

**FAST SAMPLING AND ANALYSIS OF OFFGAS DIOXINS/FURANS USING A
THERMAL DESORPTION-GAS CHROMATOGRAPHY-HIGH RESOLUTION MASS
SPECTROMETRY METHOD**

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ABSTRACT

The United States Department of Energy is using or evaluating several Alternatives-to-Incineration (ATI) technologies for treating hazardous wastes and low-level mixed wastes. ATI treatment technologies may have the potential for generating gaseous or other emissions of polychlorinated dioxins/furans, a class of highly toxic compounds which are regulated to very low levels. At present, the emission limit for dioxins/furans from hazardous waste incinerators is 0.2 ng TEQ/dscm (0.4 ng TEQ/dscm w/TC). Emissions from ATI technologies are expected to be subject to similar restrictions.

The regulatory method for sampling and analyzing offgas dioxins/furans is EPA Method 23. For Method 23, the offgas sample is passed through a filter to retain any particulate-bound dioxins/furans, and a resin cartridge to adsorb any vapor phase dioxins/furans. For all sample media, offgas, liquid, or solid, the overall procedure for extraction and analysis is complex and labor intensive, and requires specialized laboratory facilities as well as specialized sampling and analysis equipment. Sampling and analysis turnaround time is normally several weeks. The cost and complexity, and turnaround time, make Method 23 impractical as a tool for process optimization or routine process monitoring. A faster and simpler method for dioxin/furan sampling and analysis is needed. Simplifying or eliminating sample preparation steps provides the most significant opportunity for reducing overall turnaround time. Thermal desorption-based sampling and sample preconcentration offers an attractive means to simplify and speed up the sample preparation process. In this approach, vapor phase and particulate-bound dioxins/furans are trapped in a conventional sampling tube packed with a suitable filter/adsorbent material. In principle, the compounds of interest can then be thermally vaporized and presented to a GC/MS or other analyzer system in a single, rapid step.

A potential shortcoming of thermal desorption-based sampling and analysis, which may be very significant for "dirty" samples, is that compared to Method 23 it offers little ability to remove interfering compounds prior to introducing the sample into a GC/MS. One approach to removing interferences is to thermally desorb the sample in stages, so that dioxins/furans and interfering compounds are presented to the GC/MS at different times. In previous work we found that gas chromatography/low resolution mass spectrometry (GC/LRMS) provided adequate compound resolution for thermal desorption of pure dioxins/furans spiked onto adsorbent media, but did not

adequately resolve or identify dioxins/furans and interfering compounds present in highly contaminated pilot-scale incinerator, marine boiler, and bench reactor offgas samples, when the samples were taken using a thermal desorption-based method.

We are evaluating gas chromatography/high resolution mass spectrometry (GC/HRMS) as a means to analyze similarly highly contaminated samples. As expected, we have found that GC/HRMS provides much improved identification and quantitation of dioxins/furans in the presence of background interfering compounds, and also allows identification of many of the interfering compounds. Identification of the interfering compounds will allow improvements in staged thermal desorption, and other techniques, for the purpose of reducing interfering compounds presented to a GC/MS.

INTRODUCTION

Objective

The objective of the work described in this paper was to use gas chromatography/high resolution mass spectrometry (GC/HRMS) to resolve analytical interferences previously observed in thermal desorption-based sampling and analysis of offgas dioxins/furans¹, and to develop thermal desorption-based procedures to minimize the transport of interfering compounds into a GC/MS, or other analyzer/detector.

In the previous work we found severe analytical interferences and low analyte recoveries for thermal desorption-based analysis of samples taken from a pilot-scale hazardous waste incinerator and a research marine boiler (1,2). The low recoveries of dioxins/furans from real offgas samples were observed even though the same time and temperature programs gave essentially 100% recovery of dioxins/furans spiked into sampler tubes. Accordingly, further method development appeared to require the use of real or simulated offgas samples.

Because of the prohibitive cost of generating offgas samples with a pilot-scale system, we constructed a bench-scale reactor for the purpose of generating simulated offgas samples. The bench reactor design and operating conditions were derived from a system reported by Gullet et al.(3), Thornton, et al.(4), and Lemieux, et al.(5) to generate high concentrations of offgas dioxins/furans. The bench reactor system produced offgases containing elevated concentrations of dioxins/furans and elevated concentrations of interfering background substances, as discussed below.

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 recently 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, or 0.4 ng TEQ/dscm under some circumstances.

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* (6). 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 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 investigated here consists of three steps: (1) Sampling and preconcentration, (2) Thermal desorption of the analyte compounds, and (3) Analysis of the desorbed analyte compounds. In the present work, 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.

