# PCDD/F MEASUREMENTS IN EMISSIONS OF A BELGIAN SINTERING PLANT AN EXEMPLARY LOOK AT THE UNCERTAINTY

# Peter Luthardt<sup>1</sup>, Johan Dhaese<sup>2</sup>, Andreas Hovemann<sup>1</sup>, Regine Keymeulen<sup>2</sup>, Matthias Opel<sup>1</sup>, Klaus Reichel<sup>1</sup>

- eurofins | GfA Gesellschaft f
  ür Arbeitsplatz- und Umweltanalytik mbH, P.O. Box 41 01 28, D-48065 M
  ünster-Roxel, Germany
- 2 SIDMAR N.V., John-Kennedylaan 51, B-9042 Gent, Belgium

#### Introduction

The 'Uncertainty of measurements' has triggered an intense discussion during recent times. To find a middle course between empirical estimations and mathematic calculations regarding the reproducibility or to favour one of these methods here among others forms the centre of consideration. In this respect the GUM (Guide to the expression of uncertainty in measurement)<sup>1</sup>, the DIN V ENV 13005:1996-06<sup>2</sup> (Guide to the expression of uncertainty when measuring) as well as the QUAM (Quantifying uncertainty in analytical measurement)<sup>3</sup> currently serve as decisive guidelines.

#### Scope of investigations

From July 1998 to December 2002 the GfA performed more than 600 PCDD/F emissions measurements at the sintering plant 1 and 2 of the SIDMAR N.V. in Gent.

The actions taken by Sidmar since 1998 starting with process-integrated measures and ending with the use of adsorbents on the basis of activated carbon resulted in a significant reduction of the PCDD/F emissions of both sintering plants. During the measurement period the average concentration per annum decreased from about 6.6 ng I-TEQ/m<sup>3</sup> in 1998 to a tenth in 2002 which means that an average output (weighed on the basis of the different mass flows of both plants) of 69 g I-TEQ/a in 1998 (calculation basis: hrs/a x m<sup>3</sup>/ h x I-TEQ/m<sup>3</sup>) was reduced below 4.9 g I-TEQ/a in 2002. From the pool of data depicted in Figure 1, the results of 4 individual measurements in different I-TEQ ranges were selected for the calculation of the measurement uncertainty. The selected 4 individual measurements have been conducted at the same sintering plant. The results are summarised in Table 1.

# **Methods and Materials**

The individual samplings were made as grid measurements on two axes in the flue gas channel. Figure 2 exemplary shows a cross-section of the channel at sampling height and Figure 3 shows the velocity profiles in context to the selected measurements.

All flue gas samplings reported here were carried out according to the European standard EN 1948 ("cooled probe method"). All analyses were conducted by HRGC/HRMS on HP 5890 A/VG AutoSpec systems.

Fig. 1: I-TEQs of the flue gas measurements at two sintering plants of the SIDMAR N.V. in Gent between 1998 and 2002 (selected results for the calculation of the measurement uncertainty are stressed as black rhombus).

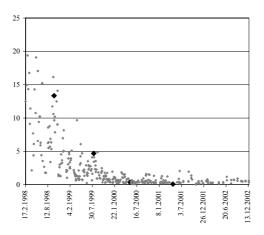
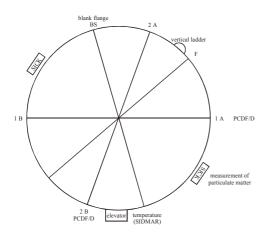


