



Project Summary

Validation of Emission Test Method for PCDDs and PCDFs

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The precision and accuracy of the Modified Method Five (MM5) sampling and analysis scheme for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) in municipal waste combustor (MWC) stack gas have been determined. This was accomplished using a dynamic spiking system designed to continuously deliver stable isotopic PCDD/PCDF congeners into the MM5 sampling train upstream of the particulate filter during sampling of incinerator stack gas. Field validation tests to measure the recovery of statically and dynamically spiked PCDD/PCDF during stack gas sampling indicated that the resin effectively retained the static spike during operating conditions. Dynamic spike recoveries were inadequate, partially due to the use of dichloromethane as the extraction solvent. Toluene was subsequently shown to be more appropriate than dichloromethane for obtaining enhanced recoveries of PCDD/PCDF.

Experiments were conducted to determine if increasing filter box temperatures provoked increased migration of the PCDD/PCDF towards the back components of the MM5. Back-half glassware was coated with Apiezon-L grease to enhance PCDD/PCDF recovery. Recovery of the static spikes was quantitative. Dynamic spike recovery was mostly greater than 60%, but reproducibility was inconsistent between some of the replicate trains, possibly due to inconsistencies in Apiezon-L coatings or the inability to effectively remove the Apiezon during extract cleanup. Increasing the temperature of the

filter box resulted in a redistribution of dynamically spiked PCDD/PCDF toward the back components of the MM5 at all sampling locations. The native dioxins and furans did not undergo analogous redistributions.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Municipal incineration of waste, coupled with energy recovery, is a practice that is gaining favor in current efforts directed at finding economic, effective, and efficient alternatives to land burial. The U.S. Environmental Protection Agency has undertaken to regulate municipal waste incinerators and to characterize their emissions in order to allay public concerns about their emissions. Among pollutants of such concern are the polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

A Modified EPA Method 5 (MM5) sampling train, incorporating an ice-water chilled condenser and XAD-2 resin cartridge, has been used to collect medium volatility organic compounds from stack gases for a wide range of combustion sources. The configuration and operating procedures for this system in determining PCDDs and PCDFs in municipal waste combustor (MWC) emissions were standardized by a workshop sponsored by the American Society of Mechanical Engineers, the U.S. EPA, and the U.S.

Department of Energy held in September 1984. The product of the workshop was a draft sampling and analysis procedures document known as the ASME protocol.

The ASME protocol has become a *de facto* industry standard for sampling stack gases for PCDDs, PCDFs, PCBs, and many other semivolatile organics. However, low recoveries for specific PCDD isomers spiked into MM5 sampling trains were observed during pilot and field evaluation studies conducted under contract to U.S. EPA's Environmental Monitoring Support Laboratory (EMSL), now the Atmospheric Research and Exposure Assessment Laboratory (AREAL). Since these observations were based on limited experiments, additional data were needed to determine the precision and accuracy of the MM5 system for collecting and recovering PCDD and PCDF emissions.

The overall objective of the current study was to characterize the precision and accuracy of the MM5 sampling system using stable isotopically labeled PCDD and PCDF compounds spiked during MWC flue gas sampling.

Procedures

The study was conducted in several phases. During Phase 1, a dynamic spiking system for continuously introducing ¹³C-labeled PCDD/PCDF congeners into the MM5 train during sampling was designed and tested. The dynamic spiking system was then tested using MWC flue gas background to determine method reproducibility and accuracy during Phase 2 of the study. Based on the results obtained during Phase 2, additional laboratory tests were conducted (Phase 3) to investigate the influence of extraction solvent and carbon content on PCDD and PCDF extraction from MWC ash. Phase 4 used the information gleaned from the previous phases to investigate alternative PCDD/PCDF recovery enhancement procedures from the MM5 sampling train. Finally, Phase 5 used the recovery enhancement procedures to determine precision and accuracy of modified MM5 sampling and analysis techniques with MWC flue gas background. Table 1 summarizes the phases of this study and identifies the MM5 sampling runs associated to each phase. Because of the complexity of the study, the phase-specific methods utilized will be discussed concurrently with the results noted at each phase. The following procedures were used throughout the study.

Table 1. Summary of the Investigation with Associated MM5 Sampling Runs

Phase 1	Run 1	Laboratory tests of
	2	the dynamic spiking
	3	system
Phase 2	Run 4	Laboratory tests to
	5	demonstrate recovery
		of PCDD/PCDF at two
		spiking levels using
		MM5 sampling train
Phase 3	6	Field tests to
	7	determine MM5
	8	sampling and analysis
	9	method reproduc-
	10	ibility and accuracy
	11	using MWC flue gas
Phase 4	Run 12	Laboratory tests to
	13	investigate sample
	14	recovery enhance-
	15	ment procedures for
	16	the MM5 sampling
17	train	
Phase 5	Run 18	Field tests to deter-
	19	mine the distribution
	20	of PCDD/PCDF within
	21	the MM5 sampling
	train for high filter	box
	temperature and to	determine the precision
	and accuracy of	the MM5 protocol
	using sample recovery	enhancement
	procedures studied in	Phase 4

The MM5 sampling train consists of four main sections (Figure 1): a nozzle/probe assembly (front-half glassware), a heated filter assembly with a cyclone for trapping particulates, an ice water-chilled condenser (back-half glassware) for trapping moisture, and an XAD-2 resin cartridge. Each sampling train was assembled and leak-checked prior to collection of the samples. During collection of actual MWC flue gases, the trains were not traversed but rather set up as single, average, velocity points. Each of the two average velocity points sampled concurrently were considered to be replicate sampling locations. The ambient air or stack gases were sampled for a minimum of three hours and the train leak-checked after the sampling run. Posteriorly, the MM5 trains were dis-

assembled, each section capped, and the components taken to a clean area. The front-half and back-half glassware was then rinsed with appropriate solvents and the rinsates stored in bottles.

In the laboratory, only one of the components from each of several sampling trains was spiked with the Method Internal Standards (MIS, i.e., surrogates) prior to solvent extraction. This was done for individual MM5 components which were composited prior to analysis. For those sampling trains which were composited, a different component was spiked with surrogates before extraction. The solid samples (i.e., XAD-2 resin and combined particulates/filter) were Soxhlet-extracted for 16 to 22h. XAD-2 resin extracts and front-half and back-half glassware rinses were back-extracted using reagent grade water. The sample extracts were passed through sodium sulfate to effect extract drying. Each extract was rotoevaporated to a final volume of 1 to 2 mL. A small volume (25 μ L) of tridecane keeper was added to each extract and then further concentrated using a nitrogen evaporator. Hexane was added to the extracts to a final volume of 1 mL.

