DETERMINATION OF THE LEVEL OF QUANTIFICATION FOR 2,3,7,8 - TCDD AND 2,3,7,8-TCDF IN PULP AND PAPER MILL EFFLUENTS

Chiu,C.[A] ,Halman, R.[A], Atkinson, G.[B],Poole,G.[A],Thomas,R.[A] Turle,R. [A],Bumbaco, M.[A]
[A] Environment Canada, Technology Development Branch, River Road Environmental Technology Centre, Ottawa, Ontario, Canada, K1A OH3
[B] Environment Canada,Office of the Science Advisor,PVM,Hull,Quebec,Canada,K1A 0H3

INTRODUCTION

Environment Canada, in support of the Canadian Environmental Protection Act (CEPA) regulations governing the release of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in pulp and paper mill effluents[1], has developed a reference method[2] to identify and quantify these compounds at ultra-trace levels using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Under the regulations, effluents must not contain a "measurable concentration" of either 2,3,7,8-TCDD or 2,3,7,8-TCDF. A "measurable concentration of 2,3,7,8-TCDD" is defined in the regulations as a concentration greater than the Level of Quantification (LOQ) established using the reference method. A "measurable concentration of 2,3,7,8-TCDF" is defined as a concentration that is greater than the LOQ and that, when multiplied by 0.1, exceeds 5 ppq (i.e. value greater than 50 ppq). The magnitude of interlaboratory variability which can be expected from use of this reference method with samples containing near-detection-limit concentrations of TCDD/TCDF must be known in order to establish LOQ values. An interlaboratory study was therefore carried out to generate the data from which reasonable and valid LOQ values could be established.

STUDY DESIGN

With assistance from the Pulp and Paper Research Institute of Canada (PAPRICAN), the most current available effluent data from the 47 bleached chemical pulp mills across Canada were assessed to identify candidate effluents for use as samples for the interlaboratory study. Nine pulp mills were selected as candidates and effluent samples from these mills were collected for dioxin analysis. Two mills were finally chosen as sample sources on the basis of appropriately low TCDD and TCDF concentrations in their final effluents.

Approximately 210 litres of composite effluent from the final outfall of the treatment system of each of these two pulp mills were collected, homogenized and split into 180 one-litre bottles. Homogeneity was confirmed by weighing the suspended particulate of randomly-selected sub-samples. The standard deviation of the five measurements for each effluent was less than 5% of the mean value.

Each participating laboratory received 8 one-litre sub-samples of each effluent, plus

various solutions of native and isotopically-labelled PCDD/PCDF congeners, including a set of four GC/MS calibration standards. Calibration standards contained TCDD/TCDF at concentrations ranging from 0.25 to 25 pg/uL. Laboratories were instructed to adhere to the key procedural elements and performance criteria specified in the reference method. This method allows users a large degree of freedom in the choice of sample preparation techniques.

RESULTS AND DISCUSSION

Ten laboratories participated in this study. Participants included commercial, industrial and governmental laboratories in Canada and the United States.

Two laboratories' results were rejected because their initial calibration and calibration verification data very clearly did not meet applicable performance specifications. Analytical performance of the remaining eight participants are summarized in Table 1. In general, laboratories performed very well, although only three laboratory demonstrated that they had satisfied all requirements. No more than two laboratories experienced difficulty with any single performance specification. Lab E failed to achieve method detection limits of 4 ppq for 2,3,7,8-TCDD and 2,3,7,8-TCDF. Surrogate recoveries reported by Labs A and G for effluent I replicates were generally lower than the required minimum recovery of 40% for both TCDD and TCDF. Contamination did not appear to be a problem on the basis of the glassware proof rinse and method blank data that was submitted. Criteria for gas chromatographic performance, mass resolution, calibration linearity, and ongoing verification of calibration stability were met by all laboratories listed in Table 1.

Both the Grubbs and Dixon tests, at the 5% significance level, were applied to detect within-laboratory outliers in reported concentration values. Consequently, one TCDD value from Lab H (effluent I) and one TCDF value from each of Labs C and G (effluent II) were rejected as outliers. Standard deviations of the replicate analyses for 2,3,7,8-TCDD and 2,3,7,8-TCDF in each effluent sample were then calculated for each laboratory. Interlaboratory comparison indicated that mean concentration values for lab A were either significantly higher or lower than the means for the other labs, and lab A precision was relatively poor for both analytes in both effluent samples. Consequently, lab A's data was excluded from the statistical calculations for the determination of LOQ values.

The interlaboratory comparison of 2,3,7,8-TCDD and 2,3,7,8-TCDF concentration data for the seven remaining laboratories, in terms of mean and median values, is shown in Table 2. The agreement among laboratories is considered fairly good. The maximum difference between any laboratory-mean value and the interlaboratory median is 35% for effluent I. For effluent II, Lab G's mean concentration value for 2,3,7,8-TCDD was 92% larger than the interlaboratory median concentration. Such a result was not surprising in view of the much lower concentration of 2,3,7,8-TCDD in this sample compared to effluent I.