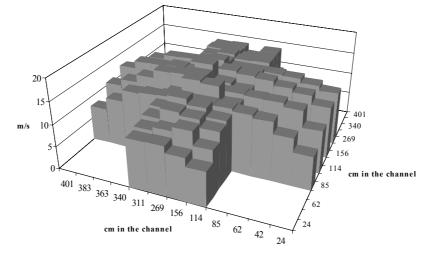
Table 1: Selected PCDD/F-results in the flue gas of a sintering plant of the SIDMAR N.V. in Gent

| plant                    | SIFA 1                                   |      |      |       |
|--------------------------|--|------|------|-------|
| dimension                | ng/m <sup>3</sup> (0 °C, 1,013 hPa, dry) |      |      |       |
| measurement date         | 1998                                     | 1999 | 2000 | 2001  |
| total Tetra to OctaCDD/F | 667                                      | 265  | 21.7 | 0.82  |
| I-TEQ excl. LOD          | 14.4                                     | 5.42 | 0.39 | 0.014 |
| I-TEQ incl. LOD          | 14.4                                     | 5.42 | 0.39 | 0.015 |
| WHO-TEQ excl. LOD        | 14.9                                     | 5.59 | 0.41 | 0.013 |
| WHO-TEQ incl. LOD        | 14.9                                     | 5.59 | 0.41 | 0.015 |

Fig. 2: Cross-section of the sampled channel of sintering plant SIFA 1



sampling site: SIFA I internal- $\emptyset = 4,258$  m area = 14,29 m<sup>2</sup> external- $\emptyset = 5,00$  m perimeter = 15,70 m



## Fig. 3: Velocity profile of the 4 selected measurement days at the sintering plant SIFA 1

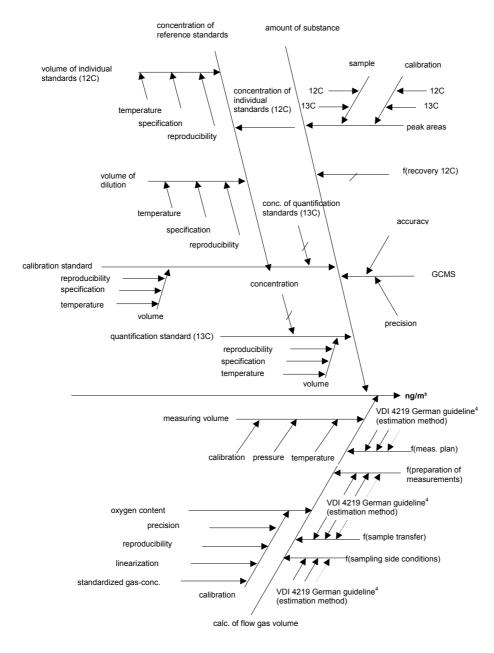
#### **Results and Discussion**

The uncertainty has been determined in accordance with the methods of GUM, DIN V ENV 13005:1999-06 and QUAM. The data taken for the determination of the uncertainty are based both on repeated measurements and range estimations. The following 'cause and effect diagram' (Figure 4) gives an overview on the impact parameters taken into consideration.

The calculated uncertainty of measurement with regard to the determination of the PCDD/F concentration in the flue gas of the sintering plant based on the whole procedure (planning of sampling, sample preparation, peripheral sample conditions and sample transport excluded) ranges between I-TEQ/WHO-TEQ  $\pm$  9 % and I-TEQ/WHO-TEQ  $\pm$  12 %. The calculations show that the use and the mastery of the state-of-the-art technique in sampling and analyses can provide reliable results with a slight uncertainty, not influenced by the factor 1000-scale of the concentration considered. The reported uncertainty is an expanded uncertainty calculated by a coverage factor 2 which gives a level of confidence of approx. 95 %. However, the variation caused by influences resulting from the plant operation have to be critically included into the assessment of measurement results as well.

### References

- 1. GUM Guide to the expression of uncertainty in measurement (1995)
- 2. German version DIN V ENV 13005:1999; Guide to the expression of uncertainty in measurement
- 3. EURACHEM/CITA Guide (Second Edition 2000) Quantifying uncertainty in analytical measurement
- 4. VDI 4219/Draft (August 2000) Quality assurance-Determination of the uncertainty of emission measurements-Systematic estimation of the contributions to the uncertainty of a measurement result



# Fig. 4: Cause and effect diagram (uncertainty of PCDD/F flue gas measurements)