ABSTRACT

The recently promulgated standard for dioxin/furan emissions from hazardous waste incinerators is 0.2 ng TEQ/dscm. The regulatory method for sampling and analyzing for offgas dioxins/furans is EPA Method 23/0023, which is labor intensive and normally requires a turnaround time of several weeks. A faster and cheaper method for dioxin/furan sampling and analysis would permit more routine monitoring of offgas emissions for dioxins/furans, and could also be used to reduce dioxin/furan emissions through optimization of process conditions.

Screening experiments were conducted to identify promising techniques for accelerated sampling and analysis of offgas dioxins/furans. A thermal desorption-based technique using commercially available equipment appeared to hold the greatest promise for speed and simplicity. Initial method development experiments consisted of spiking selected tetra- through octa-chlorinated dioxin/furan liquid standards onto candidate adsorption media. Based on these experiments, porous glass beads, a diatomaceous earth, and alumina were selected for testing with real offgas samples.

Offgas samples were taken from a pilot scale hazardous waste incineration test system and a hazardous waste-firing marine utility boiler test system. Both systems were operated under conditions expected to produce high concentrations of offgas dioxins/furans.

Thermal desorption-based samples were taken and compared to Method 23 sampling and analysis. Dioxin/furan recoveries relative to Method 23 were approximately 10%, depending on the particular dioxin/furan homolog class. More chlorinated dioxins/furans appeared to yield higher retention/thermal desorption efficiencies than did less chlorinated homologs. Severe background interferences were noted. Individual compound detection limits for thermal desorption of a 7.5 liter offgas sample, analyzed by gas chromatography/low resolution mass spectrometry (GC/LRMS), were approximately 70 ng/dscm. Possible approaches to obtaining a lower detection limit include identifying or developing a more selective and retentive adsorbent medium, using a more sensitive detector, or taking a larger offgas sample. Incomplete thermal desorption of dioxins/furans from offgas particulate may also have contributed to the dioxin/furan recoveries observed in the present experiments, and may be problematic.

Subsequent to the pilot-scale and marine boiler sampling activities, a bench reactor was constructed in order to generate particulate laden, high-dioxin offgas samples at lower cost than is possible with pilot-scale systems. The bench reactor will be used for further development of thermal desorption-based sampling and analysis. Those investigations will assess whether issues of detection limits, interferences, and recoveries can be resolved by thermal desorption techniques alone. If it appears that they cannot, then alternative techniques, for example, carbon dioxide-based supercritical fluid extraction, will be considered.

INTRODUCTION

Objective

The objective of the work described in this paper was to assess thermal desorption-based techniques as a method for sampling and analyzing offgases for dioxins/furans.
Background

The DOE is using or evaluating several thermal and non-thermal technologies for treating hazardous wastes and low-level mixed wastes. Treatment technologies often have the potential for generating gaseous emissions of polychlorinated dioxins/furans, a class of highly toxic compounds which are regulated to very low levels under the recent promulgated MACT Rule. For example, under the MACT Rule, the limit for emissions of dioxins/furans from hazardous waste incinerators is 0.2 ng TEQ/dscm.

The regulatory method for offgas sampling and analysis for dioxins/furans is EPA Method 23, Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources (1). Normal turnaround time for Method 23 and other standard methods of dioxin/furan sampling and analysis is one month or more. To better understand factors affecting dioxin/furan formation, in order to control and minimize dioxin/furan emissions, it would be helpful to have a faster dioxin/furan sampling and analysis method. Accordingly, under the direction of the DOE Transuranic and Mixed Waste Focus Area, MSE Technology Applications, Inc. (MSE), originated and is now testing an accelerated sampling and analysis system based on analytical thermal desorption techniques. This sampling and analysis system is expected to have a turnaround time of as little as 2 hours, or potentially less than 2 hours where higher detection limits resulting from abbreviated sampling times (less than 1 hour) are permissible.

In addition to the specific concerns of DOE, there is the broader public concern that dioxins/furans are generated by many processes other than hazardous waste treatment, including steel making, coking ovens, cement kilns, and petroleum combustion. A rapid screening method would be useful for improved assessments of emissions from these sources.

