

For Proceedings of 1996 International Incineration Conference

Development of PIC Target Analyte List for Hazardous Waste Incineration Processes

Jeffrey V. Ryan and Paul M. Lemieux
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division
Research Triangle Park, NC 27711

Christopher Lutes and Dennis Tabor
Acurex Environmental Corporation
PO Box 13109
Research Triangle Park, NC 27709

Abstract

Current analytical schemes for measuring organic emissions from hazardous waste incineration (HWI) processes do not characterize the full spectrum of products of incomplete combustion (PICs) that may be emitted. In fact, required incineration emissions measurements are oriented towards quantifying principal organic hazardous constituents (POHCs) and other noncombustion related organic compounds. As a result, the emissions measurement approach is based more on what is fed into the incinerator than what may be emitted by the incineration process. Experiments were performed to generate, collect, and characterize the organic emissions from a pilot-scale rotary kiln hazardous waste incinerator using a complex, surrogate hazardous waste mixture in order to develop an analyte list representative of volatile, semivolatile, and nonvolatile organic HWI emissions that includes PICs. Organic emissions were collected and analyzed using a combination of conventional and nonconventional techniques. Emphasis was placed on expanding the capabilities of existing methodologies, such as gas chromatography/mass spectrometry (GC/MS), to identify and quantify nontarget analytes. Analytes identified include: alkylated, chlorinated, brominated, and mixed bromochloro aromatics, alkanes, alkenes, and alkynes; chlorinated, brominated, mixed bromochloro, alkylated, oxygenated polyaromatic hydrocarbons; and chlorinated, brominated, mixed bromochloro dibenzodioxins and furans. Of the volatile and semivolatile organic species found, less than half have been identified. Less than 25% of those found were actual target analytes.

Introduction

The current regulatory approach for hazardous waste incineration (HWI) is based on assessing the destruction of principal organic hazardous constituents (POHCs). As a result, associated EPA test methods specifically focus on identifying and quantifying these compounds. Concerns are increasing over the products of incomplete combustion (PICs) that may be emitted as a result of incineration. Required analytical schemes for measuring organic emissions from HWI processes do not fully characterize the spectrum of PICs that may be emitted. Because POHCs are "target analytes" for identification and quantitation, only a small number of PICs are typically identified. As a result, the number of PICs identified may be relatively small compared to the actual number present.

The EPA's Office of Solid Waste (OSW) is interested in including PICs in their risk assessments for hazardous waste combustors (HWCs). HWCs are defined as hazardous waste incinerators, hazardous-waste-burning cement kilns, and hazardous-waste-burning lightweight aggregate kilns. A comprehensive list of hazardous PICs from HWC sources is needed to augment risk assessments. While considerable data are available on PICs from HWI processes, the data generated have been primarily collected using conventional methodologies -- the EPA test methods that focus on the quantitation of POHCs. As a result, they are not considered to encompass the breadth of potential PICs. More innovative sampling and analytical approaches are required.

To support OSW's Combustion Strategy, the EPA's National Risk Management Research Laboratory (NRMRL), Air Pollution Prevention and Control Division (APPCD), Air Pollution Technology Branch (APTB) conducted a study to help develop a target analyte list for PICs from hazardous waste incinerators.

Experimental

The incineration tests were performed using the EPA/APPCD Rotary Kiln Incinerator Simulator (RKIS) located in the EPA Environmental Research Center HWI research laboratory in Research Triangle Park, NC. The facility has a Research Conservation and Recovery Act (RCRA) Research, Development, and Demonstration (RD&D) permit to burn actual and surrogate hazardous waste. The RKIS, shown in Figure 1, consists of a 73 kW (250,000 Btu/hr) rotary kiln section, a transition section, and a 73 kW (250,000 Btu/hr) secondary combustion section. The RKIS was designed for the testing of liquid and solid surrogate hazardous waste materials.

