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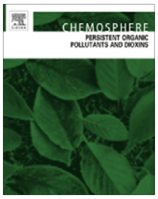

# Interlaboratory comparison of the determination of chlorinated dibenzo-*p*-dioxins and dibenzofurans according to regulatory methods EN 1948 and EPA 1613b

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## ABSTRACT

Four laboratories participated in a collaborative study to determine differences in analytical results generated according to two different compliance methods, US EPA Method 1613b and European Union Method EN 1948 for the determination of chlorinated dibenzo-*p*-dioxins and dibenzofurans (CDD/CDFs). Various sample matrices containing the analytes at levels ranging from parts-per-quadrillion (ppq) to parts-per-billion (ppb) were used to illustrate differences and similarities between the two analytical methods. The choice of the sample matrices analyzed in this study was made to mirror many of the real-world samples that are of interest to Dow and also to test the laboratories on many different, complex matrices. For this reason, commercially available performance evaluation samples were not used. The study results indicate that the 1613b requirement for confirmation of analyte identity and concentration on a second, polar gas chromatographic column for 2378-tetrachlorodibenzofuran (TCDF) only may lead to quantitative results which are biased high compared to EN 1948 which additionally requires confirmation for all 2378-substituted tetra – through hexachlorodibenzo-*p*-dioxins and dibenzofurans.

## 1. Introduction

Because of the global breadth of The Dow Chemical Company, environmental projects frequently span international borders; and data generated to demonstrate compliance with national regulations must conform to nationally-mandated analytical methods. Frequently, these compliance methods are designed to be rugged, reproducible, and expedient; but they may not always deliver absolutely accurate results due to some inherent biases. We have found that, occasionally, researchers wish to compare data generated according to the different compliance analytical methods. However, comparison of results of analyses performed according to similar compliance methods such as those in use in the United States and the European Union should not be attempted unless the correlation of the two methods has been established. For example, a previous comparison of three national compliance methods (US EPA Method 23 and German VDI 3499/2 and 3499/3) for the collection of incinerator stack gas emissions for the measurement of chlorinated dibenzo-*p*-dioxins and dibenzofurans (CDD/CDFs) demonstrated that there was a distinct bias in the sample collection procedures(Wallbaum et al., 1995).

In this report, a variety of sample matrices (wastewater, biological sludge, process by-products, and carbon adsorption media) were analyzed for CDD/CDFs according to US EPA Method 1613b(Telliard et al., 1994) and following the principles of the European Standard Method EN 1948(Standard EN, 1948) by four different laboratories skilled in the application of these methods. The results obtained from the laboratories have been compared; and, in some cases, additional confirmatory analyses were performed in order to better define and minimize the differences between the methods.

## 2. Materials and methods

The laboratories were selected to participate in the collaborative study based upon their experience in analyzing samples according to the methods defined in Table 1 below. These laboratories routinely participate in international collaborative studies on the determination of CDD/CDFs in many different matrices. Because of the experience of SGS in analysis according to both EPA 1613b and EN 1948, this laboratory was chosen to perform the

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**Table 1**
Participating laboratories and methods used for the analysis

| Laboratory | Analytical method |
|---|---|
| Alta Analytical, El Dorado Hills, CA, USA | EPA 1613b |
| Dow Chemical Co., Midland, MI, USA | EPA 1613b (modified) |
| GfA, Münster, Germany | EN 1948 based |
| SGS, Antwerp, Belgium | EPA 1613b (optimized) and EN 1948 based |

analyses by both of the methods in order to eliminate any interlaboratory variables. The participants were instructed to follow their standard laboratory protocols which are based on the defined methods. No special cleanup or separation steps were to be implemented unless there were standard practice for the laboratory or were allowed by the method (e.g., extended Soxhlet extraction time for samples containing activated carbon).

In summary, the analytical methods that were used for the analyte measurements are described below:

Alta, SGS EPA 1613b – Extraction with toluene, chromatographic cleanup on mixed (acid/base) silica, alumina, and carbon; HRGC–HRMS analysis on 60 m × 0.25 mm DB-5MS column with confirmation analysis for 2378-TCDF only on 30 m × 0.25 mm DB-225 (Alta), or confirmation for 2378-TCDF, 23478-PeCDF, 234678-HxCDF, and 123789-HxCDF on 60 m × 0.25 mm SP-2331 (SGS).

GfA, SGS EN 1948 – Extraction with toluene, chromatographic cleanup on mixed (acid/base) silica, silver nitrate/silica, alumina, carbon; HRGC–HRMS analysis on 60 m × 0.25 mm DB-5MS column with confirmation analysis for selected furan isomers (2378-TCDF, 23478-PeCDF, 234678-HxCDF, and 123789-HxCDF) on 60 m × 0.25 mm SP-2331.