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 not containing particulates. By controlling desorption conditions it may be possible to selectively desorb dioxins/furans.

Analysis - The desorbed compounds are separated, detected, and quantified. In the present work, a gas chromatograph/low resolution mass spectrometer (GC/LRMS), and a gas

chromatograph/high resolution mass spectrometer (GC/HRMS) were used to separate, detect, and quantify the compounds of interest. It should be noted that 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 any dioxins/furans present in vapor, condensed, or adsorbed phases, and then quickly transfer the analyte dioxins/furans to the analyzer as a gas.

Similarly to the thermal desorption approach, Method 23 involves three steps: (1) Sampling, (2) Extraction and cleanup, and (3) 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.

With some modification thermal desorption techniques may also be applicable to liquid and solid waste streams generated during waste treatment by Alternative to Incineration (ATI) technologies now being investigated by DOE.

EXPERIMENTAL

Bench Reactor

A bench reactor system was constructed for the purpose of generating simulated offgas samples containing readily measurable concentrations of dioxins/furans. The bench reactor was built around two commercially available tube furnaces, which were used to heat quartz or stainless steel reaction lines. The bench reactor system consisted of inlet gas controls, solution injectors, two series connected tube furnaces, a catalyst ampoule containing cupric chloride (CuCl_2) and a sampler module, as shown in Fig. 1. The first furnace was used to vaporize injected aqueous concentrated hydrochloric acid and injected liquid phenol, and to preheat reactant air and nitrogen. The second furnace was operated at temperatures expected to be conducive to dioxin formation. Reaction conditions for the two furnace system are shown in Table I. These conditions, including residence times, choice of reagents, reagent injection rates, and reaction temperatures, were adapted from bench reactor experiments previously reported by Gullett, et al.(3), Thornton, et al.(4) and Lemieux, et al.(5).

Thermal Desorption Analysis Systems

Two commercially available thermal desorption-based analysis systems were used. A TDS-A™ thermal desorption system (Gerstel Inc., Baltimore, MD) was used in conjunction with a low resolution mass spectrometer, while a Model TD-4 SIS Short Path Thermal Desorption™ system (Scientific Instrument Services, Inc., Ringoes, NJ) was used with the high resolution mass spectrometer. The two systems are conceptually similar. Both thermal desorption systems utilize relatively small sampling tubes (~6 mm o.d.) which may be packed with various adsorbent materials. After sampling, the sampling tubes are placed in a heater assembly which is then heated to a temperature expected to thermally desorb dioxins/furans. During heating, the desorbed dioxins/furans are flushed by a purge gas into a GC inlet.