Conceptually, the thermal desorption-based technique being reported here consists of three steps: sampling and preconcentration, thermal desorption of the analyte(s), and analysis of the desorbed analyte(s). In the present work, each of these steps include the following:

Sampling

The gas sample is drawn through a sampling cartridge containing a suitable adsorbent/filtration material. To lower the detection limit, but at the expense of longer sampling times, a large volume of sample can be drawn through the cartridge. In effect, the sample is concentrated in the sampling cartridge. The cartridge must be capable of both adsorption and filtration, because dioxins/furans may be present in “gaseous” waste streams as a vapor, as a condensed phase, or adsorbed on particulate. In order to reduce interference problems in the later analysis step, an ideal adsorbent cartridge would retain only dioxins/furans and allow all other compounds to freely pass through the cartridge. Actual adsorbent cartridges may be partially selective for dioxins/furans. Identification or development of efficient and selective adsorbent/filtration materials was one of the issues addressed in the present work.

Desorption

The sampling cartridge is heated and purged with an inert gas, in order to desorb the compounds of interest and transfer those compounds as a vapor to a suitable analyzer/detector. Dioxins/furans are high boiling compounds which may adsorb very strongly to native particulate present in offgas samples, therefore application of the thermal desorption technique to dioxins/furans presents technical problems that are not encountered with lower boiling compounds, nor with offgases that do not contain particulates. By controlling desorption conditions it may be possible, to some degree, to selectively desorb dioxins/furans. Desorption efficiency and selectivity are issues that were investigated in the present work.
Analysis

The desorbed compounds are detected and quantified. In the present work, a gas chromatograph/mass spectrometer (GC/MS) was used to separate, detect, and quantify the compounds of interest. While GC/MS is a versatile and widely used technique for quantifying organic compounds, other detectors are also possible. Of particular interest, the EPA and DOE are sponsoring the development of an analyzer designed specifically to be highly sensitive and selective for vapor phase dioxins/furans. This analyzer has the potential to be much faster and more sensitive than GC/MS for the analysis of dioxin/furans, however, as with GC/MS the compounds to be analyzed must be presented to the analyzer in the vapor phase. Accordingly, this analyzer, also, will require a sampling system that can trap and preconcentrate dioxins/furans, which may be present in vapor, condensed, or adsorbed phases, and then quickly transfer the dioxins/furans to the analyzer as a gas.

Similarly to the thermal desorption approach, Method 23 involves three steps: sampling, extraction and cleanup, and analysis. For Method 23, the extraction and cleanup step requires approximately two days to complete, involves the use of complex glassware and heating equipment and relatively large volumes of purified solvents, and must be performed in a specialized chemical laboratory. The thermal desorption approach has the potential to reduce the “extraction” step to a few minutes and eliminate the need for solvents, glassware, and laboratory space. That is, the thermal desorption approach has the potential to provide fast dioxin/furan analyses in a field setting.

The thermal desorption-based method development reported here will be specifically applicable to offgas waste streams, but is expected to be readily adaptable also to solid (particulate) waste streams, and with some modification to aqueous waste streams.

EXPERIMENTAL

Experimental activity consisted of developing methods for thermal desorption-based sampling and analysis of dioxins/furans, by spiking dioxin/furan standards onto candidate adsorption media, and then testing the more promising adsorption media by obtaining concurrent thermal adsorbent and Method 23 offgas samples from a pilot scale incineration system and a hazardous waste-firing marine boiler test system.

Thermal Desorption Analysis Equipment and Procedures

A Hewlett-Packard™ 6890 PLUS™ gas chromatograph (GC) equipped with a Hewlett-Packard 5972A mass selective detector (MSD or MS) and a Gerstel™ TDS-2A thermal desorption system (TDS) front end was used to desorb and analyze thermal desorption tube samples. A high resolution capillary column (HP-5 MS, 5% diphenyl/95% dimethylsiloxane stationary phase, 30 m x 0.32 mm x 0.25 μm) was used for analyses. The MSD was operated in either scanning or selected ion monitoring (SIM) mode. Samples could be injected into the GC/MS either through the Gerstel programmable temperature vaporizing (PTV) inlet (which interfaces the TDS to the GC) or through the standard GC liquid injection port.