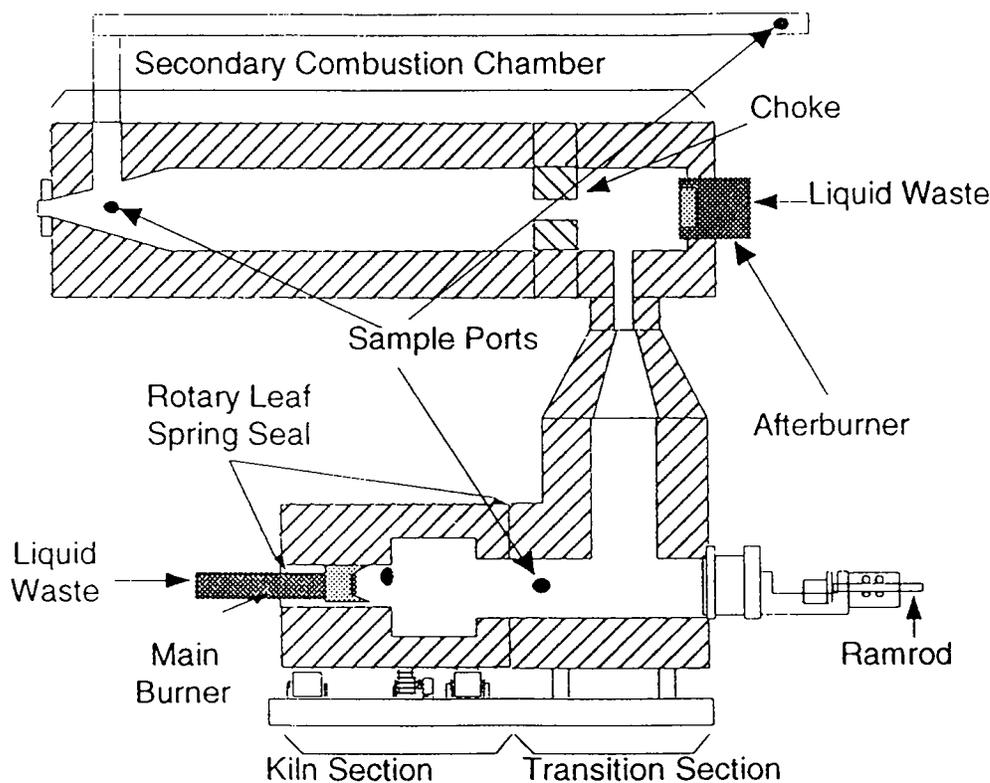


Figure 1. Rotary kiln incinerator simulator

The RKIS was designed to contain the salient features of full-scale kilns, but still be sufficiently versatile to allow experimentation by varying one parameter at a time or controlling a set of parameters independently. The rotating kiln section contains a recess which contains the solid waste during incineration. The recess was designed with a length to diameter (L/D) ratio of 0.8, which is 20 to 25% of a full-scale system. The main burner, based on an International Flame Research Foundation (IFRF) variable swirl design, is the primary heat source for the system. Natural gas was used as the primary fuel during startup and idle, then was switched over to the surrogate waste feed used throughout testing.

From the kiln section, the combustion gases enter the transition section. The gases then flow into the experimental secondary combustion chamber (SCC). The SCC consists of three regions: the mixing chamber, the plug flow section, and the stack transition section. A replaceable choke section separates the mixing chamber from the plug flow section. A conical refractory insert has been installed into the first plug flow sub-section to provide a gradual divergence from the choke diameter to the plug flow section diameter and minimize recirculation zones downstream of the choke. The afterburner, also based on an IFRF variable swirl design, provides heat and flame to the SCC, and was also fired with natural gas during startup and idle times, then switched to the liquid surrogate waste during the tests.

Combustion gases exiting the afterburner pass through a water-jacketed convective cooling section of 20.3-cm (8-in) diameter stainless steel (SS) ducting. Further cooling is achieved by adding ambient dilution air via a dilution damper located upstream of the 9.9-m (35-ft) sampling duct. Emissions samples were collected at sampling locations 66.7-cm (169.5-in) and 98.6-cm (250.5-in) downstream of the dilution damper. These sampling locations

are oriented to meet isokinetic sampling requirements.