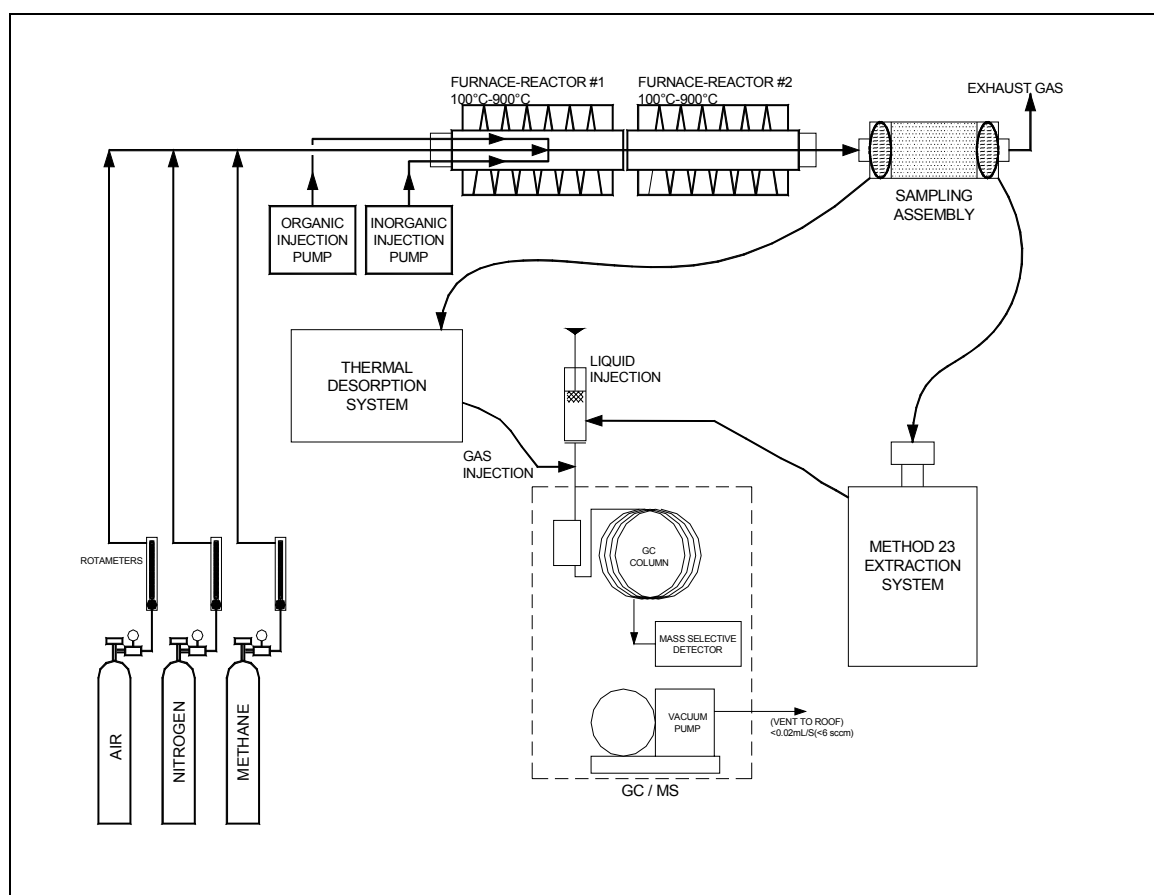


Fig. 1. Schematic of bench reactor system.

Table I. Bench reactor conditions.

Furnace 1 Temp. (°C)	Furnace 2 Temp. (°C)	Air Flow (L/min)	Nitrogen Flow (L/min)	HCl Injection Rate (mL/hr)	Phenol Injection Rate (mL/hr)	Catalyst	Sampling Time
200	350	0.025	0.025	1.0	0.60	CuCl ₂	1 hr

The Gerstel system requires a special temperature programmable GC inlet assembly, which is used to condense and then rapidly volatilize analyte compounds. The SIS system uses the normal heated GC injection inlet, and instead condenses analyte compounds onto the front end of the GC column. In the SIS system, subsequent heating of the column releases the analyte compounds for GC separation and MS detection.

Conceptually, the Gerstel and SIS systems are similar, the principle difference being that the Gerstel system transfers analyte from the sampling tube to the GC/MS through a heated transfer line approximately 5 cm in length while the SIS unit, termed a "short path" system by the manufacturer, transfers analyte from the sampling tube through an injection needle inserted directly into the conventional GC/MS heated inlet. For both systems, operation involves relatively slowly desorbing analyte compounds from the sampling tube, recondensing the compounds at the GC inlet or on the front of the GC column, and then quickly revolatilizing the analyte compounds for subsequent GC/MS analysis. If the sampling tubes could be heated quickly enough to avoid chromatographic peak broadening (initial analyte volatilization in approximately one second, or less), the recondensation and revolatilization steps would be unnecessary, however this does not appear to be possible for conductive/radiative heating of a single tube large enough to sample the gas volumes required for acceptable dioxin/furan detection limits. We previously proposed a resistively heated bundled capillary concept, which would enable flash heating of sample and eliminate the need for intermediate condensation followed by revolatilization.

Operation of the Gerstel system for adsorption/thermal desorption of dioxins/furans, followed by GC/LRMS analysis, has been previously described (1,2). Operation of the SIS system in conjunction a GC/HRMS is described below.

Sampler for Bench Reactor

Bench reactor samples were obtained by routing the outlet gas flow from the second tube furnace into a Gerstel or SIS sampling tube, as indicated schematically in Fig. 1. The sampling tubes were then either thermally desorbed and analyzed by GC/MS, or taken through the Method 23 extraction procedure, and then analyzed by GC/MS.

Method 23 Extraction

Selected samples were taken through the Method 23 (6) extraction procedure, except that for cost reasons the present method development samples were generally not spiked with isotopically labeled dioxins/furans. Method 23 consists of a 16 hour Soxhlet extraction with toluene, followed by several sample cleanup steps and final evaporative concentration of the sample prior to analysis. For the present experiments, the sample extract was concentrated to a final volume of ~100 μ L. In some instances, the toluene extract was split before cleanup, in order to compare background interferences in the toluene-extracted sample and thermally desorbed samples.

Gas Chromatograph/Low Resolution Mass Spectrometer (GC/LRMS)

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 μ m) 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.

