Effects of inorganic chlorine sources on PCDD/Fs formation via heterogeneous synthesis on fly ash surfaces

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Introduction

Currently available sample collection methods for determination of the emissions of chlorinated dibenzo-p-dioxins and dibenzofurans (CDD/CDFs) from incineration devices predominately focus upon the measurement of these analytes for compliance purposes. As such, the usual methods of sample collection conform to the requirements defined by various government agencies. For example, in the United States, EPA Method 23a [1] is required for all compliance measurements. European analyses may be predicated upon the procedures defined in the VDI 3499-2 [2] or the subsequent EN1948-1 [3]. The common feature for all of these methods is that the sample collection time is relatively long, 4-6 hours. Recently, procedures have been described for the long-term monitoring of stack emissions through the use of continuous on-line samplers [4-6]. All of the previous methods are useful for monitoring long-term (many hours) emission trends; but in examining the short-term variations in incinerator operation, information may be lost. In studies to improve incinerator operation, it is frequently necessary to measure the effects of operational upsets that may range from 15 minutes to 1 hour in duration.

Over the period of the last 8 years, the number of analyses of stack gas emissions samples collected for the measurement of CDD/CDFs that have been undertaken at The Dow Chemical Company has increased dramatically, primarily because of company-initiated emission reduction projects. These initiatives have resulted in an increase in the number of sample analysis requests from approximately 10-20 per year in 1995 to ~150 per year in 2002 and 2003. EPA –defined sampling procedures are required to demonstrate compliance with emissions regulations.

Because of the complexity of the sample collection procedures for stack gas emissions samples and the limited resources available to meet the ever-increasing sample analysis demands, steps were initiated by Dow Analytical Sciences Lab to reduce the complexity of EPA-defined procedures [1] while not adversely affecting data quality of analytical results. The modified stack gas collection train has been in use for the collection of data to document process improvements undertaken to reduce dioxin emissions from incinerators. This document is intended to 1) describe a simplified stack gas sample collection train which has been used for a number of years at The Dow Chemical Company for the collection of research samples of gaseous emissions from incinerators; 2) explain the procedural differences compared to standard methods; 3) compare data generated by the techniques; and 4) discuss any potential biases in samples collected by this method.

Materials and Methods

Figure 1 shown on the following page illustrates the differences between the EPA Method 23a (1a) sample train and the Dow SSS (1b) sample collection train. Basic changes incorporated in the SSS train are:

- Replacement of the heated sample probe with an unheated probe.
- Elimination of the “hot box” to contain the heated filter and associated connecting glassware.
- Elimination of the quartz-fiber filter.
- Elimination of the condenser to cool the heated gases exiting the “hot box”.
- Connection of the gaseous and particulate effluent directly to the XAD-trap to utilize the absorptive properties of the XAD to capture CDD/CDFs from both vapor phase and condensed liquid phase and to filter the particulates from the gas phase.
- The original design incorporated collection of the condensate after XAD and extraction for possible CDD/CDFs that may have passed through the XAD. Subsequent testing showed that >98% of CDD/CDFs were collected on the XAD, and this condensate trap was eliminated.
- All gas measuring parameters necessary to insure correct measurement of the dry gas volume and collection of isokinetic samples remain the same in both trains.
- Because of the shorter sample collection time, the SSS collection is done on a single traverse only rather than two perpendicular traverses for the Method 23.

- Shipment of the entire sample train to analytical laboratory and rinsing and extraction of all components with benzene to remove CDD/CDFs from the interior of the train. Rather than rinsing and brushing with solvent in the field.

Discussion

As summarized above, one of the main driving forces for the development of a simplified stack gas sampling train was to decrease the amount of time (and hence, expense) associated with the actual collection of emissions samples from waste incinerators. There were, however, other significant reasons for modifying the sample collection process:

- Reducing the number of glassware pieces in the train resulted in lower logistical costs of maintaining an inventory of train components, cleaning parts between uses, and shipping costs. Fewer glass connections in Dow SSS train reduced the likelihood of leaks detected during the pre-test and post-test leak checks. Leak test failures can result in invalidation of a test sample and the need to repeat a test.
- The shorter sample collection time of one hour compared to the four hour sample time could allow multiple data points to be collected in the same amount of time if there were a need to assess the short-term (hourly) variability of a unit. Short-term emission level variations, which are not readily detectable when averaged over a four-hour period, may be more easily detectable by means of the shorter sample collection cycle of the simplified stack gas sampling train.
- The use of the Teflon® filter holder for the trapping of particulates in the hot box may also adsorb CDD/CDFs from the vapor phase. This phenomenon may affect the analyte concentrations in an unknown manner. Under some circumstances the Teflon® may absorb CDD/CDFs from the gas phase and bias results low. Generally, the ratio of the absorbed analyte to the total amount in the gaseous phase is small and may not significantly reduce analyte concentrations for any single sample [7]. Under other circumstances, previously absorbed CDD/CDFs from a higher concentration sample may desorb the analytes and bias a relatively clean sample higher than normal [8].

- The approach of reducing the amount of heated glassware was predicated on the concept that reactive gases in the effluent could change the composition of the analytes as they are trapped on a heated filter for up to four hours. Generally, this is not a problem with emission samples that have been purified through an efficient Air Pollution Control Train; but in some of our initial incinerator improvement studies, we wished to evaluate the CDD/CDF content in gases before the acid absorbing towers. These samples contained significant levels of chlorine and hydrochloric acid, which would have adversely affected the measured CDD/CDF concentrations. The ability to accurately measure the CDD/CDF content of gaseous emissions upstream of the air pollution control system was instrumental in isolating process conditions that could be responsible for the formation or emission of CDD/CDFs.

Data illustrating the quantitative comparison of the two sample collection trains are shown in Table 1 below. In these experiments, specific incinerator effluent samples were simultaneously collected using the different sample trains. Since the normal collection times that were employed for the two trains were not identical (four hours vs. one hour), absolute comparison is not possible. In most cases there is good agreement between the SSS and the Method 23a (M23a) for TEQ, generally within ~20%.

One sample from Unit#5 shows both TEQ and total CDD/CDFs levels that are about twice as high for the SSS sample. Possible explanations for this difference are: the possible reaction of CDD/CDFs adsorbed on trapped particles reacting with reactive chemicals in the effluent in the M23a train while being retained on the heated filter for the extended sampling period; or a short-term upset condition that was occurred during the time when both the M23 and the SSS were being collected. The incinerator returned to normal operation and the higher emission level was average down in the M23 sample.

Another obvious sample difference is exemplified in the data shown for the sample Unit#4. This unit was part of the Magnesium Production operation and not a true incinerator. This unit consisted of two furnaces that recycled chlorine between them for the production of magnesium chloride. The gas that was collected was the recycle gas between the units and not true stack gas emission, but the information is included here to illustrate the point that there could be significant differences between samples collected by the M23a train and the SSS train. It has been surmised that the heated portions of the sample train provided an environment that was conducive to the reaction of adsorbed dioxins on the filtered particulates with chlorine in the gas phase and may have resulted in the actual loss of analyte through degradation of CDD/CDFs from the sample.

The comparison for total CDD/CDFs shows a slightly greater amount of variation than for the TEQ; but it is important to point out that in every case except one (Unit#1) both the total and TEQ values reported for the SSS are higher than the M23 results. Possible explanations include:

1) The M23a collection is not as efficient as the SSS train and some analyte is lost by passing through the M23a train.
2) Larger air leaks in the M23a train due to the greater number of, and stress on, glass connections have biased the sample volumes high and, hence, the analyte concentrations low.
3) The SSS-train is inherently more efficient at trapping the CDD/CDFs because they enter the XAD trap in both the gaseous and aqueous phase rather than totally in the condensed aqueous phase.
4) Poor recovery of analytes in the M23a due to inefficient elution/rinsing from the many glass pieces of the M23a train.
5) Reaction of CDD/CDFs on the heated components of the M23a train.
6) The SSS-train is biased high because CDD/CDFs are produced under certain conditions on the SSS train.

Definitive explanation of the causes of the differences in analyte concentrations is beyond the scope of this report and could be the subject of a more extensive collaborative research project. However, regardless of the reason for the differences, the results obtained from samples collected with SSS train: 1) do not underestimate the CDD/CDF concentrations relative to the Method 23a train; 2) may, under some conditions, be more accurate than Method 23a; 3) are usually within commonly accepted “experimental error” (±25%) for these types of measurements.