Interlaboratory standard deviation values for 2,3,7,8-TCDD and 2,3,7,8-TCDF were calculated by pooling all within-laboratory values. As shown in Table 3, pooled standard deviations for 2,3,7,8-TCDF were higher than the pooled standard deviations for 2,3,7,8-TCDD determination. This result is considered to be a direct consequence of the fact that 2,3,7,8-TCDF was present at a higher concentration that 2,3,7,8-TCDD in both effluent samples. Since the measurement process for both congeners is exactly the same, a LOQ

Table 1 Summary of Analytical Performances for 2,3,7,8-TCDD and 2,3,7,8-TCDF Determination

Specifications		Laboratory A	B	C	D	E	F	G	H
Performance Test:	1. Results for both 2,3,7,8-TCDD and 2,3,7,8-TCDF determination are withinin 20% of the spike levels	P	F	P	P	P	P	P	P
	2. RSD for both analytes <20%	P	P	P	P	P	P	P	P
	3. Surrogate recoveries are within range of 40-130%	P	P	P	P	P	P	P	P
Contamination:	4. Each analyte in the glassware combined rinse <4 pg/L	-	P	P	P	P	-	-	P
	5. Each analyte in method blanks <4pg/L	F*	P	P	P	F*	P	P	P
GC Performance:	6. Adequate resolution of 2,3,7,8-TCDD from neighbouring isomers (peak valley <25%)	P	P	P	P	P	P	P	P
Mass resolution:	7. Demonstration of mass resolution of 10,000 minimum	P	P	P	P	P	P	P	P
GC/MS Calibration	8. RSD of the Relative Response Factors for 4-point calibration <20%	P	P	P	P	P	P	P	P
	9. Calculated concentrations for analytes in Calibration Verification Standard are within 15% of their actual values	P	P	P	P	P	P	P	P
	10. Calculated surrogate recoveries for Calibration Verification Standard are within range of 75-125%	P	P	P	P	P	P	P	P
Detection Limit (DL)	11. Instrumental DL ≤0.2 pg for both TCDD and TCDF	P	P	P	P	P	P	P	P
	12. DLs for method blanks and glassware rinses ≤ 4 pg/L	F	P	P	P	F	P	P	P
	13. DLs for effluent I ≤ 4 pg/L	-	P	P	P	F	P	P	P
	14. DLs for effluent II ≤ 4 pg/L	-	F	P	P	F	P	P	P
Surrogate Recovery:	15. Surrogate recoveries for method blanks and glassware rinses are within range of 40-130%	P	F	P	P	P	P	P	P
	16. Surrogate recoveries for effluent I are within range of 40-130%	F	P	P	P	P	P	P	P
	17. Surrogate recoveries for effluent II are within range of 40-130%	P	P	P	P	P	P	F	P

* Not detected at the DL above 4 pg/L
'P ' Passed; 'F' Failed; '-' Data not available

value based on data for the lower concentration congener can apply to both 2,3,7,8-TCDD and 2,3,7,8-TCDF. The LOQ is defined as ten times the standard deviation of the measured concentration at near-detection-limit level[3]. Pooling the standard deviations for both effluent samples, the LOQ for 2,3,7,8-TCDD was calculated to be 15.46 ppq. A value of 15 ppq was therefore adopted to serve as the LOQ value for both 2,3,7,8-TCDD and 2,3,7,8-TCDF. When measuring these two compounds at or near the LOQ concentration, the precision (uncertainty) is expected to be 5 ± ppq at the 99% confidence level.

Table 2 Interlaboratory Comparison of 2,3,7,8-TCDD and 2,3,7,8-TCDF Concentration in Effluents I & II

		Effluent I		Effluent II	
		2,3,7,8-TCDD	2,3,7,8-TCDF	2,3,7,8-TCDD	2,3,7,8-TCDF
Interlab Median (pg/L)		20.25	31.74	3.98	29.00
Interlab Mean (pg/L)		21.53	33.75	4.31	28.58
		Lab Mean / Interlab Median			
Lab:	B	0.87	1.09	0.98	1.00
	C	0.83	**	0.88	1.24
	D	0.98	1.01	0.64	0.77
	E	1.00	0.93	*	0.93
	F	1.30	0.99	1.02	0.96
	G	1.35	1.35	1.92	1.02
	H	1.11	1.01	1.06	1.05

* All Measurements were reported as "Not Detected"
** Data was rejected

Table 3 Interlaboratory Means and Pooled Standard Deviations

		No.of Labs	Mean (pg/L)	Pooled Standard Deviation	Degrees of Freedom	% Relative Standard Deviation
Effluent I:	2,3,7,8 TCDD	7	21.53	1.825	48	8.5
	2,3,7,8-TCDF	6	33.75	2.744	42	8.1
Effluent II:	2,3,7,8-TCDD	6	4.31	1.152	42	27
	2,3,7,8-TCDF	7	28.58	2.432	47	8.5

REFERENCES

1 Department of the Environment, Canada Gazette,PartI, December 14, 1991 *Pulp and Paper Mill Effluent*, Chlorinated Dioxins and Furans Regulations.
2 Environment Canada, *Reference Method for the Determination of PCDDs and PCDFs in Pulp and Paper Mill Effluents*, Report EPS 1/RM/19, February, 1992.
3 Keith, L.H., et al, *Analytical Chemistry*, Vol 55, No 14, P.2217, December 1982.