

## Experiences with the Analysis of Incinerated Ashes and Associated Matrices for Chlorinated Organics by HRGC/LRMS

- M.G. Foster Roberts<sup>A</sup>, K. Nicol<sup>A</sup>, H. Donison<sup>A</sup>, W. Mills<sup>B</sup>, B. Prucha<sup>C</sup>  
A Zenon Environmental Laboratories, Burlington, Ontario, Canada  
B Woodward-Clyde Federal Services, Rockville, Maryland, formerly of Proctor and Redfern Ltd, Toronto, Canada  
C Proctor and Redfern Ltd, Toronto, Canada

### Introduction

The incineration of PCB contaminated waste has been carried out in a variety of Canadian locations as a means of site remediation. Wastes such as soils, oils, metal drums and concrete are incinerated in a mobile rotary kiln incinerator in order to destroy the PCB contamination. The process is designed with the intention of minimising the formation of PCDD/PCDF and other chlorinated contaminants which could be emitted or generated in the sample matrix. The regulatory requirements of such incineration processes require the reduction of PCB to a level of 0.5 µg/g (ppm) in the incinerated waste samples, so that disposal of the incinerated material can be conducted without the need for secure landfilling.

The intention of our study was to investigate an analytical approach which would enable high quality data to be produced under very short time frames and with a wide variety of sample matrices requiring analysis for PCB by HRGC/LRMS and PCDD/PCDF by HRGC/LRMS. Several of the matrices posed interesting analytical challenges which required the investigation of the effects of particle size, moisture content, and sample heterogeneity on the quantitative data generated for the incinerated materials.

This paper presents the experiences encountered during the course of a recent project involving the analysis of over 900 incinerated ash samples and the analytical approaches developed to resolve the difficulties of the generation of high quality data from such complex matrices.

### Approach

The study involved the analysis of over 900 incinerated ash samples during the course of the incineration of materials contaminated with PCB. Each sample of incinerated ash was removed from a storage bin containing 12 tons of waste material. On arrival at the laboratory, several samples were composited into a single sample. The composite sample was analysed by GC/MS. If the levels determined in the composite were above the defined regulatory limits of 0.5 ppm for total PCB, each individual sample used to generate the composite sample was analysed separately. This would enable the container which contained contaminated material to be identified. On several occasions, the levels of PCB found in the individual samples were different from and lower than the levels found in the composite sample. Several experiments were devised in order to investigate the reason for the discrepancy found in the data generated.

### 1. Size Fraction experiment:

Two typical incinerated ash samples were combined and the sample mixed well. A portion of the sample was analysed "as is". A portion of the remaining moist sample was separated visually into large particles and small particles and the two portions analysed separately for PCB. The remaining portion of the moist sample was dried at 105° C. Half of the dried sample was separated visually into large and small particles and each analysed separately. The rest of the dried sample was separated into three size fractions using a set of sieves with 8 and 30 mesh sizes. Each sample was analysed for PCB by HRGC/LRMS as described below.

### 2. Homogeneity Experiment:

This study involved a series of four samples requiring a composite to be prepared for analysis. A total of 5 separate composite samples were prepared from the individual samples and these were analysed for PCB by HRGC/LRMS.

### Methods

The analysis of PCBs by GC/MS was developed for this project in order to provide a detection limit of 0.05 µg/g (ppm) in each sample matrix analysed within 24 hours of receipt of the samples. It is based on a method developed by Environment Canada <sup>1</sup>, modified to enable the turnaround time requirements to be met. The QC/QA protocols used, in support of the data generated, were stringent and included the analysis of method blanks, surrogate spikes representing each congener group from Cl<sub>3</sub> to Cl<sub>8</sub>, duplicate analyses and reference standards.

Each sample was mixed with sodium sulphate, spiked with <sup>13</sup>C<sub>12</sub> labelled PCB standards as internal standards, extracted with hexane/acetone using a wrist - action shaker and cleaned up with alumina. The cleaned-up extract was spiked with a <sup>13</sup>C<sub>12</sub> labelled PCB standard as an injection standard prior to analysis by HRGC/LRMS using selected ion monitoring, in order to improve detection limits to a level compatible with regulatory requirements, while retaining the specificity required. Calibration of the instrument was carried out using 5 concentration levels of standards and quantification was carried out using the relative response factor calculated for each congener group.

### Results

The results for the total PCB found in each sample analysed are presented in Table 1. The size fraction study demonstrated that, for both wet and dry incinerated ashes, as the particle size decreases, the concentration of PCB's increases. The evaluation of the data from the different sized fractions indicated that the concentration found in the small size fraction was a factor of ten higher than that found in the large size fraction. In the dried ash, the concentration found in the smallest size fraction is somewhat higher than that found in the fraction between mesh size 8 and 30. The results from the evaluation of the size fractions defined visually and defined by the sieves in the dried sample indicated comparable data for the concentration of PCB in each of the large and small fractions. The difference in distribution of the PCBs in the different sized fractions is likely caused by the absorption of the PCB's onto the surface of the incinerated particles. This demonstrates the importance of the sampling protocol for the generation of quality data.

**TABLE 1**

**Size fractionation of Incinerated ashes**

	TOTAL PCB µg/g
Normal moist ash selected visually to be representative	1.8
WET Ash - large particles	0.22
WET Ash - small particles	2.3
DRY Ash - large particles	0.19
DRY Ash - small particles	1.8
DRY - > 8 mesh	0.25
DRY - < 8 mesh	1.3
DRY - < 30 mesh	1.7

The ash samples which had been dried at 105°C prior to analysis presented with a reduction in concentration of total PCB compared to the incinerated ash analysed in the moist state. The loss shown was over 20%. The reduction is greater in the concentration of the di-, tri-tetra and penta chlorinated biphenyls. The higher chlorinated biphenyls showed no effect on drying, because of their lower volatility. The drying process has, therefore been shown to be detrimental to the provision of accurate data because of the losses of the more volatile PCB's.

The homogeneity study provided data on 5 equivalent composite samples. Four of the composite samples provided data which were comparable. One of the samples, however, was found to have levels of PCB more than an order of magnitude higher than the other four. This result confirms our experiences during this project, which have highlighted the difficulty in reproducing a high concentration level of PCB found in a composite of incinerated ash.

### Conclusions

The generation of a representative sample for the analysis of ultra-trace levels of organics contaminants is a difficult analytical challenge. The approaches of coning and quartering which have been used for generating representative sub-samples for inorganics analysis depend, for their success, on a dry sample. Drying of solid samples prior to organics analysis will be associated with losses of the more volatile contaminants of interest as confirmed in this study for the lower chlorinated PCB homologues. This approach, therefore, would provide inaccurate data for organics. The sub-sampling process must take into account, the size distribution of the particles within the sample and attempt to use a truly representative sample and provide data which are accurate for the evaluation of the success of the PCB incineration process.

<sup>1</sup> A Method for the Analysis of Polychlorinated Dibenzo-para-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Polychlorinated Biphenyls (PCBs) in Samples from the Incineration of PCB Waste. *Chemistry Division, River Road Environmental Technology Centre, Conservation & Protection, Environment Canada. Report EPS 1/RM/3, June 1989.*