The principle of operation for the TDS is to adsorb and concentrate organic analyte vapor onto a suitable adsorbent medium. The analyte is then thermally desorbed from the adsorbent material and transferred to the GC/MS through a heated transfer line. Desorption is accomplished by programmed heating and purging of the adsorbent material. In the Gerstel TDS, the analyte is recondensed in a cold trap, or cooled injection system (CIS), which is also the GC column inlet. This is done while the relatively slow desorption step is taking place. The adsorbent material itself is contained in a standard-sized glass tube 0.25 inches o.d. by 7 inches in length (6.4 mm o.d. x 178 mm length). After purging analyte from the adsorbent material, the cold trap is rapidly heated to quickly transfer the analyte to the GC column. The cold trap may be heated in stages, permitting some interfering compounds to be vented off before transferring the analyte to the GC column.
In principle, the analyte could be transferred directly from the adsorbent material to the GC column; however, good compound separation on the GC column requires that the analyte be transferred to the column very quickly, in a few seconds or less. In the Gerstel configuration, the adsorbent material cannot be heated and desorbed quickly because the heat must be transferred through the walls of the glass tube containing the adsorbent material, and because of the mass and relatively poor thermal conductivity of the adsorbent material itself.

The CIS can be heated at rates from 0.1 °C per second to 12 °C per second and can be held at two programmable temperature plateaus. Liquid nitrogen can be used to cool the CIS to below ambient temperatures. The maximum heating rate for the TDS (that is, the desorption tube) is 20 °C/min. The desorption assembly can be heated up to 450 °C; the CIS assembly can be heated to 350 °C.

For initial method development and adsorbent screening experiments liquid dioxin/furan standards containing selected tetra- through octa-chlorinated dioxins and furans were spiked onto candidate adsorbent materials contained in TDS glass sampling tubes, which were then carried through the thermal desorption process. Spike levels of 50 pg, 500 pg, and 5,000 pg of each selected dioxin/furan compound were used. Chromatograms from spiked adsorbents were then compared to the same liquid standards injected into the conventional GC inlet port. This process was repeated, varying adsorbent materials, desorption times and temperatures, and CIS trapping and desorption times and temperatures in an effort to identify optimum thermal desorption conditions.

**Offgas Sampling and Analysis**

Thermal desorption tube offgas samples and comparison Method 23 samples were taken from nearly adjacent sampling points on a pilot scale incineration test system and a marine boiler test system, both operated under conditions expected to produce high concentrations of offgas dioxins/furans. The combustor systems are described below.

Method 23 samples were taken and analyzed following procedures described in the published method (1), except that the marine boiler Method 23 samples were analyzed by gas chromatography/low resolution mass spectrometry (GC/LRMS) rather than high resolution mass spectrometry (HRMS).

Obtaining desorption tube samples required construction of a sampling probe, shown in Fig. 1.

The probe was designed to be interchangeable with a standard Method 23 sampling probe so that existing Method 23 sampling ports could be used. The exterior dimensions of the probe are 3.5 inches diameter by approximately 24 inches in length. Internally, the probe contains two thermal desorption tubes, a sample tube, and a breakthrough tube, connected in series. The sampling tubes are mounted inside individual cooling/heating jackets through which...
Air is circulated as a heating or cooling fluid. At lower temperature sampling points, the circulated air must be preheated to prevent liquid condensation within the thermal desorption tubes. Preheating is supplied by a small in-line electric heater. A thermocouple mounted at the outlet of the second thermal desorption tube is used to control power to the electric in-line heater.

Preliminary flow tests indicated that the maximum practical sampling rate for a thermal desorption tube packed with adsorbent material was approximately 200 mL/min. A sampling rate of approximately 125 mL/min was used for the pilot scale incinerator and marine boiler tests. The effective nozzle diameter for thermal desorption tube sampling was 4 mm, that is, the inside diameter of the thermal desorption tubes. This nozzle diameter and a 125 mL/min sampling rate resulted in under-isokinetic sampling for the stack velocities of the pilot-scale and marine boiler combustion systems. The expected effect of under-isokinetic sampling is over-sampling of large particulate. Depending on the particle size distribution and the ratio of absorbed (bulk) and adsorbed (surface) dioxins in the offgas particulate, under-isokinetic sampling could result in biased-high dioxin measurements.