A 1- x 10-cm tapered column was slurry-packed in hexane with 1 g of silica gel followed by 4 g of 40% (w/w) sulfuric acid modified silica gel. A second column (1 x 30 cm) was also slurry-packed, but with 6 g of acid alumina followed by 1 g of sodium sulfate, also in hexane. The two columns were set such that the silica gel column drained directly into the acid alumina column. The sample extract was applied to the silica gel column and drawn into the packing together with three rinses of the concentrated extract container. The silica gel column was eluted with 45 mL hexane into the alumina column, which was then eluted with 20 mL hexane. A solution of 20% (v/v) methylene chloride/hexane was used to elute the alumina column (20 mL). Finally, 20 mL of a 50% methylene chloride/hexane solution was used to elute the column and collected. The three separate fractions were collected separately and archived. The 20% methylene chloride/hexane fraction was concentrated to 2 to 3 mL, transferred to a reaction vial, amended with 25 μ L of tridecane and the volume reduced to 25 μ L. This cleaned up extract was spiked with recovery internal standards and analyzed for PCDD/PCDF by GC/HRMS.

GC/MS conditions were as per Table 2. A three-point calibration curve was analyzed and relative response factors calculated. All sample and standards

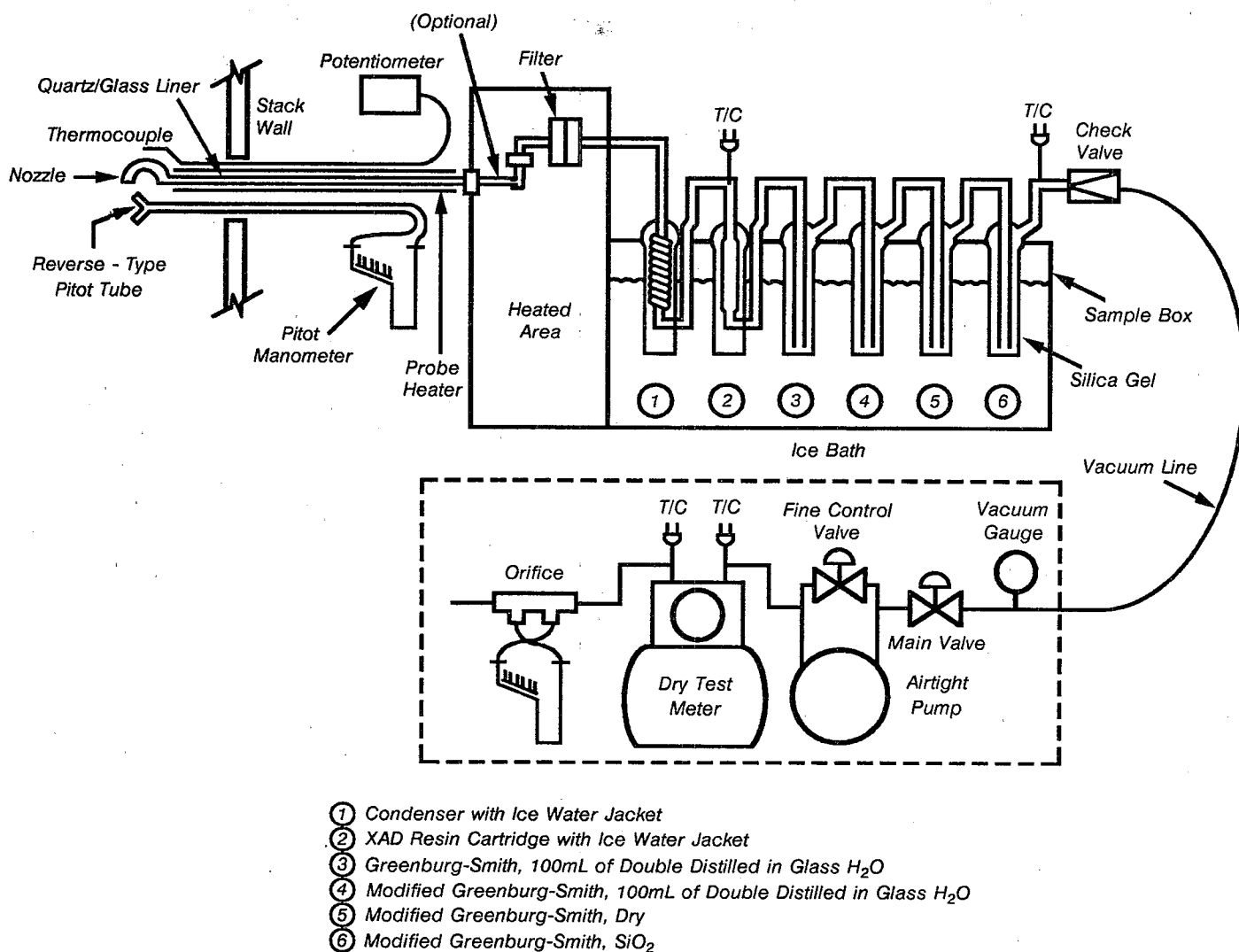


Figure 1. MM5 sampling train configuration used during the study.

were analyzed in the selected ion monitoring (SIM) mode. Table 3 presents the ions monitored during data acquisition.

Results and Discussion

Phase 1 - Development of a dynamic spiking system - A dynamic spiking system was designed to continuously deliver the spike compounds at a consistent and known rate in the vapor phase during the 3- to 5-h duration of a typical sampling run. Dual syringe injection units were installed just ahead of the MM5 filter box (Figure 2). The injection port was heated and located at an angle to facilitate rapid vaporization and

mixing with influent sample gases. Syringe pumps were used to inject relatively small volumes of a concentrated dynamic spiking solution in toluene. All system parts in contact with dioxins or sample gas were in glass or PTFE except for the stainless steel syringe needle. The system was tested under laboratory conditions to address proper vaporization of the spiking compounds and the use of toluene as the solvent. A large glass preheater was installed to maintain a stable temperature at the injector. An MM5 train assembly was connected to the dynamic injection system and operated for 4h sampling ambient air. A low spike (5ng) and a high

spike (500ng) were used. Each of the PCDD/PCDFs dynamically spiked into the system was extracted and analyzed by GC/ECD.

Table 4 presents the results of the initial laboratory tests. Results of the high spike test indicate that recovery was quantitative for each PCDD/PCDF spiked. Furthermore, most of the dynamically spiked compounds recovered were impinged in the back-half glassware. The low spike tests resulted in somewhat lower recoveries of the dynamic spikes, but the distribution of spiked compounds also favored the back-half glassware. However, some congeners were found in notable amounts in the filter extracts. The

Table 2. Operating Parameters for the Capillary Column Gas Chromatographic System for Analysis of Tetra-Octa CDD and CDF

Mass spectrometer	KRATOS MS-50
Gas chromatograph	Carlo Erba MFC 500
Column	60 n x 0.25 ID fused silica
Liquid phase	DB-5
Liquid phase thickness	0.25 μ m
Carrier gas	Helium
Carrier gas velocity	20-40 cm/s
Injector	"Grob" (splittless mode)
Injector temperature	270°C
Injection volume	1-5 μ L
Initial column temperature	200°C (2 min hold)
Column temperature program	200-220 (5°C/min) hold 16 min 220-235 (5°C/min) hold 17 min 235-330 (5°C/min)
Transfer line temperature	280-300°C
Scan range	202-472 amu
Scan time	0.5-1 s
Resolution	3,000 or greater

data indicate that the development of the dynamic spiking system was successful and that it could be used as a field spiking technique.