The surrogate hazardous waste that was fed during tests was designed to possess representative compounds from many common classes of organic hazardous wastes. The composition of the surrogate hazardous waste feed was developed based on recommendations from members of OSW. Table 1 lists the composition of the surrogate waste feed. In addition to the organic surrogate waste, an aqueous mixture of metal salts, including zinc nitrate hexahydrate, nickel nitrate hexahydrate, and copper nitrate hexahydrate, was also fed into the kiln. The purpose of the metals injection was to provide a representative supply of metal catalyst to promote any heterogeneous reactions forming polychlorinated dibenzodioxins and furans (PCDDs/PCDFs). The liquid surrogate waste was injected as fuel into both the primary burner and afterburner. The liquid was injected using a pump, and was metered using calibrated rotameters.

Table 1. Waste Feed Composition

Class	Compound	Formula	Mass %
carrier liquid	No. 2 fuel oil	n/a	50.0
chlorinated non-aromatic	methylene chloride	CH ₂ Cl ₂	15.93
	chloroform	CHCl ₃	8.94
	carbon tetrachloride	CCl ₄	4.79
chlorinated aromatic	monochlorobenzene	C ₆ H ₅ Cl	6.65
	dichlorobenzene	C ₆ H ₄ Cl ₂	7.69
	chlorophenol	C ₆ H ₅ ClO	3.00
non-chlorinated aromatic	toluene	C ₇ H ₈	10.40
	xylene	C ₈ H ₁₀	10.43
alcohol	isopropanol	C ₃ H ₈ O	4.71
ketone	methyl ethyl ketone	C ₄ H ₈ O	9.67
nitrated waste	pyridine	C ₅ H ₅ N	11.79
non-chlorinated polyaromatic	naphthalene	C ₁₀ H ₈	3.00
brominated non-aromatic	bromoform	CHBr ₃	1.50
	ethylene dibromide	C ₂ H ₄ Br ₂	1.50

Several different RKIS operating conditions were employed during the incineration tests. These operating conditions were designed to simulate several operating modes for the incinerator system, including off-specification combustion. Since this is a small idealized system, the RKIS was operated in a slightly off-specification mode to produce measurable quantities of diverse PICs. The operating test conditions used are listed in Table 2.

Table 2. Test Conditions

Run	Date	Description
5	5/3/95	Baseline conditions, kiln T ≈ 800 °C, SCC T ≈ 1000 °C
6	5/4/95	Baseline conditions, kiln T ≈ 800 °C, SCC T ≈ 1000 °C
9	5/12/95	Low SCC temperature, SCC T ≈ 650 °C
10	5/16/95	Low SCC temperature, SCC T ≈ 650 °C
13	8/14/95	SCC fuel-rich, afterburner stoichiometric ratio ≈ 0.9
14	8/16/95	SCC fuel-rich, afterburner stoichiometric ratio ≈ 0.9

The RKIS was equipped with a continuous gas analysis and data acquisition system consisting of two sets of continuous emissions monitors (CEMs) for oxygen (O₂), carbon monoxide (CO), carbon dioxide (CO₂), nitric oxide (NO), and total hydrocarbons (THCs), with sample locations at both the kiln and SCC exits.

Standard EPA sampling methodologies were used to collect volatile, semivolatile, and nonvolatile organic emissions. Volatile organics (VOCs) were collected using two different methods: Method 0040 (TedlarBag)¹ and the Volatile Organic Sampling Train (VOST)². Semivolatile organics (SVOCs) were also collected using two different methods: Modified Method 5 (MM5)³ and the Source Assessment Sampling System (SASS)⁴. Dioxins were collected using Method 23⁵. These are the same standard methods that would be used during actual compliance testing.

The volatile, semivolatile, and nonvolatile organic samples were analyzed following the analytical methodologies associated with each respective sampling method. Additional analytical procedures were incorporated to expand the range of qualitative analyses.