Thermal desorption tube samples were analyzed using the thermal desorption equipment and procedures described above, except that two of the adsorbent tube samples were taken through the Method 23 Soxhlet extraction procedure and analyzed by GC/HRMS. Soxhlet extraction was done in order to measure the adsorption efficiency, rather than combined adsorption and desorption efficiency, of the TDS sampling tubes.

Pilot Scale Incineration Test System

The pilot scale incineration test system, located at the MSE Technology Applications, Inc. test facility in Butte, Montana, consists of a primary stream and a slip-stream test bed (SSTB), as shown in Fig. 2. For the present test series, the primary chamber heat source was a 1.6 MBtu/hr oxygen-enriched natural gas-fired combustor (OEC). Normal offgas flow rate from the primary combustion chamber (PCC) is approximately 3.6 kg/min (8 lb/min). Offgas exiting the PCC flows through a secondary combustion chamber (SCC) that nominally operates at 1,090 °C (2,000 °F) and has a design exit mass flow rate of 7.3 kg/min (16 lb/min). At design conditions the SCC provides a 2-second offgas residence time.

The slip stream test bed was designed to provide a means for testing small-scale emission control systems and processes under steady flow conditions. Offgas is drawn through the SSTB from the outlet of the SCC at a rate of 0.9 to 1.8 kg/min (2 to 4 lb/min), and after flowing through the SSTB, is returned to the primary system upstream of the quencher.

During testing, the target stack oxygen concentration was 8%, controlled by varying the oxygen flow rate into the PCC oxygen lance. Measured stack oxygen concentrations varied from 6% to 17%. For these tests, a 1:1 mix of PVC and ABS plastic was batch fed into the PCC at two minute intervals. Batch sizes varied from 400 to 454 grams. Batch feeding caused momentary oxygen-deficient conditions and visible sooting in the PCC, which was expected to cause dioxin/furan formation. While batch feeding, the PCC caused momentary oxygen-deficient conditions at the upstream end of the system, however, the time-averaged excess global oxygen and buffering effects due to downstream mixing maintained stack oxygen above 5%.

In addition to batch feeding plastic into the PCC, a 4%(w/w) solution of 3,4-dichlorophenol in 1,1,1-trichloroethane and an inorganic powder slurry were continuously metered into system piping between the PCC and the SCC, at 10 to 20 mL/min and 10 g/min, respectively. The inorganic powder slurry consisted, by weight, of 50% ferric oxide, 30% silicon dioxide, 10% cupric oxide, 5% aluminum oxide, 2% calcium oxide, 1% sodium carbonate, 1% magnesium oxide, and 1% potassium carbonate. The 3,4-dichlorophenol was expected to act as a dioxin/furan precursor; the inorganic powder was expected to act as a dioxin-forming catalyst.

For the present test series, samples were taken downstream of the SCC, at measured sampling temperatures of 704 to 760 °C (1300 to 1400 °F), and downstream of the hot high efficiency particulate air (HEPA) filter, at measured
sampling temperatures of 188 to 210 °C (370 to 410 °F). The pilot scale test system and test conditions are described in greater detail elsewhere (2).

Marine Boiler Test System

The North American Package Boiler (NAPB) facility is located at the EPA Environmental Research Center (ERC) in Research Triangle Park, North Carolina. The NAPB is a 2.5 x 10^6 Btu/hr, three-pass, fire-tube, Scotch marine utility boiler capable of firing natural gas or #2 through #6 fuel oils. The boiler is capable of generating up to 11 ton/hr (24,000 lb/hr) of saturated steam at up to 1.02 atm (15 psig). The NAPB system is equipped with multiple sampling ports.

