manual method. Continuous sampling throughout the year is comprehensive.

Thus, for monitoring results with unquestionable compliance control value, inclusion of the automated sampling method in the standard, as now envisaged by CENTC264, would be beneficial. Several such systems are now commercially available.

### *Acknowledgements*

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### *References*

1. Result of one year continuous monitoring of the PCDD/PCDF emissions of waste incinerators in the Walloon region of Belgium with AMESA, J. Reinman, Dioxin2002, Barcelona
2. <http://environnement.wallonie.be/data/air/dioxines/>