Gas Chromatograph/High Resolution Mass Spectrometer (GC/HRMS)

A Hewlett-Packard 5890 Series II Plus gas chromatograph (GC), interfaced to a VG 70E-HF double focusing (EB) magnetic mass spectrometer, was used for the high resolution GC/MS studies. The front end of the GC included a Scientific Instrument Services (SIS) thermal desorption system (SIS model TD-4) to desorb the collected offgas material from the desorption tubes. A high resolution capillary column (Phenomenex ZB-5, 5% diphenyl/95% dimethylsiloxane stationary phase, 30 m x 0.25 mm x 0.25 μ m), similar to the column used for GC/LRMS analyses, was used for all GC/HRMS analyses. The mass spectrometer was operated in either scanning or selected ion monitoring (SIM) mode, with a respective mass resolution of 2000 and 10,000 (fwhm²). Perfluorokerosene (PFK) reference masses were used as reference lock masses for the SIM experiments to self-correct the instrument electronics for minute drift away from true mass centroids of interest during the course of the experiment. The ion source was maintained at 230°C for all experiments.

As noted above, the SIS thermal desorption system works, in principle, the same way as the Gerstel unit interfaced to the GC/LRMS. The SIS unit can be used in either a manual or automatic mode. The desorption tube can be purged for a period of time with an inert gas to remove traces of solvent, water, or oxygen that may pose problems with regard to chromatography columns or that may result in unwanted reactions with components of interest within the tube during the high temperature desorption cycle. The unit can be temperature ramped at up to 40 °C per minute with desorption times ranging from 1 second to 100 minutes. The desorption tubes are fitted into a pneumatically driven device which automatically injects the needle from the tube into the

standard injection port of the gas chromatograph while simultaneously enveloping the tube with a heating device for the desorption process. The entire assembly sits directly above the heated injection port with the needle of the tube in the injection port, an arrangement that is expected to minimize cold zones that may result in loss of the desorbed sample. The desorption tubes are commercially available in standard stainless steel or glass lined stainless steel. Both types of tubes were used in these experiments.

For most experiments, the desorption program was: (1) purge for 30 seconds with helium at ambient temperature, (2) ramp heat to 125 °C in 3 minutes, (3) ramp heat to 310 °C at 30 °C per minute, (4) hold at 310 °C for 10 minutes.

RESULTS AND DISCUSSION

GC/HRMS Analysis of Dioxin/Furans Standards Spiked onto Adsorbent Media

The initial investigation of the recovery of dioxins/furans from the SIS thermal desorption system indicated an approximate recovery efficiency of only 10% based on a comparison of liquid standard injected in the GC inlet vs the same standard injected onto the top of the desorption tube. It was found that poor gas flow characteristics from the desorption unit, through the injection port of the gas chromatograph, and into the column, resulted in the poor recovery efficiency. A modification of the desorption process utilized an uncoated 0.53 mm i.d. fused silica capillary connected to the injection port of the GC as a precolumn. This precolumn was left unconnected from the analytical column during the desorption process to permit a higher and unrestricted gas flow through the desorption system. The effluent was cold-trapped on the precolumn. After the cold trapping, the precolumn was connected to the analytical column utilizing a fused silica connector (Supelco #23628). The modification also allows venting of low molecular weight material, for example water or other condensable liquids collected from the off-gases, to prevent contamination of the analytical column and mass spectrometer. The result for liquid standard spiked into an adsorption tube was virtually 100% recovery of the spiked standard.

An example thermal desorption of liquid dioxin/furan standard spiked onto porous glass beads is shown in Fig. 2. The VG 70E-HF GC/HRMS system was operated in low mass resolution scanning mode.

GC/HRMS Analysis of Bench Reactor Offgas Samples Following Method 23 Soxhlet Extraction

To determine the yields of dioxins/furans from the bench reactor, and to identify interfering compounds using the EPA reference method, the contents of a thermal desorption tube used to take a bench reactor offgas sample (one hour reaction time and one hour sampling time) were extracted using Method 23 procedures. Specifically, the sample was taken through a 16 hour

Soxhlet extraction procedure, a two-column cleanup procedure, consisting of a silica gel column with a hexane rinse followed by an alumina column with a methylene chloride/hexane rinse, and then the extract was reduced to a final volume of 90 μL .

Two 2 μL aliquots of this extract were used for GC/HRMS analysis. The GC/HRMS was set up first in low resolution (LR) scanning mode ($R = 1,500$, fwhm), and then in high resolution (HR) selected ion monitoring (SIM) mode ($R=10,000$, fwhm) to monitor only the mass peaks of dioxins and furans of a specific chlorine number. The full-scan LR chromatogram and the HR SIM chromatograms of the tetra-, hexa-, and octa-chlorinated furans are shown in Fig. 3.