Table 1: Quantitative Comparison of Method 23 and Dow SSS Sampling Trains

		M23		SS			Relative
TTU	Date	Total	TEQ	Total	TEQ		TEQ
Unit#1	06/12/95	198.1	3.12	156.1	3.14		101%
Unit#1	06/13/95	150.4	3	160.3	3.07		102%
Unit#2	06/13/95	60.97	0.83	84.36	0.84		101%
Unit#2	06/14/95	71.97	0.77	89.33	0.77		100%
Unit#3	08/03/95	178.8	3.05	246	3.83		126%
				211.1	3.47		114%
Unit#4	08/05/95	6.83	0.18	100	3.7		2056%
Unit#5	08/03/95	193.2	1.93	407.4	3.54		183%
	08/03/95	156.6	1.61	195.2	1.74		108%

Conclusion

The productivity enhancements that are discussed have reduced the cost of sample collection for stack gas emissions samples by more than ~70% based on previous experience using EPA Method 23 methodology. This reduction came by implementing a shorter sample collection time, which allowed a much greater number of samples to be collected in an 8-hour workday and a greatly reduced amount of collection train glassware. Five SSS trains could be collected in an 8-hour workday, but only one Method 23a sample could be collected in approximately 6 hours. This allows many more samples to be collected for use in process control or process improvement studies. The less complicated (fewer glassware pieces) sample collection train: 1) reduced the amount of glassware precleaning; 2) reduced the possibility of collection train leaks, before and after sampling; and 3) eliminated the need for the particulate filter in the sample train. Analysis of the impinger water collected after passage through the XAD-trap demonstrated that ~98% of the CDD/CDFs are removed on the XAD-trap in the improved configuration, by acting as a vapor and liquid absorbent, that is employed for the SSS train.

Inherent problems with the heated particulate filter and sample probe include the possibility of reactive gases (e.g. Cl_2, HCl) in the sample reacting with compounds adsorbed on the trapped particulates and changing analyte concentrations. Hazardous waste incinerators burning chlorinated wastes have the possibility under extreme conditions or equipment failure of emitting small amounts of HCl or Cl_2 in the gaseous effluent. Normally, these compounds are efficiently removed in the Air Pollution Control System; but occasionally, these components may fail. The reaction of CDD/CDFs with these active gases will change the characteristics of the resulting analytes in an unknown manner. Elimination of the heated portion of the sample train was intended to reduce this possibility.

In summary, the information presented above supports the use of this simplified stack gas collection train for the measurement in CDD/CDFs the gaseous effluent from hazardous waste incinerators operating under a variety of process conditions. Data obtained can certainly be used for process optimization, trouble-shooting, and some emissions estimates. With appropriate validation, we feel that this could also be a cost-effective alternative to Method 23a for the collection of samples for compliance monitoring.

References:

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Figure 1a: EPA Method 23a Train

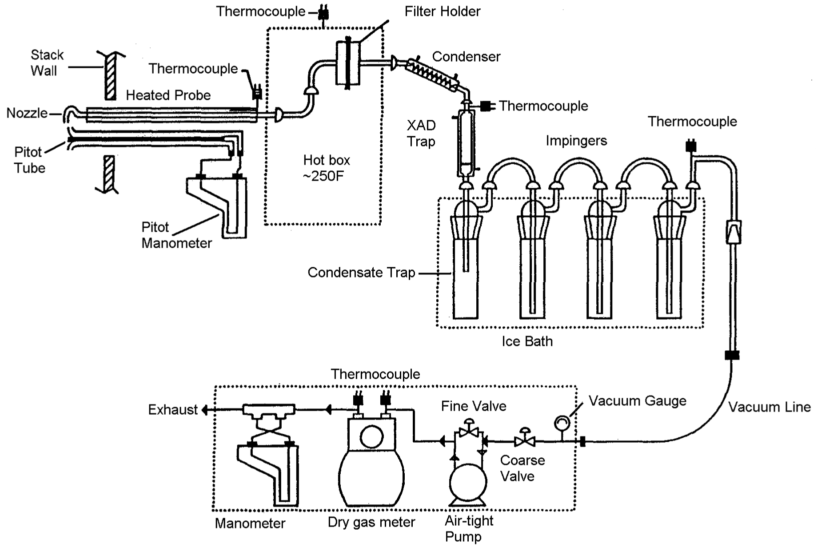

Figure 1b: Dow SSS Train