Phase 2 - Determination of dynamic spiking method precision and accuracy - Laboratory and field verification studies were conducted to determine the accuracy and precision of dynamic spikes using the dynamic spiking system. In the laboratory, replicate MM5 sampling trains equipped with the dynamic spiking system were assembled. The trains sampled ambient air for 4h using the dynamic spiking system at two spiking levels: 5 and 500 ng (Runs 4 and 5). All extracts were analyzed by GC/ECD and in some cases, by GC/HRMS. Field tests (Runs 6 to 11) were also conducted to subject the dynamic spiking system to a realistic sample matrix from a mass burn waste combustor burning municipal refuse. In addition, a ¹³C-labeled pentachlorinated dibenzofuran was statically spiked onto the XAD-2 resin prior to sample collection. This set of tests used three static and dynamic spiking levels: 5, 50, and 500 ng. All sample extracts were analyzed by HRGC/HRMS-SIM. The experimental

design is shown in Table 5. The design provided for replication of one spike level per each test day.

Analyses of the laboratory test runs of the dynamic spiking system indicated adequate (>60%) recovery of the spiked compounds at both spiking levels (Table 6). The results also indicated that, in the absence of particulate matter, gas phase dioxins and furans were impinged in the back half glassware of the MM5 sampling train, specifically the condenser.

Field tests using realistic sample matrices resulted in lower recoveries of the dynamically spiked components (average of 22% recovery) but high recoveries of the static spike (Table 7). The majority of the dynamic spike compounds recovered using a realistic matrix were found on the filter (Table 8). Recoveries of method internal standards (surrogates) indicated no analytical problems during the analysis of the samples.

Phase 3 - Laboratory tests to investigate the influence of carbon content and extraction solvent on PCDD and PCDF extraction from MWC ash - Two composite municipal refuse incinerator fly ashes were augmented with unburned carbon (carbon black) such that the total carbon content was approximately 10% and 20% more than the original content. Duplicate extractions and analyses were performed for each ash (native and amended) using each of three extraction solvents (dichloromethane, benzene and toluene). Prior to extraction and during sample cleanup, each ash aliquot was spiked with the isotopically labeled PCDD and PCDF congeners as indicated in Table 9. The ashes were Soxhlet-extracted, cleaned up, and analyzed for the spiked compounds.

Average recoveries of ¹³C-PCDD/PCDFs spiked directly into Ash No.1 ranged from 13% to 84% using dichloromethane, from 72% to 92% using benzene, and from 69% to 100% using toluene (Figure 3). Ash No.2 showed average recoveries of ¹³C-PCDD/PCDFs spiked directly into the ash ranging from 5% to 78% using dichloromethane, 50% to 83% using benzene, and 59% to 90% using toluene (Figure 3). Since sample preparation and analysis were completely randomized across the three variables under consideration (i.e., ash type, percent carbon, and extraction solvent), it appears that overall extractability of dioxins and furans from ash is extraction solvent and ash-dependent. For both ashes, the labeled compounds added to the cleanup columns were recovered

quantitatively, indicating no loss of material from cleanup to analysis.

Benzene and toluene were the more efficient extraction solvents, although the addition of unburned carbon to the native fly ashes resulted in an enhancement of the recovery efficiency of spiked compounds in the dichloromethane extracts. A parallel effect was not noted for toluene and benzene extractions. There was also some specificity on the extraction efficiency based on the degree of chlorine substitution on the spiked compounds.

Phase 4 - Investigation of sample recovery enhancement procedures from the MM5 sampling train - Since the recovery of dynamically spiked ¹³C-labeled dioxins and furans using dichloromethane as the extraction solvent during Phase 2 of the study were unacceptably low, and because Phase 3 of the study indicated that dichloromethane does not effectively extract dioxins and furans from ashes, additional studies were designed to test the hypothesis that the use of an alternative solvent (i.e., toluene) would result in better recoveries of spiked dioxins and furans. Furthermore, the results from Phase 1 of the study indicated that, in the absence of particulates, most of the spiked dioxins and furans were impinged in the back-half glassware. However, the results from Phase 2 indicated that, in the presence of particulates, most of the dioxins and furans were impinged in the filter. Therefore, in order to enhance dioxin and furan recovery in the back-half glassware of the sampling train, the back-half glassware was coated with Apiezon-L chromatographic grease.

A total of six laboratory runs (Runs 12 to 17) were conducted by sampling ambient air and exhaust gas from a kerosene combustor. Dynamic spiking levels were 25 and 500 ng. The back-half glassware of the MM5 sampling train was coated with Apiezon-L for six of the MM5 sampling trains, and the other six trains used uncoated back-half glassware.

The results of the dynamically spiked labeled compounds are presented in Table 10. Overall, the results indicate that Apiezon-L effectively increased the recovery of the ¹³C-labeled PCDD/PCDF dynamically spiked congeners.

Phase 5 - Determination of precision and accuracy using modified recovery procedures with a MWC flue gas background - The sample recovery modifications investigated during Phase 4 and the dynamic spiking system were used during a field test while sampling incinerator flue gas laden with high levels of particulate matter. Replicate runs were

Table 3. Characteristic Ions for Tetra-Octa CDD/CDF Analysis

Compound	Ion (Relative Intensity)		
	Primary [M+2] ⁺	Secondary [M] ⁺	Ratio Range
Stable Isotopes (Field Spiked Analytes)			
13C-1,2,3,7,8-PeCDF ^a	351.9005 (100)	349.9035 (61)	0.49-0.73
13C-1,2,3,4,7,8-HxCDF ^a	385.8615 (100)	387.8586 (87) ^c	0.66-0.98
13C-OCDF ^a	455.7806 (100) ^c	453.7836 (87) ^d	0.70-1.04
13C-1,2,3,4-TCDD ^a	333.9344 (100)	331.9373 (76)	0.61-0.91
13C-1,2,3,7,8,9-HxCDD ^a	401.8564 (100)	403.8535 (82) ^c	0.66-0.98
13C-PCDD ^a	471.7755 (100) ^c	469.7785(87) ^d	0.70-1.04
Native (Calibration Standard)			
2,3,7,8-TCDF	305.8987 (100)	303.9016 (76)	0.61-0.91
2,3,7,8-TCDD	321.8936 (100)	319.8965 (76)	0.71-0.91
1,2,3,7,8-PeCDF	339.8597 (100)	337.8627 (61)	0.49-0.73
1,2,3,7,8-PeCDD	355.8546 (100)	353.8576 (61)	0.49-0.73
2,3,4,6,7,8-HxCDF	373.8207 (100) ^b	375.8178 (82) ^c	0.66-0.98
1,2,3,7,8,9-HxCDD	389.8156 (100) ^b	391.8127 (82) ^c	0.66-0.98
1,2,3,4,6,7,8-HpCDF	407.7817 (100) ^b	409.7787 (98) ^c	0.78-1.18
1,2,3,4,6,7,8-HpCDD	423.7767 (100) ^b	425.7737 (99) ^c	0.79-1.19
OCDF	443.7398 (100)	441.7428 (87)	0.70-1.04
OCDD	459.7347 (100)	457.7377 (87)	0.70-1.04
Stable Isotopes (Method Internal Standard)			
13C-2,3,7,8-TCDF	317.9395 (100)	315.9424 (76)	0.61-0.91
13C-2,3,7,8-TCDD	333.9343 (100)	331.9373 (76)	0.61-0.91
13C-1,2,3,4,6,7,8-HpCDD	435.8175 (100) ^b	437.8145 (99) ^c	0.79-1.19
Recovery Internal Standard			
13C-1,2,3,7,8,9-HxCDD	401.8564 (100) ^b	403.8535 (82) ^c	0.66-0.98