For the work described here, Method 23 samples were taken at the third pass sampling port (the last fire tube pass before the stack), while APSA samples were taken at the stack sampling port, approximately 1.5 m (5 ft) downstream of the third pass sampling port. Before these samples were taken, the NAPB system was operated under conditions intended to coat the boiler tubes with soot and copper-containing compounds, which were expected to facilitate the formation of offgas dioxins/furans. For the present samples, the system was operated under “Sooting/Formation Conditions” previously shown to generate dioxins in excess of 250 ng/dscm (summed concentration, mono- through octa-chlorinated species)(3,4). The NAPB system and planned operating conditions
RESULTS AND DISCUSSION

Dioxin/Furans Spiked onto Adsorbent Media

Selected tetra- through octa-chlorinated dioxins and furans were spiked onto candidate adsorbent materials in 50 pg, 500 pg, and 5,000 pg quantities. Adsorbent media tested were bare glass tubes, quartz wool, porous glass beads, Tenax™, Tenax GR, GasChromST™, GasChromR™, neutral alumina, and basic alumina. Particulate media investigated were either 45/60 mesh or 60/80 mesh. Of these media, porous glass beads, GasChromR, and alumina appeared to give usable desorption efficiencies and to have acceptable thermal stabilities (stable above 350 °C). An example chromatogram of thermal desorption of a dioxin/furan mix (500 pg/compound) spiked onto porous glass beads is shown in Fig. 3. For this adsorbent, relative to the same compounds injected into the GC/MS through a conventional liquid injection port, thermal desorption showed recoveries from less than 10% to 100%, depending apparently on the molecular weight of the analyte. Higher molecular weight compounds showed poorer thermal desorption recoveries, probably as a consequence of their higher boiling points.

Pilot Scale Incineration System Sampling and Analysis

Nine thermal desorption tube samples were taken during pilot scale tests conducted in March 2000. Porous glass beads, GasChromR, and alumina adsorbent media were used. Two of the thermal desorption tube samples were taken through the Method 23 extraction and analysis procedure, in order to directly measure the dioxin/furan
retention efficiency of the adsorbent material. Two Method 23 comparison samples were taken and analyzed.

An example chromatogram of thermal desorption of a HEPA outlet offgas sample, porous glass bead adsorbent, is shown in Fig. 4. The chromatogram shown is background corrected; the original chromatogram showed a high background, apparently due to interfering compounds present in the offgas. Qualitatively, the background corrected chromatogram indicates identifiable dioxin/furan peaks. As previously noted, for these experiments the TDS/GC/MS system was calibrated with only seven of the 210 possible dioxin/furan congeners. Accordingly, thermal desorption chromatographic peaks were quantified only by dioxin and furan homolog class, that is, by degree of chlorination.

<table>
<thead>
<tr>
<th>Time</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>10</td>
<td>1500</td>
</tr>
<tr>
<td>20</td>
<td>1800</td>
</tr>
<tr>
<td>30</td>
<td>2000</td>
</tr>
<tr>
<td>40</td>
<td>2200</td>
</tr>
<tr>
<td>50</td>
<td>2400</td>
</tr>
<tr>
<td>60</td>
<td>2600</td>
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<tr>
<td>70</td>
<td>2800</td>
</tr>
<tr>
<td>80</td>
<td>3000</td>
</tr>
<tr>
<td>90</td>
<td>3200</td>
</tr>
<tr>
<td>100</td>
<td>3400</td>
</tr>
</tbody>
</table>

Fig. 4. Chromatogram of thermal desorption sample taken at the HEPA filter outlet, porous glass bead adsorbent material.

Table I shows comparison results for sampling and analysis at the HEPA outlet, by Method 23, desorption tube/Soxhlet extraction, and desorption tube/thermal desorption. Porous glass beads were used as the adsorbent material for the Soxhlet extracted tube samples and the thermally desorbed tube samples. The samples listed in the table were all taken on the same day, under similar test conditions, but over two different time intervals. Examination of data in the table indicates the following:

- The method 23 samples, taken at different times, yielded a 29% difference in total dioxin/furan concentrations, which is within the accuracy interval usually expected for the method, and represents the probable best case for sample-to-sample variation.

- Soxhlet extraction of desorption tube samples showed nearly 20% breakthrough (total dioxins/furans) to the second tube, indicating saturation of the primary tube adsorbent, or incomplete retention of analyte on the adsorbent, or both.