The Tedlar bag samples were analyzed using two separate analytical procedures based on target analytes. Gas chromatography with flame ionization detection (GC/FID) was used to screen for C1 through C4 straight chain alkanes, alkenes, and alkynes. The actual target analyte list is presented in Table 3. The Tedlar bag samples were also analyzed by gas chromatography/mass spectrometry (GC/MS) following the procedures described in SW-846 Methods 5040 and 8240^{6,7}. Method 8240 quantifies VOCs with boiling points ranging from ~-30 to ~ 200 °C. The Method 8240 VOC target analyte list for these tests is presented in Table 4.

The VOST samples were also analyzed by SW-846 Methods 5040 and 8240. The target analyte list presented in Table 4 was also used for the VOST analyses.

Table 3. C1 - C4 Target Analytes

Methane	Acetylene (Ethyne)
Ethene	Ethane
Propyne	Propene
Propane	n-Butane

Table 4. Target Volatile Organic Compounds

Dichlorodifluoromethane	Bromodichloromethane
Chloromethane	cis-1,3-Dichloropropene
Vinyl Chloride	2-Hexanone
Bromomethane	trans-1,3-Dichloropropene
Chloroethane	1,1,2-Trichloroethane
Trichlorotrifluoromethane	Dibromochloromethane
1,1-Dichloroethene	1,2-Dibromoethane
Iodomethane	Bromoform
Carbon Disulfide	4-Methyl-2-pentanone
Acetone	Toluene
Methylene Chloride	Tetrachloroethene
1,2-Dichloroethene (total)	Chlorobenzene
1,1-Dichloroethane	Ethylbenzene
Chloroform	1,1,1,2-Tetrachloroethane
1,2-Dichloroethane	m/p-Xylene
2-Butanone	o-Xylene
1,1,1-Trichloroethane	Styrene
Carbon Tetrachloride	1,1,2,2-Tetrachloroethane
Benzene	1,2,3-Trichloropropane
Trichloroethene	trans-1,4-Dichloro-2-butene
1,2-Dichloropropane	Pentachloroethane
Dibromomethane	1,2-Dibromo-3-chloropropane

The MMS samples were analyzed in general accordance with SW-846 Methods 3542 and 8270^{8,9}. The front half (filter), back half (XAD-2), and condensate sample fractions were extracted separately. In addition, the front half and back half sample fractions were extracted with acetone, and then toluene, following the dichloromethane extraction, to enhance the recovery of organic compounds with differing polarities. Each dichloromethane extract was analyzed separately. The Method 8270 semivolatile organic target analyte list used for these tests is presented in Table 5.

Table 5. Target Semivolatile Organic Compounds

N-Methyl-N-nitroso-ethanamine	Dimethylphthalate
bis(2-chloroethyl)Ether	2,6-Dinitrotoluene
Aniline	Acenaphthene
Phenol	4-Nitroaniline
2-Chlorophenol	2,4-Dinitrophenol
1,3-Dichlorobenzene	Dibenzofuran
1,4-Dichlorobenzene	Pentachlorobenzene
1,2-Dichlorobenzene	2,4-Dinitrotoluene
Benzyl alcohol	2,3,4,6-Tetrachlorophenol
bis(2-chloroisopropyl)Ether	4-Nitrophenol
2-Methylphenol	Fluorene
Acetophenone	Diethyl phthalate
Hexachloroethane	4-Chlorophenyl phenyl ether
Methylphenol	2-Methyl-4,6-dinitrophenol
N-Nitrosodipropylamine	Diphenylamine
Nitrobenzene	4-Bromophenyl phenyl ether
1-Nitrosopiperidine	Phenacetin
Isophorone	Hexachlorobenzene
2,4-Dimethylphenol	Pentachlorophenol
bis(2-chloroethoxy)Methane	Pentachloronitrobenzene
2,4-Dichlorophenol	Phenanthrene
1,2,4-Trichlorobenzene	Anthracene
Naphthalene	Dibutyl phthalate
2-Nitrophenol	Fluoranthene
2,6-Dichlorophenol	Pyrene
Hexachloropropene	P-Dimethylaminoazobenzene
4-Chloroaniline	Benzyl butyl phthalate
Hexachlorobutadiene	Chrysene
N-Butyl-N-nitroso-butanamine	Benzo(a)anthracene
4-Chloro-3-methyl-phenol	di-N-Octyl phthalate
2-Methylnaphthalene	Benzo(b)fluoranthene
1,2,4,5-Tetrachlorobenzene	7,12-Dimethylbenz(a)anthracene
Hexachlorocyclopentadiene	Benzo(k)fluoranthene
2,4,6-Trichlorophenol	Benzo(a)pyrene
2,4,5-Trichlorophenol	3-Methylcholanthrene
2-Chloronaphthalene	Indeno(1,2,3-cd)pyrene
2-Nitroaniline	Dibenz(a,h)anthracene