a = Quantitation was on the primary ion + secondary ion.

b = [M]⁺

c = [M+2]⁺

d = [m+4]⁺

conducted at both inlet and outlet sampling ports (relative to the electrostatic precipitator), and each of the field analytes was dynamically spiked at two levels (25 and 500 ng). In addition, the filter box temperature was run at 250°F and at 420°F for each spiking level at the inlet and outlet locations to determine if the filter box temperature affected the distribution and impingement of spiked and native PCDDs and PCDFs within the MM5 sampling train. The incinerator was the same as that used during Phase 2 of this study. A total of 16 MM5 runs (Runs 18 to 21) were collected at both inlet and outlet location in duplicate. The test matrix is shown in Table 11. Toluene was used as the solvent for rinsing all glassware components (front-half and back-half) after the sampling runs.

Static spike recoveries are presented in Table 12. In most cases, the spike recoveries were quantitative. Inlet static spike recoveries were somewhat lower when the filter box temperature was set at 420°F as compared to when the lower temperature was used. Overall, outlet static spike recoveries were higher than inlet spike recoveries, especially at the higher temperature.

The results for the recovery of the dynamic spikes collected at the inlet are presented in Table 13. The average of the sum of the dynamic spike recoveries ranged from 49.5% to 70.6%. The 49.5% average recovery was from the high spike, high filter box temperature sampling train, in which one of the replicate trains was lost due to a leak.

The relative percent difference (RPD) between each replicate sampling train

provides an indication of sampling precision. An RPD value of 35% or less was chosen arbitrarily to indicate reproducible sampling of the stack material. Overall, the majority of the replicate results had less than 35% RPD (39 of 60 replicate measurements). For the low temperature, low spike inlet samples, the OCDF had poor RPD for each portion of the sample train analyzed. At the high temperature, low spike samples, poor precision was accounted mostly by the back-half and XAD subsamples. This may reflect some difficulty in consistently mobilizing the compounds trapped in the cyclone/ filter by increasing the temperature of the filter box. The largest variability between the replicates at the low temperature, high spike samples was observed on the cyclone/filter subsamples, and of these, it was observed on the

HxCDF, TCDD, and HxCDD. This may be indicative of variable trapping of these congeners on the cyclone/filter. No evaluation of precision of the field samples for the high temperature, high spike sample trains can be made

because one of the replicate trains leaked, invalidating its results.

Table 14 presents the results of the recoveries of the dynamic spikes at the outlet location. The average of the sums

of recovery for each sampling train ranged from 62.9% to 107%.

Precision between the field replicates of the outlet samples was lower than the inlet samples. Fifty-eight of 80 replicate values had RPDs exceeding 35%. For

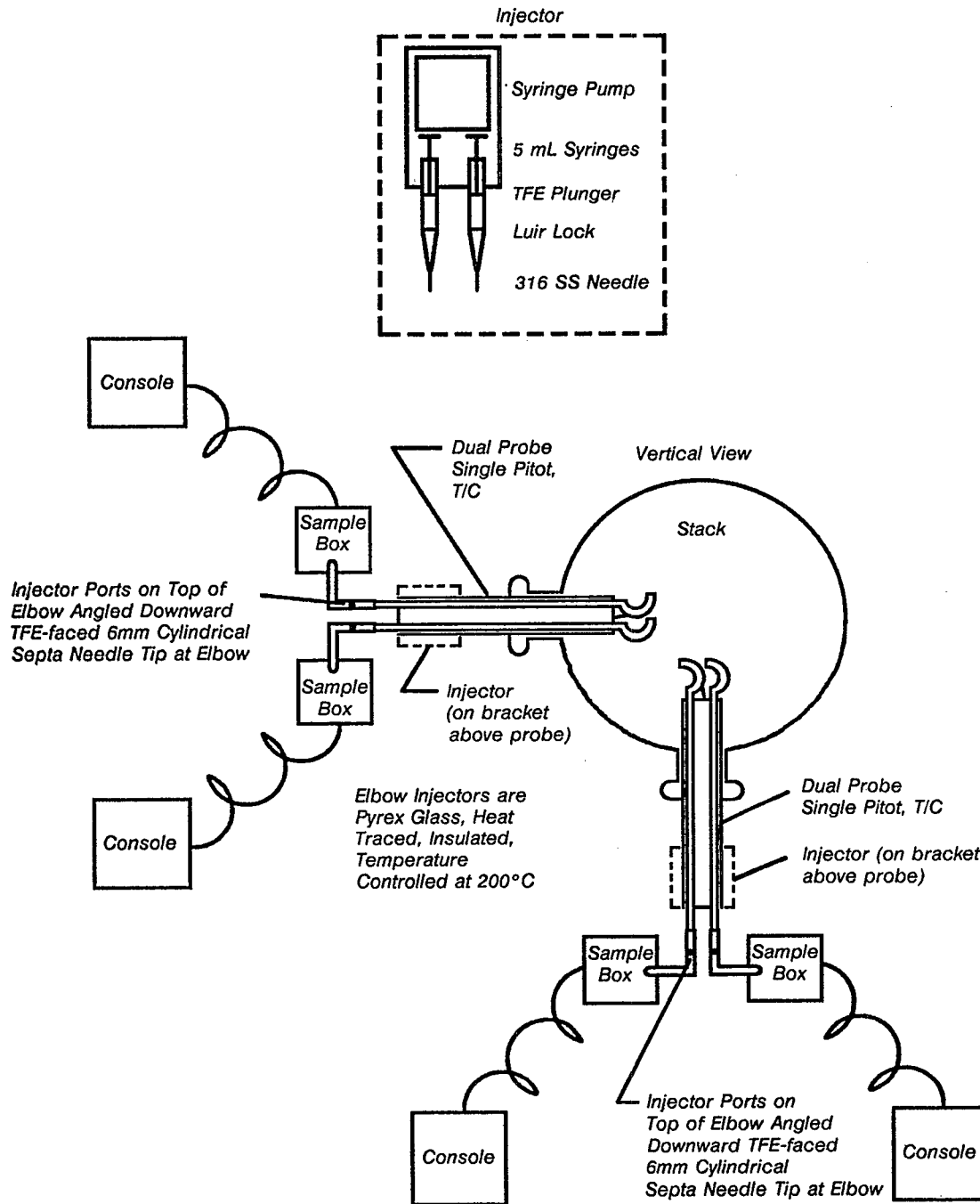


Figure 2. Dynamic spiking system configuration relative to the MM5 sampling train.