- Soxhlet extraction recovery (total dioxins/furans basis) relative to Method 23, summed for both the primary and breakthrough tubes, was 7%, indicating incomplete retention on the adsorbent material, and possibly also
saturation of the primary tube adsorbent material.

- For Soxhlet extraction, higher molecular weight dioxins/furans appeared to be better retained on the adsorbent, based on summed results of the primary and secondary tubes, but breakthrough to the second tube appeared to be slightly worse for the higher molecular weight furans.

- Similar trends were evident for thermal desorption: total recovery was 11% relative to Method 23, some breakthrough to the second sampling tube was evident, and recoveries for the higher molecular weight furans was better than for the lower molecular weight compounds.

Individual compound detection limits for thermal desorption of tube samples was expected to be approximately 7 ng/dscm, based on a 50 pg detection limit for the LRMS and a sample volume of 7.5 liters (125 mL/min for 60 min). For 10% recovery of dioxin/furans, the idealized detection limit would increase to approximately 70 ng/dscm, and would be higher when interfering compounds are present, as appeared to be the case here.

Table I. Sampling and analysis of pilot scale incinerator HEPA outlet offgas by Method 23, by Soxhlet extraction of desorption tubes, and by thermal desorption of desorption tubes, porous glass bead adsorbent material. “APSA” in the table is an acronym for the thermal desorption tubes.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Designation</td>
<td>Run 3 Loc 4</td>
<td>SP-4-3-Pri</td>
<td>SP-4-3-Sec</td>
<td>SP-4-3-Sum</td>
<td>Run 4 Loc 4</td>
<td>SP-4-5-Pri</td>
</tr>
<tr>
<td>Date Sampled</td>
<td>3/14/00</td>
<td>3/14/00</td>
<td>3/14/00</td>
<td>3/14/00</td>
<td>3/14/00</td>
<td>3/14/00</td>
</tr>
<tr>
<td>Location Description</td>
<td>HEPA Out</td>
<td>HEPA Out</td>
<td>HEPA Out</td>
<td>HEPA Out</td>
<td>HEPA Out</td>
<td>HEPA Out</td>
</tr>
<tr>
<td>Sampling Temp. (C)</td>
<td>194.3</td>
<td>194.3</td>
<td>194.3</td>
<td>194.3</td>
<td>194.3</td>
<td>194.3</td>
</tr>
</tbody>
</table>

Individual compound detection limits for thermal desorption of tube samples was expected to be approximately 7 ng/dscm, based on a 50 pg detection limit for the LRMS and a sample volume of 7.5 liters (125 mL/min for 60 min). For 10% recovery of dioxin/furans, the idealized detection limit would increase to approximately 70 ng/dscm, and would be higher when interfering compounds are present, as appeared to be the case here.

Conversely, thermal desorption detection limits could be improved by using a more sensitive detector, by modifying the thermal desorption temperature/time program to reduce or eliminate interferences, by using more retentive adsorbents, and by taking a larger sample volume, either by increasing the flow rate through the sampling tube, or by sampling for a longer time. For the thermal desorption equipment used in this work, the sampling rate probably cannot be increased, and sampling for periods significantly longer than an hour would defeat the purpose of a “fast” sampling and analysis method, therefore reducing interferences, using a better adsorbent, and using a more sensitive detector appear to be the more practical alternatives. Future work will focus on these issues.
Marine Boiler Sampling and Analysis

On August 2, 2000, one Method 23 and two thermal desorption tube samples were taken from the EPA North American Package Boiler (NAPB). The Method 23 sample was taken at the last section of fire tubes before the stack, and the thermal desorption tube samples were taken at the stack. Sampling temperatures were 257 °C and 259 °C, respectively. Dioxin/furan homolog analyses for the samples are shown in Table II. The toxicity equivalent for the Method 23 sample was 18.4 ng TEQ/dscm, not corrected to 7% oxygen. The total concentration of tetra-through octachlorinated homologs was 1,550 ng/dscm.

For the present implementation of the thermal desorption method, dioxins/furans were marginally detectable in the NAPB offgas. Dioxins/furans were not detected in the breakthrough tubes, but “normal” breakthrough, based on the pilot scale incinerator results above, would not have been detectable for this offgas.