(continued)

Nontarget organic compounds present in both volatile and semivolatile organic samples were tentatively identified primarily through mass spectral matching. The mass spectra from unknowns were compared to known mass spectra contained in a database. Through probability-based matching, tentative identifications were assigned. The quality of the match, along with the analyst's judgement, were the primary basis for tentatively assigning identification to unknowns. Confirmation with known standards has not been performed at this time. The number of compounds identified for spectral matching is based on the analytical system response of individual compounds relative to the other compounds present in the sample. Typically, the 10-20 nontarget compounds with the greatest system response are identified for spectral matching. For these analyses, the number was 30.

PCDDs/PCDFs were analyzed by an approach that is similar to Method 23, except that: the analyses were performed by low resolution mass spectrometry (LRMS) as opposed to high resolution mass spectrometry (HRMS); and the target analytes were expanded to include mono-, di-, and tri- CDD/CDF congeners. The 2,3,7,8 isomers were not confirmed as required by Method 23. All PCDDs/PCDFs are reported as total mass per congener.

The PCDD/PCDF sample extracts were also analyzed to screen for the presence of polybrominated dibenzo dioxins and furans (PBDDs/PBDFs) and mixed bromochloro dibenzodioxins and furans (MBCDDs/MBCDFs). Standardized analytical techniques for these target compounds do not exist. The analysis for MBCDDs/MBCDFs is particularly hindered by the lack of both isotopically labelled and unlabelled standards. Because of the lack of the standards, the screening approach targeted only those PBDD/PBDF and MBCDD/MBCDF isomers for which standards could be obtained. These included BrCl₃DD, Br₂Cl₂DD, Br₄DD, Br₅DD, BrCl₃DF, Br₄DF, and Br₅DF. Samples were analyzed by LRMS using isotope dilution techniques similar to those used to analyze for PCDDs/PCDFs. Prior to extraction, the samples were spiked with known amounts of isotopically labelled Br₄DD and Br₄DF. These were used as internal standards to quantify the target native PBDDs/PBDFs and MBCDDs/MBCDFs as well as assess method performance.

Results and Discussion

It must be emphasized that the results reported here are both preliminary and incomplete. Test conditions in addition to those presented in Table 2 were also evaluated. Most importantly, the tentative nontarget analyte identifications are just that, tentative. Their identities have not been confirmed. Readers are cautioned to keep these considerations in mind when drawing information from this paper.

Tedlar bag results are limited at this time. No C1 - C4 alkenes, alkenes, or alkynes were detected. Estimated minimum detection limits are on the order of 1 - 2 ppm. The VOC GC/MS data have not yet been interpreted.

The VOST analytical results indicate that a significant number of VOC PICs have been identified both as target analytes and as tentatively identified compounds (TICs). For the analytical data evaluated, PICs identified both as target analytes and TICs are presented in Tables 6 and 7, respectively. Of the 44 target analytes, 38 were detected. It should be noted that several of these compounds are POHCs. Over 50 nontarget analytes were tentatively identified as PICs. However, a large number of PICs present in the VOST samples were not identified. To aid in perspective, at least 82 compounds were detected in a single sample. Of those, 28 were identified as target analytes, 21 were tentatively identified, and 33 remained unidentified.

An interesting comparison was made of the C1 and C2 halogenated alkanes, alkenes, and alkynes. A table was made of the possible chloro, bromo, and mixed bromochloro organics with one and two carbons (Table 8). With only several exceptions, each compound was detected in at least one sample. These C1 and C2 compounds are of particular interest as these species are considered to be precursors in aromatic ring propagation reactions leading to higher molecular weight PICs¹⁰.