Table 4. Recovery of 13C-PCDD/PCDFs from Preliminary Tests of Dynamic Spiking System

Run	Spike Level	Spike Compound	Percent Recovery				Sum of Recoveries
			FH Rinse	Filter	BH Rinse	XAD	
2	500 ng	13C-TCDD	ND	8	87	4	99
		13C-HxCDD	ND	1	108	4	113
		13C-HxCDF	<1	<1	113	4	117
		13C-OCDF	<1	5	113	4	121
3	5 ng	13C-TCDD	*	*	*	*	*
		13C-HxCDD	ND	*	56	8	64
		13C-HxCDF	ND	31	51	*	82
		13C-OCDF	ND	13	76	3	92

* Chromatographic interference.

Table 5. Experimental Design for Initial Field Evaluation Testing

Stack Location	Field Spiking Level ^a for Test Run Number:					
	6	7	8	9	10	11
1	L	L ^b	M ^b	M ^b	H	H
2	L ^c	M	M ^b	H	H	L
3	M	L ^b	H	L	M	H ^d
4	H	H	L	M ^b	L	M

^a Field static and dynamic spiking levels: L = low (5 ng); M = medium (50 ng); and H = high (500 ng).

^b The MM5 train components of these test runs were analyzed individually.

^c The XAD spike (static) was 50 ng instead of 5 ng.

^d The XAD spike (static) was 25 ng instead of 500 ng.

the low spike, low filter box temperature run, the relative percent difference between the replicate recoveries of almost every congener collected in the front half, back half, and XAD exceeded 35%. All of the samples from the first replicate train of this run had high amounts recovered on the back-half and low on the XAD, whereas the second replicate train samples exhibited the opposite, namely higher recoveries in the XAD than in the back half. This may be the result of differential coating of the Apiezon in both trains or of the inability to totally remove the Apiezon from the extracts during cleanup. For the sampling trains from the low spike, high filter box temperature run, a large degree of variability can be observed in the replicate front component recoveries. However, the actual sample concentrations were close to the detection limits, so that random variability can be important. For the high spike, low filter box temperature run, significant variability was encoun-

tered for all congeners from the front components.

The average recoveries for each subsample in the train were normalized to the sum of these recoveries and plotted as stacked bar plots in Figure 4 for the dynamic spikes at the inlet and outlet. This plot aids in determining the distribution of the spiked compounds in the MM5 sampling train components. For each set of congeners, consecutive stacked bars represent low and high filter box temperatures, respectively.

For the dynamically spiked compounds collected at the inlet, there was a change in the overall distribution of each one favoring the back part (back half plus XAD) of the sampling train at the higher filter box temperature. This was observed for both the low and high spikes. This suggests that increasing the filter box temperature produced less adsorptivity of spiked dioxins and furans in the cyclone/filter assembly. The dynamic spike recoveries for the outlet location show that, as was the case for the inlet sampling locations, the higher filter box temperature increased the relative percentage of material being trapped in the back-half train components, of the sampling train. Note that at low spike levels, the high filter box temperature decreased the amount of 13C-labeled dioxin and furan congeners being trapped on the XAD relative to that collected in the back-half glassware, while at high spike level, a relatively greater proportion of the compounds were trapped in the XAD with high filter box temperatures. A potential explanation for this was described above, related to differential Apiezon-L coating on the trains or residual Apiezon in the sample extracts, and this is not reflected in the bars.

The concentrations of each native dioxin and furan congener in each portion of the sampling train were normalized to their sum and plotted in stacked bar graphs similar to those discussed above. These are shown in Figure 5. Increasing

the filter box temperature had little or no mobilization effect on the native dioxins and furans collected at the inlet and outlet locations. This is in stark contrast to the 13C-labeled dynamic spikes, whereby significantly lower adsorption of these compounds in the front parts of the train was achieved by raising the temperature of the filter box. Furans were more easily mobilized by increasing the filter box temperature than dioxins. This would suggest that the native dioxins and furans are differentially associated with the particles. The difference between the dioxins and furans likely reflects differences in their chemical structure and ability to sorb to particles.

All the evidence points to a previous association between flue particles and the native compounds that is dissimilar to that for the spiked compounds with the same particles. The residence time of the natives in the incinerator system (from incineration to sampling port) is in the order of 10s or less, whereas the residence time for the dynamic spikes is about 2s. Kinetic considerations indicate that this is not sufficient time to establish the associations between the particles and the native dioxins and furans. The implication is therefore that the association was established prior to incineration, between the precursors of the solid ash particles and the precursors of the native dioxins and furans. This suggestion is clearly speculative and would require experiments to test the hypothesis.

Conclusions and Recommendations

- Results from this investigation have demonstrated that the dynamic spiking system developed is appropriate for field use. Given the proven suitability of the technique for PCDDs/PCDFs, consideration should be given to expanding its application to other semivolatile organic compounds of interest.