Dow EPA 1613b (modified) – Extraction with benzene, chromatographic cleanup on mixed (acid/base) silica, silver nitrate/silica, alumina; HRGC-HRMS analysis on 30 m × 0.25 mm Equity-5 column with confirmation analysis for selected furan isomers (2378-TCDF, 23478-PeCDF, 234678-HxCDF, and 123789-HxCDF) on 30 m × 0.25 mm DB-225.

The following sample matrices were chosen for the study based upon a variety of factors including expected analyte concentration (ppq to ppb), expected interferences (isomeric and non-CDD/CDFs), analyte extractability from the matrix, and ability to produce a homogeneous subsample (see Table 2).

The samples were homogenized prior to aliquoting and shipment to the participating laboratories. Because the main purpose of this study was the comparison of the two different compliance analysis methods and the determination of the interlaboratory precision of the CDD/CDF measurements (and not necessarily the accurate measurement of the analytes in these specific samples), some of the steps employed to homogenize the samples (drying and grinding of the solid samples and filtration of the process byproduct) may have affected the absolute CDD/CDFs concentrations in the samples. For the purposes of this discussion, the main focus will be on the relative precision of the analytical results among the participating laboratories and not on the absolute levels of CDD/CDFs that were found in the samples. Therefore, absolute analyte concentrations that may be presented in later data tables in this report should be regarded as semi-quantitative because of the possibility of analyte loss during the sample homogenization procedure.

**Table 2**
Description of sample matrices analyzed in collaborative study

| Sample number | Source |
|---|---|
| Sample #1 | Internal plant wastewater effluent A |
| Samples # 2 and #3 | Internal plant wastewater effluent B, duplicate samples |
| Sample #4 | Wastewater treatment plant solids |
| Sample #5 | Combustion gas carbon adsorber |
| Sample #6 | Intermediate process byproduct for recycle |

**Table 3**
Comparative summary of the GC columns used

| ALTA<br>EPA | DOW<br>EPA (modified) | GfA<br>EN | SGS<br>EPA and EN |
|---|---|---|---|
| DB-5MS (60 m) | Supelco Equity-5 (30 m) | DB-5MS (60 m) | DB-5MS (60 m)<br>BPX5 (only sample 5) |
| DB-225 for 2378-TCDF (30 m) and extended confirmation | DB-225 (30 m) for selected isomers | SP 2331 (60 m) for selected isomers | SP 2331 (60 m) for selected isomers |

All of the laboratories followed sample analysis procedures that complied with the requirements of the respective matrices and methods with the exception of the data generated by the Dow laboratory. In this case, the gas chromatographic column used for the isomer separation was shorter than the suggested 60 m column specified in EPA 1613b. This change has been implemented in order to decrease the analysis time, which increases sample throughput in the Dow laboratory with the understanding that some of the analytes could be biased high by inadequate isomeric separation. One of the secondary purposes of this study was to be able to better define the impact of the use of the shorter GC column on the quantification of 2378-substituted CDD/CDFs and the calculation of TEQ compared to the 1613b-mandated 60 m column. Table 3 describes the gas chromatographic columns that were used in the HRGC–HRMS separations.

## 3. Results and discussion

A summary of the results of the comparison of the TEQ concentrations obtained by the two methods is compiled in Table 4. In this table, the TEQ concentrations for the four listed samples are compared for the different analysis methods studied and degrees of confirmatory analysis performed. (Duplicate samples 2 and 3 are not included in this table because they contained low concentrations of analytes, ~4 ppq I-TEQ, which did not significantly change with confirmatory analysis. The description and inclusion of these samples are given to suggest that the confirmation analysis necessary only when there are significant amounts of the analytes present in the sample extract. Individual analyte concentrations are not included in this paper because they are generally below the minimum levels (ML) defined for Method 1613b.) In the process of conducting these experiments, Alta began the study with the intent of strictly following the requirements of EPA 1613b. The study plan was that the Alta analysis procedure would use the GC column for analysis and analyte confirmation for 2378-TCDF only as defined by 1613b. The data that Alta reported by following this procedure is listed in Table 4 as "EPA 1613b Orig." Comparison of these results with the EN 1948 method results from SGS and GfA indicated that there were, in two of the samples, statistically higher results from EPA 1613b than from EN 1948 because of a more extensive isomer confirmation process in EN 1948.

The data shown in Fig. 1 depict the amount of variation that was observed in analytical results obtained from the strict adherence to both EPA 1613b and EN 1948 for one exemplary sample. Other samples showed similar trends so they will not be presented here. In Fig. 1 the following data are presented. The horizontal bars represent the average congener concentration measured on the right-hand *y*-axis, from all of the participant laboratories (note the logarithmic scale). The vertical bars associated with the average values depict the minimum and maximum data values from the participants. (Longer vertical bars indicate greater variation