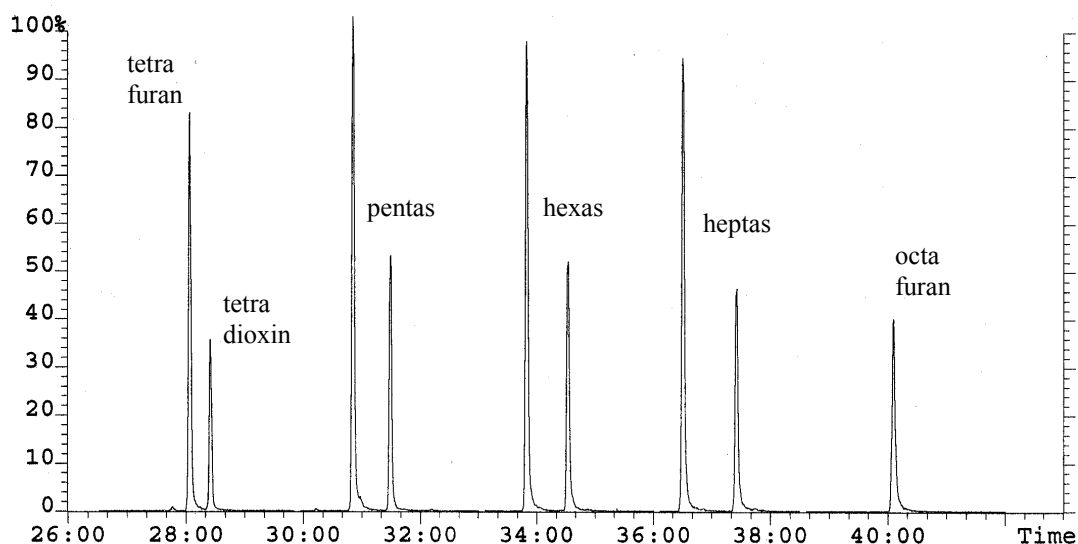


Fig. 2. Chromatogram showing thermal desorption of Cl_4 - Cl_8 dioxin/furan standards (500 pg, each compound) spiked into a thermal desorption tube containing porous glass UnibeadsTM. The first peak in each Cl-homolog series is the furan. The spike solution did not contain octachlorinated dioxin.

Chromatogram A of Fig. 3 is the full-scan data, showing the degree of extraneous background signal present throughout the GC/MS analysis. Examination of the full-scan mass spectra (not shown) for this chromatogram indicated that ions of every nominal mass were present at essentially all retention times, including the characteristic retention times of the dioxins and furans of interest. In general, the few peaks evident in Chromatogram A did not correspond to dioxin/furan retention times, and were evidence instead of the severity of background interferences. The picture was substantially improved by high resolution SIM-mode analysis of the sample, as illustrated in chromatograms B - D, of Fig. 3. These are the SIM-mode chromatograms of Cl_4 , Cl_6 , and Cl_8 furans, respectively. SIM-mode chromatograms for the Cl_5 and Cl_7 furans and the Cl_4 - Cl_8 dioxins were similar, with apparent resolution of some, but not all, of the individual dioxin/furan congeners. Comparison of the low- and high-resolution chromatograms of Fig. 3 confirms that in low-resolution scanning mode the dioxin and furan

chromatographic peaks were completely buried in background, even though this sample was taken through an extensive cleanup procedure.

One of the objectives in the GC/HRMS analysis of the sampling tube extracts was to identify interfering compounds, anticipating that this information could be used to reduce interferences during thermal desorption-based sampling and analysis, possibly by adjusting thermal desorption purge and temperature programs, by appropriate choice of monitoring ions in LRMS SIM mode, or by a combination of both. Background compounds qualitatively identified in the toluene extracts of Fig. 3 are shown in Table II. Chlorinated dibenzofurans and dibenzodioxins are included as interferences because only 17 of the 210 possible dioxin/furan congeners are classified as toxic, and must be distinguished analytically from the 193 non-toxic congeners.

Bench Reactor Reproducibility

To assess reproducibility of the bench reactor samples, three samples were taken using thermal desorption tubes packed with Unibeads. Reaction conditions and sampling times were those shown in Table I, above. After sampling, the Unibeads were transferred to a Soxhlet extractor and taken through the Method 23 extraction and cleanup process described above. The extracts were analyzed by GC/HRMS for the total concentration of dioxin/furan homologs in each homolog group. The results are shown in Table III. The estimated analytical reproducibility for these samples was $\pm 20\%$, with any additional variability due to variations in sample generation.

The experimental results shown in Table III indicate that the bench reactor produced relatively large quantities of dioxins and furans, in the microgram range, but that both the homolog profile and quantity of dioxins/furans produced could vary by orders of magnitude from one sample to the next. In general, production of furans appeared to be somewhat more consistent than production of dioxins. The variability may have been due to reactor surface corrosion, accumulating surface deposits, and/or gradual loss of the CuCl_2 "catalyst," which may in fact be a significant reactant rather than a catalyst. For example, Lemieux et al. reported that CuCl_2 "catalyst" converts to a blackened material, probably CuO , during reaction runs, and that this material may effect decomposition rather than formation of dioxins/furans (5).