Table 6. Target Volatile Organic Compounds Detected

Dichlorodifluoromethane	1,2-Dichloropropane
Chloromethane	Dibromomethane
Vinyl chloride	Bromodichloromethane
Bromomethane	cis-1,3-Dichloropropene

(continued)

Table 6 (continued)

Chloroethane	trans-1,3-Dichloropropene
Trichlorotrifluoromethane	Dibromochloromethane
1,1-Dichloroethene	1,2-Dibromoethane
Carbon disulfide	Bromoform
Acetone	4-Methyl-2-pentanone
Methylene chloride	Toluene
1,2-Dichloroethene	Tetrachloroethane
1,1-Dichloroethane	Chlorobenzene
Chloroform	Ethylbenzene
1,2-Dichloroethane	1,1,1,2-Tetrachloroethane
2-Butanone	Xylene (M,P)
1,1,1-Trichloroethane	Xylene (O)
Carbon tetrachloride	Styrene
Benzene	trans-1,4-Dichloro-2-butene
Trichloroethene	1,2-Dibromo-3-chloropropane

Table 7. Tentatively Identified Volatile Organic Compounds

Bromotrichloromethane	Propene
Chloroethyne	Methyl propene
Bromoethyne	Methyl butane
Bromochloroethyne	Butadiyne
Dichloroethyne	Butadiene
Bromoethene	Pentene
Bromochloroethene	Pentane
Dibromoethene	Hexene
Bromodichloroethene	Hexane
Dibromochloroethene	Methylcyclohexane
Tribromoethene	Heptane
Bromotrichloroethene	Methylheptane
Tribromochloroethene	Dimethylheptane
Dibromodichloroethene	Octane
Tetrabromoethene	Nonane
Bromochloroethane	Decane
Bromopropyne	Methyldecane
Bromochloropropyne	Undecane
Bromodichloropropyne	Methylfuran
Bromopropene	Benzaldehyde
Pentachloropropene	Methylpentenal
Dibromopropane	Benzonitrile
Hexachlorobutadiene	Chlorothiophene
Pentachlorobutadiene	Tetrachlorothiophene
Chlorobutane	Dibromothiophene

(continued)

Table 7 (continued)

Bromoheptane

Chlorooctane

Benzylchloride

Bromobenzene

Bromomethylbenzene

Bromodimethylbenzene

Bromochlorobenzene

Dibromobenzene

Bromodichlorobenzene

Table 8. C1 and C2 Chloro, Bromo, and Mixed Bromochloro Organics

C1 Hydrocarbons	Target Analyte	Compound Detected
chloromethane	Yes	•
bromomethane	Yes	•
dichloromethane	Yes	•
dibromomethane	Yes	•
bromochloromethane	Yes	•
trichloromethane	Yes	•
tribromomethane	Yes	•
bromodichloromethane	Yes	•
dibromochloromethane	Yes	•
tetrachloromethane	Yes	•
tetrabromomethane	No	•
bromotrichloromethane	No	•
dibromodichloromethane	No	
tribromochloromethane	No	
C2 Alkynes		
chloroethyne	No	•
bromoethyne	No	•
dichloroethyne	No	•
dibromoethyne	No	
bromochloroethyne	No	•
C2 Alkenes		
chloroethene	Yes	•
bromoethene	No	•
dichloroethene (total)	Yes	•
dibromoethene	No	•
bromochloroethene	No	•
trichloroethene	Yes	•
tribromoethene	No	•
bromodichloroethene	No	•
dibromochloroethene	No	•
tetrachloroethene	Yes	•
tetrabromoethene	No	•
bromotrichloroethene	No	•
dibromodichloroethene	No	•
tribromochloroethene	No	•
C2 Alkanes		
chloroethane	Yes	•
bromoethane	No	
dichloroethane	Yes	•
dibromoethane	Yes	•
bromochloroethane	No	•

(continued)