As indicated in Table II, thermal desorption homolog recoveries relative to Method 23 were generally 10 to 20%, comparable to the pilot scale incinerator samples, but the total dioxin/furan recoveries were lower, 3% and 1%. The lower total recoveries were probably due to several missed chromatographic peaks, both because the analyte quantity in the sampling tubes was near the instrumental detection limit, and because, as for the pilot scale samples, large background interferences were noted.

Table II. Comparison of Method 23 and thermal desorption samples from the August 2, 2000 EPA North American Package Boiler (NAPB) test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method 23, Pass 3</th>
<th>APSA, NAPB Stack, Sample 1</th>
<th>APSA, NAPB Stack, Sample 2</th>
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</thead>
<tbody>
<tr>
<td>Sample Matrix</td>
<td>M23</td>
<td>Unibeads</td>
<td>Unibeads</td>
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<td>Date Sampled</td>
<td>8/2/00</td>
<td>36740</td>
<td>8/2/00</td>
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<td>Gas Sampling Interval</td>
<td>12:43-14:43</td>
<td>15:24-16:24</td>
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<tr>
<td>Dry Gas Vol. Sampled (dscm)</td>
<td>2.59</td>
<td>0.01195</td>
<td>0.00572</td>
</tr>
<tr>
<td>Sampling Temp. (C)</td>
<td>257</td>
<td>259</td>
<td>259</td>
</tr>
<tr>
<td>Sample Fraction</td>
<td>Method 23</td>
<td>Primary Tube</td>
<td>Recovery</td>
</tr>
<tr>
<td></td>
<td>ng/dscm</td>
<td>ng/dscm</td>
<td>%</td>
</tr>
<tr>
<td>Total TCDD</td>
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<td></td>
<td>8.9</td>
</tr>
<tr>
<td>Total PeCDD</td>
<td>188</td>
<td>7.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Total HxCDD</td>
<td>141</td>
<td></td>
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<tr>
<td>Total HpCDD</td>
<td>68.3</td>
<td>10.1</td>
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<tr>
<td>OCDD</td>
<td>70.4</td>
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<tr>
<td>Total TCDF</td>
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<tr>
<td>Total PeCDF</td>
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<tr>
<td>Total HxCDF</td>
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<td>7.8</td>
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<tr>
<td>Total HpCDF</td>
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<td>11.7</td>
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<tr>
<td>OCDF</td>
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<td>18.1</td>
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<tr>
<td>Total, tetra through octa</td>
<td>1549</td>
<td>50.0</td>
<td>3.2</td>
</tr>
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</table>

# = 65 - 100 % of lowest standard

CONSTRUCTION OF A BENCH REACTOR TO GENERATE SIMULATED OFFGAS SAMPLES

The greatest cost in the experiments described above was operation of the pilot-scale systems, exceeding by more than an order of magnitude the cost of obtaining and analyzing the offgas samples. At the same time, the sampling and analysis activities described above showed that interfering compounds and apparent adsorption of dioxins/furans onto offgas particulate presented very difficult analysis problems. In order to generate offgas
samples at manageable cost, we have constructed a bench reactor intended to simulate real offgas samples containing elevated concentrations of dioxins/furans, a interfering substances, and entrained organic and inorganic particulate. The bench reactor was built around commercially available tube furnaces, which are used to heat quartz or stainless reaction tubes. Two furnaces were used. The first furnace preheats air, methane, or other reactant gases and vaporizes hydrochloric acid and dioxin precursors; the second furnace is operated at temperatures expected to be conducive to dioxin formation. In order to take offgas samples, the adsorbent tubes, described above, are connected to the outlet of the bench reactor. The entire gas flow from the bench reactor is passed through the sampling tubes, and subsequently vented to a fume hood.

Initial reaction conditions, including residence times, choice of precursor, reactant injection rates, and reaction temperatures, were derived from bench reactor work previously reported by Gullett, et al. (5), and Thornton, et al. (6). The MSE configuration of the bench reactor approach is described in greater detail in the FY2000 project test plan (7).