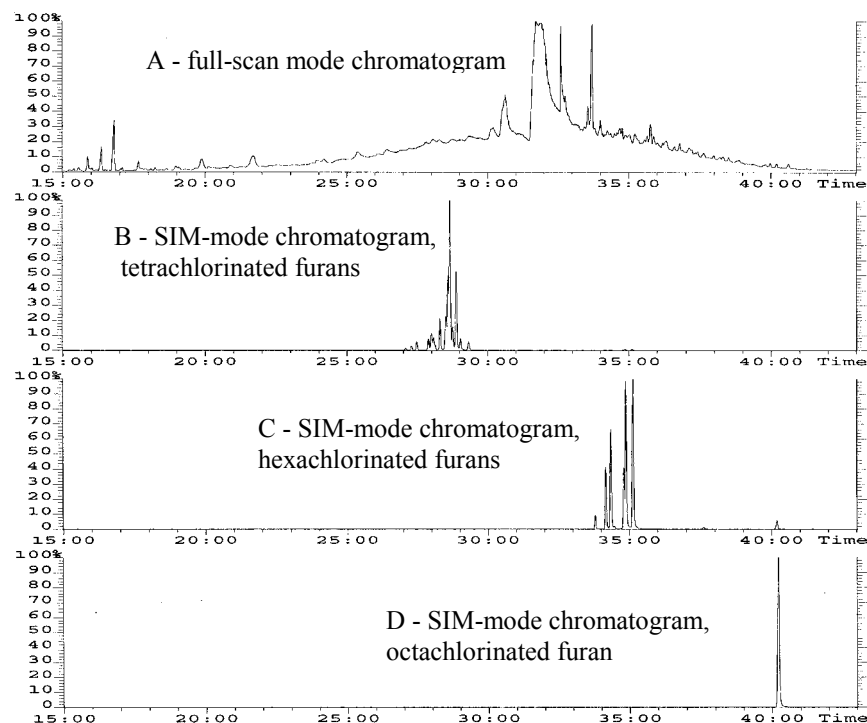


Fig. 3. Chromatogram A represents the full-scan chromatographic data ($R = 1,500$, fwhm) from the analysis of a Soxhlet extract of a thermal desorption tube containing an offgas sample from the bench-scale reactor. The extract was taken through a dual-column cleanup procedure. Chromatograms B - D are SIM data ($R = 10,000$, fwhm) for the Cl_4 , Cl_6 , and Cl_8 furans, respectively, for the same sample shown in chromatogram A.

Table II. Qualitatively identified interfering compounds or compound classes in the Method 23 extract of a bench reactor thermal desorption tube sample. Cf. Fig. 3, Chromatogram A.

Benzyl Alcohol	Phenylmethylester-formate
Methyl Phenol Isomers	Benzene Formate
Acetophenone	Nonanoic Acid
C_4 -Substituted Benzenes	Decanoic Acid
Naphthalene	Undecanoic Acid
Methylnaphthalene Isomers	Tetradecanoic Acid
Dimethylnaphthalene Isomers	Isopropyl Myristate
Diphenylethane	Hexadecanoic Acid
1-Methyl-4-(phenylmethyl)-benzene Isomers	Undecanol
Dimethylbiphenyl Isomers	Tetradecanol
Dimethyl-phenylmethane Isomers	2,6-Di-tert-butylbenzoquinone
2,4-Diisopropylphenol	Anthracene
1,2-Diphenylethylene	Phthalates
9,10-Dihydroanthracene	Cholestane or Isomers
1,2-Diphenylcyclobutane	Branched Unsaturated Hydrocarbons
Dimethyl-diphenylethene Isomers	Cl_4 through Cl_8 Dibenzodioxins
Phenylmethylester-benzoate	Cl_4 through Cl_8 Dibenzofurans

Table II. Bench reactor dioxin/furan homolog recoveries from Method 23 extraction of thermal desorption sampling tubes. Units are nanograms (ng). Quantitation was against isotopically labeled internal standards.

