

LEVEL OF QUANTIFICATION FOR MEASURING PCBs IN STACK EMISSION AND ASH SAMPLES

Chung H. Chiu, Gary Poole, Mylaine Tardif, Dominic Cianciarelli ¹ and Richard Turle

Analysis & Air Quality Division, Environment Canada, 3439 River Road, Environmental Technology Centre, Ottawa, Ontario, K1A 0H3, Canada, Emissions ¹ Research & Measurement Division, Environment Canada.

Introduction

Polychlorinated biphenyls (PCBs) were commercially produced between 1929 and 1977. It was estimated that a total of 610,000 tonnes were produced worldwide ¹ and approximately 40,000 tonnes of PCBs were imported into Canada prior to 1997 ². Because of its unique properties, PCBs were widely used as dielectric fluids in transformers and large capacitors, as heat transfer fluids, hydraulic fluids, lubrication oils and as additives in pesticides, paints, copying papers, adhesive and plastics ³.

Environment Canada has declared PCBs as toxic substances under the Canadian Environmental Protection Act (CEPA). The Toxic Substance Management Policy (TSMP), published in June 1995, provides a framework for making science-based decisions on the effective management of toxic substances. The main management objective is the virtual elimination from the environment of the Track 1 substances - toxic substances that result predominantly from human activities and that are persistent and bioaccumulative.

An assessment report ² published by Environment Canada concluded that PCBs meet all the criteria of Track 1 substances and therefore are destined for virtual elimination.

The Level of Quantification (LoQ) is defined as the lowest concentration that can be accurately measured using sensitive but routine sampling and analytical methods (CEPA section 65.1). Any measurement below the LoQ may not be reliably quantifiable. LoQ should therefore be used as a baseline to assist in establishing a virtual elimination target.

The guideline recommended by the American Chemical Society's Committee on Environmental Improvement ⁴ was adopted for the determination of LoQ. American Society for Testing and Materials has also adopted this guideline as a standard practice since 1998 ⁵. The calculation for LoQ is:

$$\text{LoQ} = 10\sigma$$

where σ is estimated as s , the standard deviation (SD) of replicate measurements of an analyte at a concentration near the detection limit (DL).

This paper summarizes the experiments for the determination of LoQ for measuring PCBs in stack emissions and incineration ash.

Materials and Methods

A stable emission combustion source with almost non-detectable or very little PCBs is an ideal site for the LoQ study. A landfill gas flare at a municipal solid waste disposal site near Ottawa was chosen for testing. A total of 12 test runs were conducted using 12 proofed sets of the modified Method-5 (MM5) sampling train glassware⁶. The sampling probe liner was cleaned and reused after each test. Before sampling, each train-filter was spiked with a cocktail of PCBs at a level around 5 to 10 times the estimated detection limit. A municipal waste incineration ash with a low level of PCBs was also selected for the study. The PCB mixture spiked onto the train filter and the fly ash contained two groups of target compounds: one group had 20 congeners for total PCB analysis, the other group had 12 dioxin-like PCBs for TEQ analysis.

Train samples recovered from the front-half and the back-half components were combined as one sample for PCB analysis. The solid portion (filter and XAD-2) of the sample was spiked with a solution containing twelve ¹³C₁₂-labelled PCB surrogates followed by Soxhlet extraction with toluene for 16 hours. The aqueous portion (condensate and diluted ethylene glycol) was extracted with dichloromethane. Both extracts were combined with the glassware rinses, changed to hexane and concentrated to a small volume before cleanup.

Approximately five grams of the ash sample was weighed out into a glass fiber thimble and spiked with native PCBs and isotope-labelled surrogates. Spiked samples were allowed to dry before placing into the Soxhlet extractor for 20 hours of extraction with toluene. Extracts were changed to hexane and reduced to a small volume before cleanup.

The concentrated extract was cleaned by passing it through a multi-layer acid/base/silver nitrate/silica column. This cleaned extract was split in half for further cleanup. For total PCB, a half portion of the extract was fractionated on an alumina column by eluting with different solvents. Environment Canada's Reference Method EPS 1/RM/31⁷ with respect to sample extraction, cleanup and GC-MS analysis was followed.

For TEQ analysis, the 12 toxic PCB congeners must be free from the interference of other PCBs. This was accomplished by fractionating the other split portion using high performance liquid chromatography (HPLC) with an ethyldimethylsilylated silica column. The fraction containing target PCBs was concentrated to almost dryness and re-dissolved in 0.05 mL recovery standard before GC-MS analysis. Detailed analytical procedures are described elsewhere⁸.