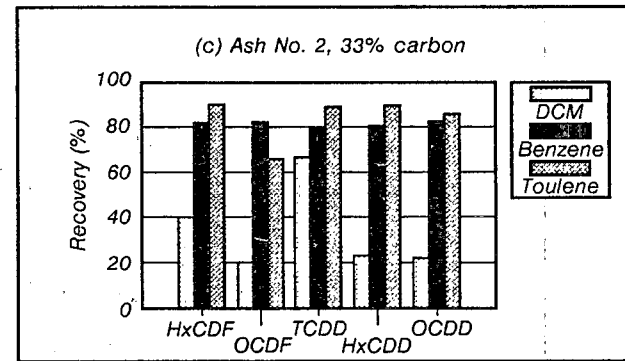
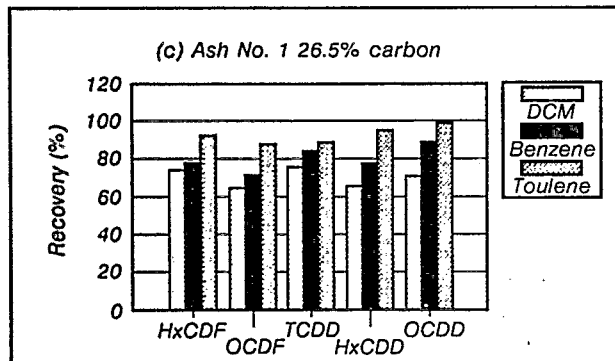
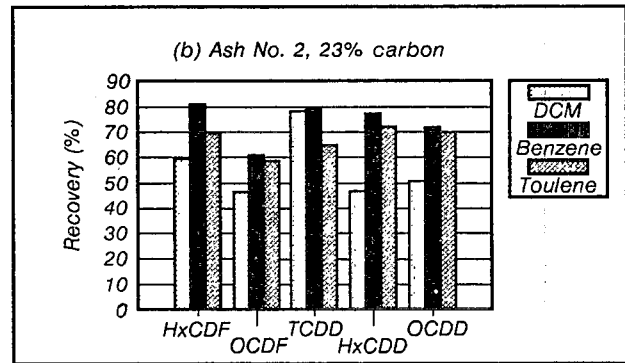
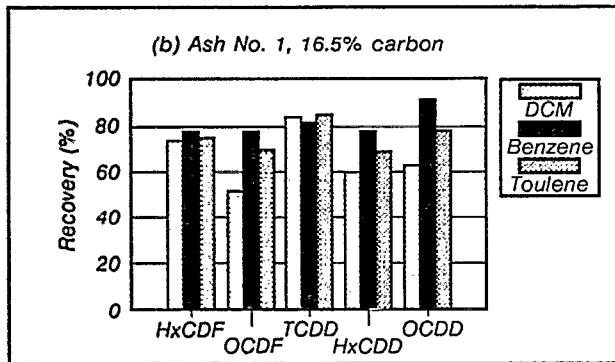
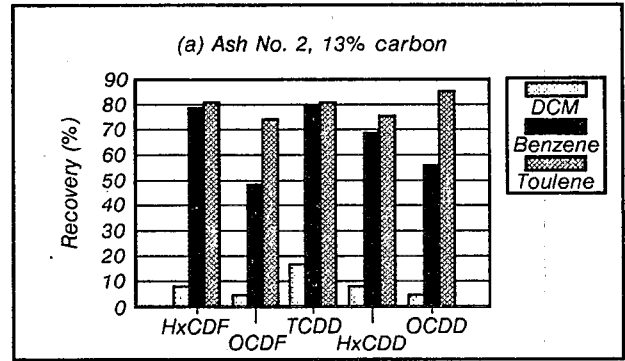
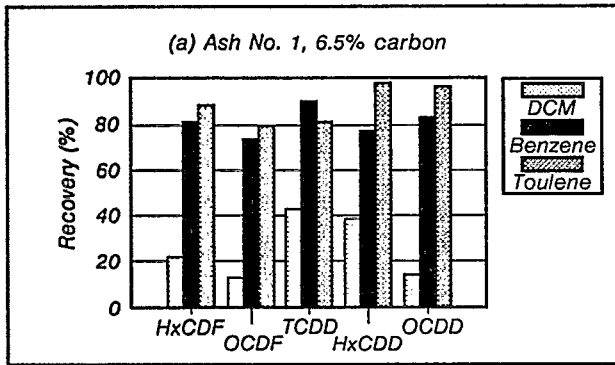


Figure 3. Recovery of ^{13}C -labeled dioxins and furans spiked into Ash No. 1 and No. 2: (a) Ash No. 1 unamended; (b) Ash No. 1 amended with 10% carbon; (c) Ash No. 1 amended with 20% carbon; (d) Ash No. 2, unamended; (e) Ash No. 2, amended with 10% carbon; (f) Ash No. 3, amended with 20% carbon..

Table 10. Recovery of ¹³C-Labeled PCDDs and PCDFs Dynamically Spiked into MM5 Trains Apiezon-L Coated and Uncoated Back-Half Glassware

Analyte	Runs 12 and 13 ^a				Runs 14 and 15 ^b				Runs 16 and 17 ^b			
	25-ng Spike		500-ng Spike		25-ng Spike		500-ng Spike		25-ng Spike		500-ng Spike	
	Back Half	XAD	Back Half	XAD	Back Half	XAD	Back Half	XAD	Back Half	XAD	Back Half	XAD
Coated Train ^c												
13C-1,2,3,4,7,8-HxCDF	129	NA	133	NA	113	2.8	212.1	86.1	NA	61.8	NA	
13C-OCDF	37.2	NA	90.6	NA	21.7	0.9	58.6	0.9	37.2	NA	47.2	NA
13C-1,2,3,4-TCDD	68.2	NA	66.8	NA	86.8	NA	118	NA	NA	NA	NA	NA
13C-1,2,3,7,8,9-HxCDD	82.6	NA	89.5	NA	74.2	2.8	156	1.2	74.2	NA	61.5	NA
Uncoated Train												
13C-1,2,3,4,7,8-HxCDF	18.9	30.3	35.3	21.2	14.0	57.7	NA	37.4	20.6	34.3	22.5	25.9
13C-OCDF	16.4	15.5	26.5	12.3	6.1	31.9	NA	19.8	21.3	22.8	13.6	13.6
13C-1,2,3,4-TCDD	8.1	NA	15.6	NA	7.3	NA	NA	NA	NA	NA	NA	NA
13C-1,2,3,7,8,9-HxCDD	12.1	20.4	21.6	14.5	10.0	49.3	NA	29.4	20.7	30.2	17.0	20.3

NA = not analyzed.

^a Flue gas from lab air.

^b Flue gas from kerosene combustor.

^c Back-half glassware was coated with Apiezon-L.

Table 11. Test Matrix for Second Field Validation Test for Recovery of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans

Test Day	Port	Location		
		Inlet Spike/F.B. Temp. ^a	Outlet Spike/F.B. Temp. ^a	Blank Train
1	1	25/250		
	2	25/250		
	3		25/250	
	4		25/250	
2	1	25/420		
	2	25/420		
	3		25/420	outlet
	4		25/420	
3	1	500/420		inlet
	2	500/420		
	3		500/250	
	4		500/250	
4	1	500/250		
	2	500/250		
	3		500/420	
	4		500/420	

^a Spike designates dynamic spike level (ng), and F.B. designates filter box.

Table 12. Percent Recovery of Static Spike^a on XAD-2 Resin During Second Field Validation Test

Sampling Location	Spike Level (ng)	Percent Recovery on XAD Resin	
		Filter Box Temp. 250°F	Filter Box Temp. 420°F
Inlet	25	99.4	78.6
		107	81.5
	500	89.0	71.9
		77.7	
Outlet	25	101	97.5
		84.3	92.4
	500	86.6	44.3
		93.4	92.6

^a ¹³C-1,2,3,7,8-pentachlorodibenzofuran.

