Data Quality Issues for Ultra Low-Level PCDD/PCDF Data Analysis

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1. Introduction

In 1985, results of a world-wide survey of PCDD/PCDF analysis capability were reported[1]. Most analytical capability at that time was based on the determination of total PCDD and PCDF congener groups. The concept of total toxicity equivalents was not developed, and - in fact - most laboratories that performed isomer-specific determinations only analyzed 2,3,7,8-TCDD and 2,3,7,8-TCDF. Few analytical standards were available, and many that were available were of questionable quality. No real-matrix reference materials for PCDD/PCDF were commercially available at that time.

The past 10 years have seen dramatic improvements to the analytical methods for PCDDs/PCDFs in almost any type of sample matrix. High resolution GC and high resolution MS methods are available today that can generate analytical results for samples where PCDD/PCDF concentrations are at parts-per-quadrillion concentrations. Good quality analytical standards are commercially available, including ^{13}C-labelled analogues of all of the 2,3,7,8-substituted PCDD/PCDF congeners. However, there still exist many discrepancies in how laboratories handle and report the results of ultra-trace PCDD/PCDF determinations. In some cases, the lack of standard data analysis and reporting protocols has resulted in confusion and even errors in the interpretation of analytical results. Some of these problems, reported initially in 1986[2], are described below. The development of data harmonization procedures could substantially alleviate these data quality problems.

2. Description of Data Quality Issues for Ultra-Trace Determinations

The principal data quality issues for ultra-trace PCDD/PCDF determinations fall into the following categories:

- ❑ incomplete descriptions of experimental procedures
- ❑ inappropriate calibration and standardization procedures (e.g. analyte response outside the calibration range)
- ❑ insufficient bench-level quality control checks (e.g. insufficient blank determinations, poor control of recoveries, no control charts or other long-term checks)
- ❑ little attention paid to the determination and reporting of precision and accuracy
- ❑ no agreement on standard protocols for the determination, reporting, and use of

basic analytical parameters such as %recoveries, detection limits, recovery corrections, use of blank data, etc.

- ❑ little attention given to the significance of reported data (e.g. too many significant figures are often reported).

3. Discussion of Issues

In a cursory examination of the recent PCDD/PCDF literature, it was apparent that the above data quality issues have yet to be resolved for the world-wide PCDD/PCDF analytical community. Some harmonization of protocols is achieved when laboratories perform contract work where the use of specific methodology is mandated by legislation. Even in these cases, however, specific data reporting protocols such as the number of significant figures are often not specified. The above data quality issues are discussed below by reference to the recent Chemosphere special volume which contains the full text of 65 papers presented at the Dioxin'92 conference[3].

Description of Experimental Procedures. Most papers described the analytical procedures followed and/or referred to previosly published works for this information. However, few references were made to the sampling procedures followed, or to the sub-aliquoting procedures followed. Few would argue that the sampling procedures are of critical importance, yet there is still so little reference to sampling methods in the published literature. This may be because many environmental samples are "grab" samples, and as such may not have clearly defined protocols. In environmental studies, samples often are difficult to collect, and may be taken out of convenience rather than because they will be the most representative.

Calibration and Standardization Procedures. Almost no discussion was given to Quality Control (QC) measures taken to ensure that the GC/MS analytical data were generated within the defined calibration range of the instrumental system used. Even when proper calibrations were performed, the frequency of recalibration is hardly ever stated. Accuracy at ultra-trace PCDD/PCDF concentrations is especially difficult to determine, in part because so few real-matrix reference materials are available commercially.

Bench-Level QC Checks. Potential problems such as sample cross-contamination are difficult to control at ultra-trace concentrations. For example, at parts-per-quadrillion concentrations, octachlorodibenzo-p-dioxin (OCDD) is likely to be present in most blanks. OCDD seems to be ubiquitous in the environment - especially on dust particles - and therefore will usually be found in airborne fine dust particles in the laboratory. Thus, the complete elimination of OCDD from blanks becomes more and more difficult as the analytical detection limit is reduced further. As this problem is experienced with increasing frequency, the question of how to treat the blank result grows in importance. Is the blank result simply subtracted from the sample result? Does each sample require its own blank determination? More consistent practices in these areas are required.

Determination of Precision and Accuracy. Increased use of real-matrix reference materials as quality checks will occur, as the commercial supply of these materials grows. However, although the precision of an analysis is relatively straightforward to determine, most PCDD/PCDF publications did not discuss this aspect of the work. There is an unfortunate

tendency to analyze more samples, rather than fewer samples with some replication. This is a direct result of the high cost of a PCDD/PCDF determination - since environmental investigators want to analyze as many different locations as possible. Frequent replicate determinations of PCDDs/PCDFs add substantially to the cost of an environmental investigation , although the quality of the data can be improved in a major way.

Percent Recoveries, Detection Limits, Recovery Correction. There is an especially urgent need to establish standard protocols in these areas. The number of methods of determining these data qualifiers are almost as numerous as the number of laboratories that perform PCDD/PCDF analyses. Much discussion has appeared in the general analytical literature of the use of these terms - especially the detection limit - but no universal agreements on defining these terms has yet emerged. To illustrate the type of problems that could be overcome with universal agreements on definitions, consider the application of recovery correction factors. If recovery of an analyte was 90%, should a recovery correction factor be applied to the data? What if the recovery was only 1%? Few would argue that a correction factor could be applied in the first case, but how many analytical chemists would be comfortable with correcting data by a factor of 100 times? How these various factors are used is an important data quality issue.

Significance of Reported Data. Of the 65 publications from Dioxin'92 that appear in the Chemosphere special volume[3], 25 of them report some data with four or more significant figures. It is the opinion of this Author that the precision of ultra-trace PCDD/PCDF analysis is insufficient to justify reporting greater than three significant figures (in the final result) - and in many cases reporting only one or two significant figures is justifiable. This is an important issue, because non-analytical chemist users of ultra-trace PCDD/PCDF data often have little knowledge of the large error estimates that must be associated with low-level data. Standardized protocols for PCDD/PCDF data reporting should include a statement of the analytical errors that are expected.

4. Conclusions

The impressive improvements in analytical capabilities over 10 years for the determination of PCDDs/PCDFs at ultra-trace concentrations have not been accompanied by a parallel improvement in data analysis and reporting protocols. Method harmonization exercises are needed to rectify this situation.

5. References

1) Clement R.E. (1986): Worldwide Survey on Chlorinated Dibenzo-p-dioxin (CDD) and Dibenzofuran (CDF) Analysis Capability. Chemosphere 15, 1941-1946.

2) Clement R.E. (1986): Reporting Chlorinated Dibenzo-p-dioxin and Dibenzofuran Data in Scientific Publications. Chemosphere 15, 1157-1164.

3) Aitio A., A. Hesso, M. Luotamo, and C. Rosenberg, eds. (1993): Chlorinated Dioxins and Related Compounds 1992. Chemosphere, Vol. 27, 1-3, 516 pp.