Results and Discussion

Each train or ash sample was spiked with 2 ng each of the 20 individual congeners for total PCB analysis. These congeners are the same congeners specified in the Reference Method as calibration standards. They represent some of the major PCB compounds in our environment and therefore are selected for the LoQ study. In addition, samples were also spiked with 0.5 each of the 12 dioxin-like PCBs.

Mean concentrations and SD for total PCB and TEQ analysis for train and ash samples are summarized in Table 1. Relative standard deviation and variance (s^2) are relatively high for PCBs that are more volatile (i.e., tri- and tetra-chlorobiphenyls) and relatively low for less volatile PCBs that have more chlorine substitutions (i.e., nona- and deca-chlorobiphenyl). The mean

concentration among congeners varied from 2.0 to 7.6 ng for the sampling train and from 1.7 to 3.9 ng for the ash. This large variation is attributed to the background level of PCBs present in the gas and ash samples. Pooled standard deviation (s_p) of the target congeners for train samples is 0.199 ng/m³ or 0.755 ng/train while s_p for the ash is 0.077 ng/g or 0.385 ng/sample. The LoQ for measuring PCBs from an emission source involving MM5 sampling train and GC-MS analysis is therefore estimated as 2 ng/m³ or 7.5 ng per sample. LoQ for the incineration ash is estimated as 0.8 ng/g or 4 ng per sample.

For TEQ analysis, the standard deviation for train and ash samples is 0.0016 ng/m³ and 0.001 ng/g respectively. The estimated LoQ for measuring PCB-TEQ in stack emissions and ash is 0.016 ng/m³ and 0.01 ng/g respectively.

Acknowledgments

The authors would like to acknowledge contributions of other team members: Ian Rigden and Stephanie Bourgeau for sampling, Anna Moudrakovskaia, Mike Lister, Aline Dombroskie and John Coltes for sample workup and Monique Lanoy and David Harnish for GC-MS analysis.

References

1. Durfee, R.L., Contos G., Whitmore F.C., Barden J.D., Hackman E.E. and Westin R.A. (1976) "PCBs in the United States - Industrial Use and Environmental Distributions", USEPA, EPA 560/6-76-005, NTIS No. PB-252 012.
2. Environment Canada, (March 1997) "Scientific Justification, Polychlorinated Biphenyls - Candidate Substance for Management Under Track 1 of the TSMP".
3. Erickson, M.D. (1997) "Analytical Chemistry of PCBs, Second Edition", CRC Press.
4. Keith, L.H., et al (1983) "Principles of Environmental Analysis", Analytical Chemistry, vol 55, no. 14, p. 2210-2218.
5. ASTM (July 1998) "Standard Practice for Determination of a Pooled Limit of Quantitation", D6259-98.
6. Environment Canada (June 1989) "Reference Method for Source Testing: Measurement of Releases of Selected Semi-volatile Organic Compounds from Stationary Sources", Report EPS 1/RM/2.
7. Environment Canada (March 1997) "Reference Method for the Analysis of Polychlorinated Biphenyls (PCBs)", Report EPS 1/RM/31.
8. Huang, E.B., Poole G. and Chiu C.H., (1997) "Isolation and Determination of Toxic Congeners of Polychlorinated Biphenyls in Environmental Samples", J. High Resol. Chromatogr., vol. 20.

Table 1 Summary of PCBs in Train and Ash Samples

Sample-Method	Concentration	Number of Replicates	Mean Concentration	s	RSD, %	s_p
Train-congener	ng/train	12	2.0-7.6	0.12-1.55	5-30	0.755
Train-congener	ng/m ³	12	0.61-2.21	0.037-0.41	6-30	0.199
Ash-congener	ng/sample	10	1.71-3.89	0.068-0.884	3-24	0.385
Ash-congener	ng/g	10	0.3-0.78	0.01-0.18	3-24	0.077
Train-TEQ	ng/train	12	0.0549	0.0058	11	
Train-TEQ	ng/m ³	12	0.0148	0.0016	11	
Ash-TEQ	ng/sample	10	0.0526	0.005	10	
Ash-TEQ	ng/g	10	0.0105	0.0010	10	

s = standard deviation; s_p = pooled standard deviation