Table 13. Percent Recovery of Dynamic Spikes from the Inlet Sampling Location MM5 Sampling Trains During Second Field Validation Test

Spike Level (ng)	13C-Labeled Analyte		Filter Box Temperature = 250°F					Filter Box Temperature = 420°F						
			Cyclone/Filter	Front Half	Back Half	XAD	Sum of Recov.	Cyclone/Filter	Front Half	Back Half	XAD	Sum of Recov.		
25	HxCDF	Average ^a	47.1	19.4	1.94	3.57	72.0	32.4	2.94	28.3	3.73	67.4		
		RPD	28.9	6.72	20.6	9.52		17.3	6.80	88.3	135			
	OCDF	Average	44.9	20.5	0.345	0.933	66.6	48.4	3.96	12.3	2.97	67.6		
		RPD	73.1	39.6	82.7	46.4		9.9	4.04	59.1	159			
	TCDD	Average	37.6	18.4	4.13	7.34	67.4	26.0	2.74	24.2	5.19	58.1		
		RPD	12.0	11.4	25.9	18.5		39.2	32.8	24.0	80.5			
	HxCDD	Average	42.5	17.7	2.26	2.69	65.1	36.4	3.34	18.9	4.81	63.3		
		RPD	24.9	6.23	6.62	5.95		5.78	0.90	56.8	87.3			
	OCDD	Average	56.1	24.6	0.576	0.822	82.0	55.0	4.37	8.69	1.71	69.7		
		RPD	32.4	20.0	85.1	7.30		7.83	2.52	69.3	200			
							\bar{x} = 70.6					\bar{x} = 65.2		
							S = 13.5					S = 8.44		
							RSD = 19.1%					RSD = 12.9%		
	500	HxCDF	Average	53.0	4.95	7.98	1.58	67.5	25.4	2.61	11.9	2.73	42.6	
RPD			60.0	11.9	44.9	18.4		NA ^b	NA	NA	NA			
OCDF		Average	55.9	9.77	3.22	0.557	69.4	45.8	4.79	6.35	1.79	58.7		
		RPD	12.7	29.2	24.8	33.9		NA	NA	NA	NA			
TCDD		Average	44.5	4.18	11.6	2.09	62.3	20.7	2.38	21.4	3.31	47.8		
		RPD	61.6	31.9	21.6	6.24		NA	NA	NA	NA			
HxCDD		Average	50.7	4.84	4.47	1.04	61.0	24.9	2.41	8.08	1.92	37.3		
		RPD	66.5	4.13	45.0	23.6		NA	NA	NA	NA			
OCDD		Average	67.5	10.0	2.65	0.421	80.5	49.4	4.90	5.38	1.53	61.2		
		RPD	28.6	25.0	1.89	45.3		NA	NA	NA	NA			
							\bar{x} = 68.1					\bar{x} = 49.5		
							S = 15.1					S = 10.3		
							RSD = 22.2%					RSD = 20.7%		

^a Average recovery of two replicate sampling points.

^b Replicate MM5 train leaked during sampling and was therefore not analyzed.

Table 14. Percent Recovery of Dynamic Spikes from the Outlet Sampling Location MM5 Sampling Trains During Second Field Validation Test

Spike Level (ng)	13C-Labeled Analyte		Filter Box Temperature = 250°F					Filter Box Temperature = 420°F						
			Cyclone/Filter	Front Half	Back Half	XAD	Sum of Recov.	Cyclone/Filter	Front Half	Back Half	XAD	Sum of Recov.		
25	HxCDF	Average ^a	1.29	0.358	46.0	28	75.5	1.85	0.382	65.3	24.8	92.3		
		RPD	0.00	57.5	72.0	73.8		83.2	200	47.2	24.2			
	OCDF	Average	3.42	0.707	37.4	18.2	59.7	3.06	0.498	97.3	33.2	134.0		
		RPD	7.91	117	66.3	126		90.2	200	28.3	3.92			
	TCDD	Average	0.827	0.124	38.0	34.0	72.9	2.03	0.505	58.1	23.9	84.5		
		RPD	17.3	102	70.4	108		77.5	200	43.4	2.94			
	HxCDD	Average	2.22	1.19	37.3	22.9	63.5	2.46	1.06	63.7	24.8	92.0		
		RPD	13.1	11.8	65.8	73.1		57.7	61.0	40.2	18.2			
	OCDD	Average	3.96	0.791	34.9	18.7	58.3	4.01	0.615	95.8	32.85	133.2		
		RPD	23.2	121	70.3	108		93.8	200	21.3	4.58			
							\bar{x} = 66.0							\bar{x} = 107
							S = 8.43							S = 25.6
						RSD = 12.8%							RSD = 23.8%	
500	HxCDF	Average	6.63	0.929	56.7	10.5	74.7	3.00	0.128	46.5	17.3	66.8		
		RPD	49.5	54.2	37.0	58.0		35.1	134	0.22	125			
	OCDF	Average	19.3	2.81	57.4	8.14	87.6	3.94	0.267	45.0	8.75	58.0		
		RPD	69.1	86.8	33.1	3.19		23.9	152	63.1	74.4			
	TCDD	Average	5.42	0.677	59.5	12.6	78.2	2.71	0.0940	44.7	20.5	67.9		
		RPD	41.3	46.1	32.3	42.7		29.5	104	6.94	110			
	HxCDD	Average	7.41	0.983	51.0	8.72	68.1	3.14	0.202	43.8	16.9	64.0		
		RPD	57.2	56.5	41.4	50.1		42.4	96.0	0.91	90.7			
	OCDD	Average	21.9	3.01	53.9	8.32	87.1	3.76	0.275	44.4	9.57	57.9		
		RPD	74.9	80.4	40.1	7.45		68.4	154	67.4	13.2			
							\bar{x} = 79.2							\bar{x} = 62.9
							S = 9.19							S = 13.3
						RSD = 11.6%							RSD = 20.9%	

^a Average recovery of two replicate sampling points.