Sample	TCD F	TCDD	PCDF	PCDD	HxCDF F	HxCDF D	HpCDF F	HpCDF D	OCDF	OCD D
BS 2	532	4,897	247	2,397	243	872	574	388	1,193	578
BS 3	283	4	47	2	24	1,555	26	0	148	19
BS 4	513	3	222	13	107	156	164	0	251	6

Consistency between bench reactor runs is desirable, since thermal desorption-based analysis is a one-shot process, that is, in contrast to Method 23, the entire sample is consumed in each analysis. Reproducibility for the thermal desorption-based analytical process can be determined only if the bench reactor sample is consistent from one run to the next. More importantly for the present purpose, bench reactor consistency is necessary for analytical method development, since the effect of changes in the method can be assessed only if each test sample has a known, or at least reproducible, composition.

The results shown in Table III are for initial runs of the bench reactor. "Burning in" the reactor through extended runs may improve reproducibility. The sampling temperature, which was not controlled for these experiments, was essentially the ambient temperature near the outlet of the second tube furnace. In future experiments we will use a purpose-built, calibrated and temperature controlled sampler. The primary objective in using a temperature controlled sampler will be to see if varying the sampling temperature reduces interferences; however, carefully controlling the temperature should also improve sampling reproducibility. If "burning in" and controlling the sampling temperature do not give adequate reproducibility, then we will try replacing the cupric chloride "catalyst" after each experimental run.

Thermal Desorption GC/HRMS Analysis of Bench Reactor Offgas Samples

Following GC/HRMS analysis of Soxhlet/toluene extracts of bench reactor sampling tubes, we generated additional samples for thermal desorption/GC/HRMS analysis. As discussed above, full-scan and SIM-mode analysis cannot be performed on the same sample injection. For the Soxhlet/toluene extracts of sampling tubes, an aliquot of the extracted solution was injected for full-scan analysis, and a second aliquot of the same solution was injected for SIM-mode analysis. For thermal desorption/GC/HRMS analysis of bench reactor sample tubes, each analysis consumed the entire sample, therefore it was not possible to analyze aliquots of a single sample. Accordingly, to compare full-scan and SIM-mode results, we analyzed two separate samples, obtained under identical bench reactor conditions. As illustrated in Table III, operating the bench reactor under identical conditions may produce sampling tubes containing widely varying quantities of dioxins.

An example of thermal desorption/GC/HRMS analysis of a pair of bench reactor samples is shown in Fig. 4. Similarly to the extraction analysis of Fig. 3, the first of the thermal desorption sample pair was analyzed at low resolution ($R=1500$ fwhm) in full scan-mode, and the second of the sample pair was analyzed in SIM-mode at high resolution ($R=10,000$ fwhm).

The full-scan chromatogram (chromatogram A) of Fig. 4 shows more structure, that is, more apparent peaks, than the corresponding full-scan chromatogram of Fig. 3, suggesting that the Fig. 4 full-scan thermal desorption chromatogram might reveal the presence of individual dioxin/furan congeners. However, comparison of the SIM-mode and full-scan chromatograms of Fig. 4 reveal that not to be the case. Similarly to the toluene extracts of Fig. 3, the SIM-mode chromatographic peaks of Fig. 4 are not discernible as full-scan peaks at the same retention times.

Qualitative analysis of thermal desorption background indicated the presence of relative high concentrations of chlorinated aromatics not identified in the Soxhlet extracts discussed above. Chlorinated aromatics identified in the thermal desorption samples but not found in the Soxhlet extraction solutions are listed in Table IV.

