Interlaboratory Comparison: Determination of Chlorinated Dibenzo-p-dioxins and Dibenzofurans by Methods EN 1948 and EPA 1613b

M. Wilken[1], Les Lamparski[1], G. D. Martin[1], T. L. Hescott[1], K. K. Mendyk[1], V. N. Fishman[1], W. J. Luksemburg[2], M. Maier[2], S. Hamm[3], W. Sunderhauf[3], M. Van Ryckeghem[4], F. Neugebauer[4], G. de Smet[4]

[1]Dow Chemical Co.
[2]Vista Analytical Laboratories
[3]Eurofins GfA
[4]SGS Belgium

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 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[1].

In this report, a variety of sample matrices (wastewater, biological sludge, and carbon adsorption media) were analyzed for CDD/CDFs according to US EPA Method 1613b[2] and following the principles of the European Standard Method EN 1948[3] by 4 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 performed in order to minimize the differences between the methods.

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. Because of the experience of SGS in analysis by both EPA 1613b and EN 1948, this laboratory was chosen to perform the 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 they were standard practice for the laboratory or were allowed by the method (*e.g.,* extended Soxhlet extraction time for samples containing activated carbon).

Table 1: Participating contract laboratories and methods used for the analysis

Laboratory	Analytical Method
Vista 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 and EN 1948 based

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/CDF), analyte extractability from the matrix, and ability to produce a homogeneous subsample.

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

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 not necessarily the accurate measurement of the analytes in the sample matrices, 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/CDF concentrations in the samples. For the purposes of this discussion, the main focus will be on the relative analytical results among the participating laboratories and not on the absolute levels of CDD/CDFs that were found in the samples.

All of the laboratories followed sample preparation 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 is shorter than the required 60 meter 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. Table 3 describes the gas chromatographic columns that were used in the HRGC-HRMS separations.

Table 3: Comparative summary of the GC-columns used

VISTA	DOW	GfA	SGS
EPA	EPA (Modified)	EN	EPA and EN
DB 5-MS (60m)	Supelco Equity-5 (30m)	DB 5-MS (60 m)	DB 5-MS (60 m) BPX5 (only sample 5)
DB 225 for 2378-TCDF (30m)	DB-225 (30m) for selected isomers	SP 2331 (60 m) for selected isomers	SP 2331 (60 m) for selected isomers

Results and Discussion

The results of the comparison of the TEQ concentrations obtained by the two methods are 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&3 are not included in this table because they contained low concentrations of analytes which did not significantly change with confirmatory analysis). In the original data packages, Vista reported data that most nearly followed the EPA provisions for analysis on a 60m "DB-5" column followed by confirmation of concentration for 2378-TCDF only. (While it is commonly assumed that DB-5 and DB-5MS are similar columns, isomeric separations are different, primarily for 2378-TCDF, 234678-HCDF and 123789-HCDF[4].) Vista subsequently repeated the confirmatory analysis for P_5CDFs and HCDFs also. Dow and SGS followed an extended confirmation procedure for their original data report (this confirmation protocol is similar to that defined in EN 1948). GfA and SGS apply this confirmation procedure routinely for matrices similar to those studied here. During the comparison of the isomeric concentrations for the extended confirmation data from Vista, we found that there are some occasions (specifically involving 234678-HCDF) in which the confirmatory analysis yields isomeric data that is actually higher than the original measurement. This is due to co-elution of isomers on the DB-225 that does not occur on the DB-5 or DB-5MS GC columns. If only the confirmatory values were to be used for reporting quantitative results, there may be additional isomeric interferences introduced into the results. This finding led to the formulation of the "optimized confirmation analysis" which specifies a comparison of results for the original and confirmation analyses for each of the “2378-substituted” TCDF, P_5CDFs, and HCDFs and selection of the lower calculated isomeric concentration for reporting purposes. The comparison of the averages of all of the pooled “optimized” data with the original 1613b data shows that in some cases there is a statistical difference between the data sets at the 95% confidence level. The relative concentrations of analytes measured by the two methods appear to be related to the dominant chemistry (chlorination or incineration *de novo*) that produces the furan isomers. The best agreement between the methods was shown for incineration produced CDD/CDFs.

The results of this study support the following conclusions:

- Strict adherence to the requirements of EPA 1613b with confirmatory measurements made for 2378-TCDF only may yield results that are biased high relative to EN 1948 based methods by ~50% (20% RPD), as observed for some of the samples in this study.
- Confirmation of analyte concentration for 2378-TCDF did not indicate any isomeric interferences for these samples when the analysis was done on either DB-5MS or Equity-5 columns. However, confirmation of analyte concentration on DB-225 or SP-2331 columns for 23478-P_5CDF and 123789-HCDF measurements can result in significantly lower concentrations due to elimination of interferences.
- Confirmatory analysis of the 234678-HCDF concentration on a DB-225 column can result in higher apparent concentrations due to isomeric interference that was not present on the DB-5MS separation.
- Excellent agreement between the EPA 1613b (modified) and EN 1948 based methods can be achieved if the optimized confirmatory analysis is used in conjunction with EPA 1613b.
- The overall variation among the four laboratories in the analysis of these four samples ranging in concentrations from ppq to ppb was between 8 and 16%.

Table 4: Summary of interlaboratory variation

		Average concentration (TEQ min) *				
Spl #	unit	EPA 1613b orig.	EPA 1613b w/optimized confirmatory analysis	EN 1948 based	Optimized EPA 1613b & EN 1948 based	Original EPA 1613b vs. optim. EPA 1613b & EN 1948 based
		Vista	Vista,Dow,SGS	GfA, SGS	Vista (opt.), Dow, GfA, SGS	Statistical diff. $^{+}$ Y / N
# 1	ppq	17.1	12.2(±1.9)	11.4(±0.5)	11.9(±1.4)	Y
# 4	ppt	316.1	275.1(±17.6)	306.6(±43)	287.7(±30.1)	N
# 5	ppt	12488	10807(±1626)	11073(±2669)	10914(±1767)	N
# 6	ppt	24.1	15.0 (±1.6)	17.3(±1.7)	15.9(±1.9)	Y

* TEQ min for TEQ calculation, analytes below the LoD are assumed to be zero.

$^{+}$ At a 95% confidence level

References

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