Table 8 (continued)

trichloroethane	Yes	•
tribromoethane	No	
bromodichloroethane	No	
dibromochloroethane	No	
tetrachloroethane	Yes	•
tetrabromoethane	No	
bromotrichloroethane	No	
dibromodichloroethane	No	
tribromochloroethane	No	

The semivolatile organic analytical results also indicate that a significant number of PICs have been identified both as target analytes and as TICs. For the analytical data evaluated, PICs identified both as target analytes and TICs are presented in Tables 9 and 10, respectively. Many of the target analytes were detected. Of the 77 target analytes, 42 were detected. It should be noted once again that several of these compounds are POHCs. Over 50 nontarget analytes were tentatively identified as PICs. Many of the PICs present in the MM5 samples were not identified. Also, the mix of PICs found on the filter sample fraction differed from that of the XAD-2 sample fraction. For a selected filter sample, at least 174 compounds were detected: 25 were identified as target analytes, 11 were tentatively identified, and 138 remained unidentified. For a selected XAD-2 sample, at least 194 compounds were detected: 18 were identified as target analytes, 17 were tentatively identified, and 159 remained unidentified. The large number of unidentified compounds is not due to an inability to identify them, but rather to the fact that only a fixed number were targeted for spectral matching. This also holds true for the volatile organic analyses.

Table 9. Target Semivolatile Organic Compounds Detected

Hexachlorobutadiene	Dibenzofuran
Hexachlorocyclopentadiene	Acetophenone
1,3-Dichlorobenzene	Naphthalene
1,4-Dichlorobenzene	2-Methylnaphthalene
1,2-Dichlorobenzene	2-Chloronaphthalene
1,2,4-Trichlorobenzene	Acenaphthylene
1,2,4,5-Tetrachlorobenzene	Acenaphthene
Pentachlorobenzene	Fluorene
Hexachlorobenzene	Phenanthrene
Phenol	Anthracene
Methylphenol	Fluoranthene
2-Nitrophenol	Pyrene
2,4,6-Trichlorophenol	Chrysene
2,4,5-Trichlorophenol	Benzo(a)anthracene
2,3,4,6-Tetrachlorophenol	Benzo(b)fluoranthene
Pentachlorophenol	7,12-Dimethylbenz(a)anthracene
Dimethylphthalate	Benzo(k)fluoranthene
Diethyl phthalate	Benzo(a)pyrene
Dibutyl phthalate	Indeno(1,2,3-cd)pyrene
Benzyl butyl phthalate	Dibenz(a,h)anthracene
di-N-Octyl phthalate	Benzo(ghi)perylene

Table 10. Tentatively Identified Semivolatile Organic Compounds

Bromomethylpropane	Methylphenanthrene
Tribromomethane	Methylanthracene
Bromotrichloroethene	Dimethylphenanthrene
Dibromodichloroethene	Bromonaphthalene
Tribromochloroethene	Bromoanthracene
Tetrabromoethene	Xanthenone
Tribromobutane	Phenalenone
Bromocyclohexane	Benzopyranone
Dibromocyclohexane	Naphthalenedione
Bromobenzene	Isobenzofurandione
Bromomethylbenzene	Anthracenedione
Bromochlorobenzene	Ethylhexanol
Dibromobenzene	Butoxyethanol
Dibromochlorobenzene	Bromocyclohexanol
Bromodichlorobenzene	Bromochlorocyclohexanol
Bromotrichlorobenzene	Bromomethoxycyclohexane
Bromodichlorophenol	Phenoxybiphenyl
Dibromochlorophenol	Hexanoic acid
Tribromophenol	Ethylhexanoic acid
Benzaldehyde	Benzoic acid, methyl ester
Benzonitrile	Butanedioic acid, dimethyl ester
Bromobenzonitrile	Dibromoacetic acid, methyl ester
Dibromothiophene	Hexanedioic acid, dimethyl ester
Chloropyridine	Decamethylcyclopentasiloxane
Dichloronaphthyridine	Dodecamethylcyclohexasiloxane
Biphenyl	Tetradecamethylcycloheptasiloxane
Nonane	Benzofuran
Decane	Trimethylhexane

PCDD/PCDF analytical results indicate that all mono- through octa PCDD/PCDF congeners were detected. Several samples indicated that PBDDs/PBDFs and MBCDDs/MBCDFs were indeed present. For the low temperature test condition, Run 10, BrCl₃DD, Br₂Cl₂DD, Br₄DF, and Br₅DF were detected.