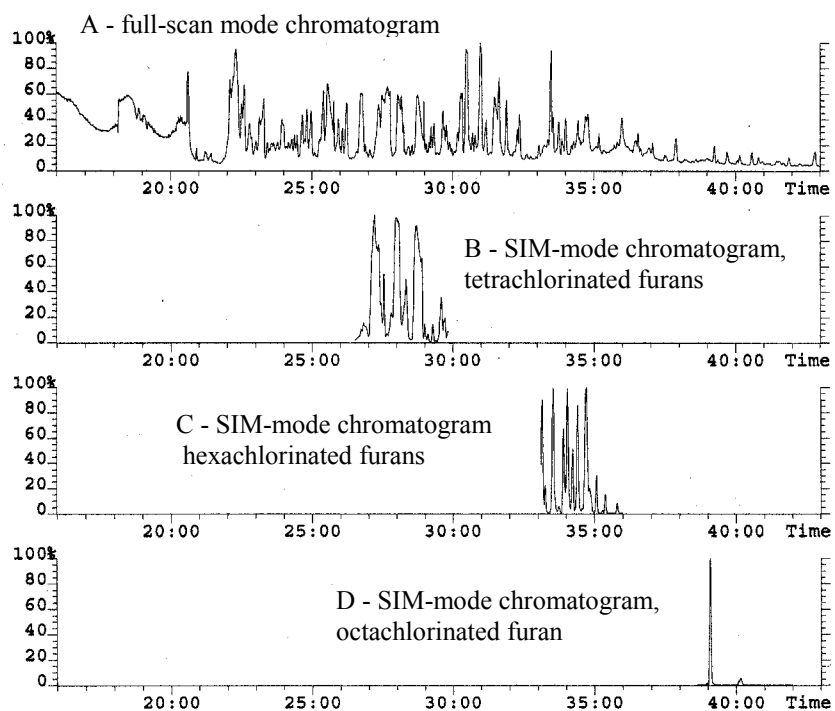


Fig. 4. Full-scan and SIM-mode chromatograms of a thermally desorbed bench reactor simulated offgas sample. Chromatogram A is derived from low resolution full-scan mass spectral data ($R=1500$ fwhm), while chromatograms B, C, and D are derived from high resolution SIM-mode mass spectral data ($R=10,000$ fwhm) for Cl_4 , Cl_6 , and Cl_8 furans, respectively.

Table III. Interfering chlorinated aromatics identified in thermally desorbed samples, but not found in Soxhlet extractions of similar bench reactor samples.

1,2 Dichlorobutyne	Octachlorostyrene
Dichloro-p-benzoquinones	Chlorinated-biphenyl-ols
Dichloro-naphthanols	Chlorinated-biphenyls
Tetrachloro-p-benzoquinone	Chlorinated-biphenyl ethers
Tetrachloro-p-benzohydroquinone	Chlorinated dibenzofurans
Hexachlorobenzene	Chlorinated dibenzodioxins

SUMMARY AND CONCLUSIONS

A bench reactor was constructed for the purpose of generating simulated hazardous waste incinerator offgas samples containing elevated concentrations of dioxins/furans. Commercially available glass or stainless steel thermal desorption sampling tubes were loaded with adsorbent media and used to take offgas samples from the bench reactor. Selected samples were taken through a Method 23-based Soxhlet (toluene solvent) extraction and cleanup procedure and analyzed by gas chromatography/high resolution mass spectrometry (GC/HRMS). GC/HRMS analysis of the extracts showed very high (microgram) quantities of dioxins/furans, and also very high levels of interfering background compounds. Using high resolution selected ion monitoring (SIM) mass spectrometry, the analyte dioxins/furans were resolved from the interfering background compounds and quantified. The dioxins/furans could not be resolved from the background interferences using full-scan low resolution mass spectrometry.

Similar bench reactor sampling tube samples were analyzed by thermal desorption of the sampling tubes directly into a GC/HRMS. The thermally desorbed samples showed more complex backgrounds than the Soxhlet extracted samples, however, high resolution SIM-mode mass spectral analysis resolved dioxins/furans from background in these samples. In contrast, full-scan GC/LRMS did not resolve dioxins/furans from background in thermally desorbed bench reactor samples.

These results indicate that direct thermal desorption of small offgas sampling tubes, coupled with gas chromatography (GC) and selected ion monitoring mode (SIM-mode) high resolution mass spectrometry (HRMS) can be adapted to dioxin/furan offgas analysis. Issues of detection limits, reproducibility, reduction of interferences, and whether GC/LRMS can be adapted to thermal desorption-based offgas dioxin sampling and analysis remain to be resolved.

FUTURE ACTIVITIES

This work was performed as part of a multi-year effort to develop a dioxin/furan sampling and analysis method capable of three hour or less turnaround time. Project objectives in FY02 will be to improve the reproducibility of bench reactor sample generation and to reduce the effects of background interferences. This will be attempted first by controlling or programming sampling

temperature and other sampling conditions, and subsequently, if necessary, by using alternative *in situ* sample cleanup procedures, including heated solvent extraction or supercritical fluid extraction. We plan to identify several alternatives, then select among these for further development and prototyping in FY03, followed by commercialization in FY04.

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FOOTNOTES

¹ "Dioxins/furans" and "dioxins" denotes the group of 210 possible chlorine-substituted dibenzo-p-dioxins and dibenzofurans. Seventeen of these "dioxin" compounds, those with chlorines substituted at the 2, 3, 7, and 8 ring positions, are regulated as toxic. The regulatory relative toxicity of each of the 17 compounds depends on the position and number of substituted chlorines. The overall dioxin toxicity of a sample is reported as a single number calculated by summing the toxicity-corrected concentration of each of the 17 toxic dioxins. For gaseous samples, the reporting units are usually nanograms toxicity equivalent per dry standard cubic meter (ng TEQ/dscm).

² Mass resolution is defined as $m/\Delta m$, where m is the approximate mass of one peak of a pair, and Δm is the difference in mass between the two peaks. By the fwhm criterion (full-width-half-maximum), two approximately equal peaks are considered to be resolved if the valley between drops to no more than half the maximum peak height.

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