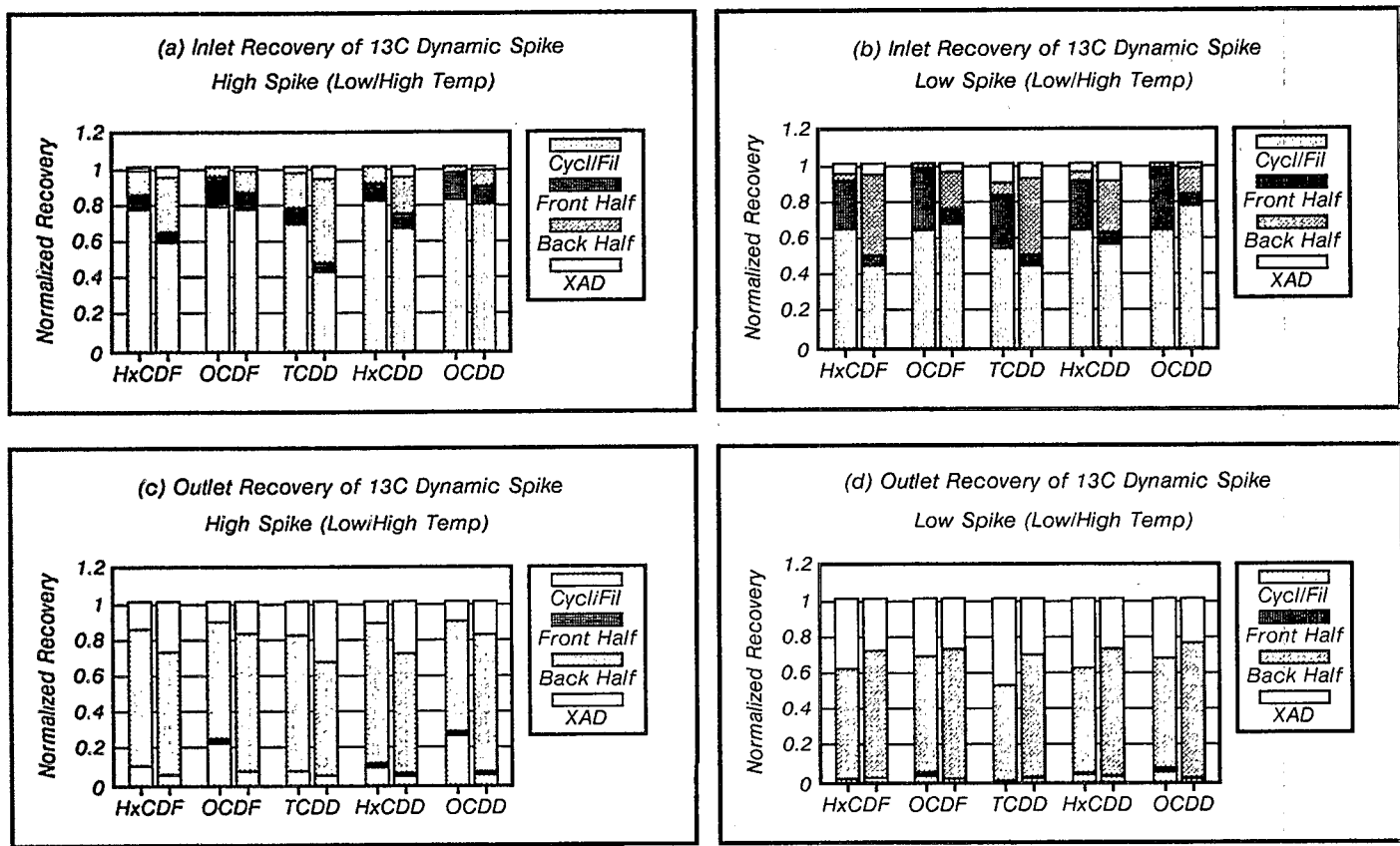


Figure 4. Normalized recoveries of ¹³C-labeled dynamically spiked compounds: (a) High spike (500 mg), inlet sampling location; (b) Low spike (25 mg), inlet sampling location; (c) High Spike (500 mg), outlet sampling location; (d) Low spike (25 mg), outlet location. Alternating bars represent low and high filter box temperature recoveries, respectively.

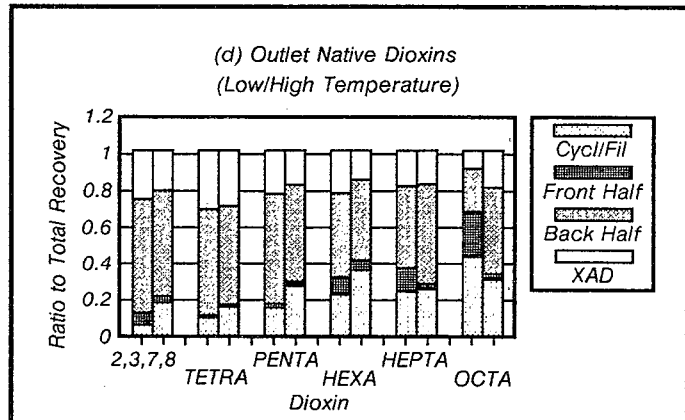
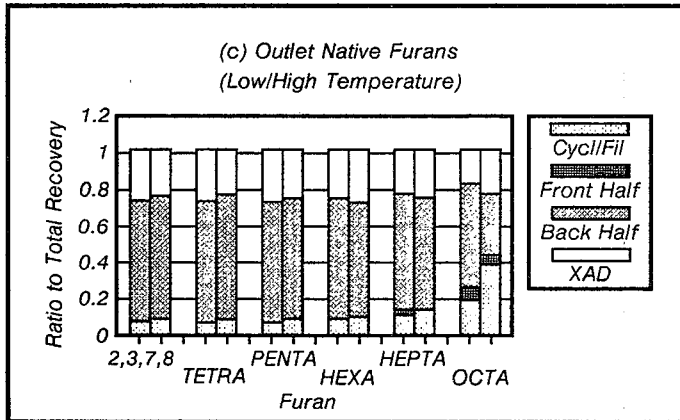
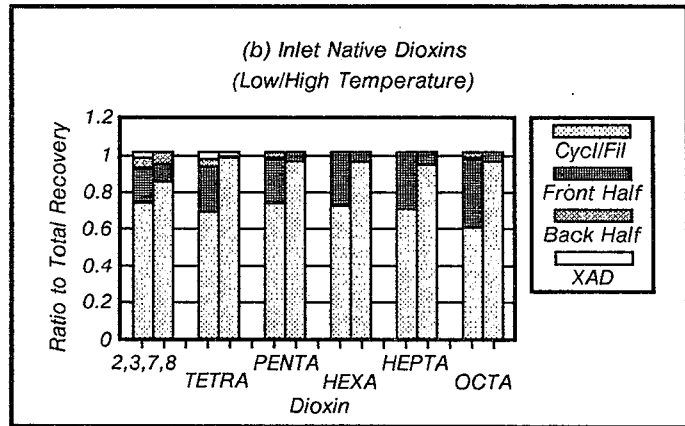
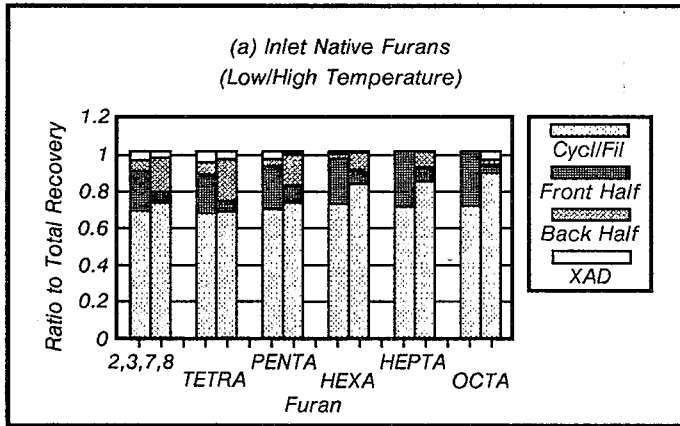


Figure 5. Normalized recoveries of native dioxins and furans: (a) inlet furans; (b) inlet dioxins; (c) outlet furans; (d) outlet dioxins. Low and high dynamic spike run results were combined; alternating bars represent low and high filter box temperature recoveries, respectively.

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The complete report, entitled "Validation of Emission Test Method For PCDDs and PCDFs," (Order No. PB 90-187 246/AS; Cost: \$53.00, subject to change) will be available only from:

*National Technical Information Service
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