Initial bench reactor experiments indicated generation of particulate-laden offgas with dioxin/furan congener profiles roughly similar to those of typical of hazardous waste incinerators, and with interfering compounds presenting analytical problems similar to those observed for the samples taken from pilot scale systems.

SUMMARY AND CONCLUSIONS

Thermal desorption-based techniques were investigated as a means for sampling and analyzing dioxins/furans in combustion offgases. The experiments were conducted using commercially available thermal desorber and gas chromatograph/mass spectrometer (GC/MS). Initial method development involved spiking dioxin/furan standards onto candidate adsorption media, which were then carried through the thermal desorption/gas chromatography/mass spectrometry analytical process. Based on initial method development experiments, porous glass beads, a diatomaceous earth, and alumina were selected as suitable adsorbent materials for offgas sampling and analysis tests.

Offgas samples were taken from a pilot scale hazardous waste incineration system and a hazardous waste-firing marine boiler test facility, and compared to the regulatory reference method, EPA Method 23. Both combustion systems were operated under conditions expected to produce high concentrations of offgas dioxins/furans. The thermal desorption-based method yielded combined retention and thermal desorption efficiencies of approximately 10% relative to Method 23, depending on the particular dioxin/furan homolog class.

In the present implementation of the thermal desorption-based method, detection limits of approximately 70 ng/m³ per individual dioxin/furan compound were observed. While suitable as a screening tool for detecting offgas dioxins/furans at levels above 70 ng/m³, the utility of the technique would be improved by lowering the detection limits, preferably to less than the regulatory limit of 0.2 ng/dscm. Possible approaches to achieving lower detection limits are to identify or develop more efficient and selective adsorbent media, use a more sensitive detector, and increase sampling volumes by increasing sampling rates or times. Incomplete thermal desorption of dioxins/furans from offgas particulate may also have contributed to the dioxin/furan recoveries observed in the present experiments, and may be problematic.

Continuing investigations will assess whether detection limit, interferences, and recovery issues can be resolved by thermal desorption techniques alone. If it appears that they cannot, then alternative techniques, for example, carbon dioxide-based supercritical fluid extraction, will be considered.

Independent efforts are underway to develop fast, sensitive, and selective dioxin/furan analyzers. These analyzers appear to be especially suitable for mono-, di-, and tri-chlorinated dioxins/furans, which are cogenerated with the more highly chlorinated toxic dioxins/furans. If formation of these less chlorinated compounds can be satisfactorily
correlated to overall dioxin/furan toxicity, then methods for sampling and preconcentrating less chlorinated
dioxins/furans will be of great interest. Because of their lower boiling points, thermal desorption techniques may be
most easily adaptable to sampling and preconcentrating these less chlorinated dioxins/furans.

The greatest cost in the present thermal desorption method development work was the cost of operating the pilot-
scale or marine boiler systems. In general, such samples from them could be justified only if the pilot-scale systems
were operated for some other purpose. While synthetic samples spiked with known concentrations of dioxin/furan
standards can be used for some method development, the work reported here has shown that desorption of
dioxins/furans from offgas particulate and separation of dioxins/furans from interfering compounds, present in real
offgas samples, are problematic for thermal desorption-based sampling and analysis, as they are for other sampling
and analysis techniques. Accordingly, a bench reactor was constructed in order to generate simulated offgases
containing dioxins/furans, interfering compounds, and inorganic and organic particulate. The bench reactor will be
used for further development of the thermal desorption-based method.

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FOOTNOTES

“Dioxin/furans” refers collectively to all chlorine-substituted dibenzo-p-dioxins and dibenzofurans. There are 210 possible dioxin/furan compounds, which vary in the number and position of chlorines substituted in the two parent compounds, dibenzo-p-dioxin and dibenzofuran. By regulation, only those 17 dioxin/furan compounds with chlorines substituted at the 2-, 3-, 7-, and 8-ring positions are considered toxic, with differing relative toxicities depending on the ring positions of additional substituted chlorines. The MACT standard regulates the summed toxicity-corrected concentration of those 17 compounds. The summed toxicity-corrected concentration is reported as a single number in units of ng TEQ/dscm.