Summary and Conclusions

Pilot-scale incineration tests have been performed under varied combustion conditions feeding a mixed surrogate waste, resulting in the generation of numerous PICs. While many of these PICs were identified as target analytes using required, standardized sampling analytical methods, the majority of PICs present in the incineration emissions were not target analytes. Although a substantial number have been tentatively identified, a considerably larger number have not been identified at this time. It can be concluded from these experiments that the current sampling and analytical schemes for characterizing HWI emissions provide an incomplete picture of the emission profile.

As a result of these experiments, an expanded list of PIC target analytes has been developed. This list is by no means complete or comprehensive. This list should be viewed in context with this particular set of experiments; i.e., waste mix. The PICs resulting from other mixed waste streams have not been evaluated.

The PICs identified fall into several chemical classes. A wide variety of chloro, bromo, and mixed bromochloro alkanes, alkenes, alkynes, aromatics, and polyaromatics were detected. In addition, nonhalogenated hydrocarbon homologues along with oxygenated, nitrogenated, and sulfonated organics were detected. Analytical

methods specifically suited to these chemical classes are needed to enhance PIC characterizations.

Future Plans

The data and chemical analyses performed to date are by no means complete. More comprehensive data and chemical analyses are intended. These include:

- Perform more rigorous spectral analysis of existing samples
- Confirm tentative identifications with known standards where possible
- For semivolatile organics, fractionate samples into functional classes and perform more thorough analyses
- Analyze the toluene and acetone sample extracts
- Use more innovative analytical techniques such as gas chromatography with atomic emission detection (GC/AED) and liquid chromatography/mass spectroscopy (LC/MS) to further characterize samples
- Conduct additional tests to verify initial results and investigate other surrogate waste mixes

References

- 1) EPA Test Method 0040 "Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar Bags" in Test Methods for Evaluating Solid Wastes, Volume II, SW-846 (NTIS PB88-239223). Environmental Protection Agency, Office of Solid Waste, Washington, DC. (August 1994)
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- 10) Tsang, W., "Mechanisms for the Formation and Destruction of Chlorinated Organic Products of Incomplete Combustion," *Combustion Science and Technology*, 74:99-116 (1990)

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completi</i>		
1. REPORT NO. EPA/600/A-96/065	2.	3.
4. TITLE AND SUBTITLE Development of PIC Target Analyte List for Hazardous Waste Incineration Processes	5. REPORT DATE	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) J. V. Ryan and P. M. Lemieux (EPA), and C. Lutes and D. Tabor (Acurex)	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANOIZATION NAME AND ADDRESS Acurex Environmental Corporation P. O. Box 13109 Research Triangle Park, North Carolina 27709	10. PROGRAM ELEMENT NO.	
	11. CONTRACT/GRANT NO. 68-D4-0005	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air Pollution Prevention and Control Division Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Published paper; 10/94-3/96	
	14. SPONSORING AGENCY CODE EPA/600/13	
15. SUPPLEMENTARY NOTES APPCD project officer is Jeffrey V. Ryan, Mail Drop 91, 919/541-1437. Presented at 15th Annual Conference on Incineration and Thermal Treatment Technologies, Savannah, GA, 5/6-10/96.		
16. ABSTRACT The paper discusses experiments that were performed to generate, collect, and characterize organic emissions from a pilot-scale rotary-kiln hazardous waste incinerator (HWI) using a complex, surrogate hazardous waste mixture in order to develop an analyte list representative of volatile, semivolatile, and nonvolatile organic HWI emissions that include products of incomplete combustion. Organic emissions were collected and analyzed using a combination of conventional and nonconventional techniques. Emphasis was placed on expanding the capabilities of existing methodologies, such as gas chromatography/mass spectroscopy, to identify and quantify nontarget analytes. Analytes identified included: alkylated, chlorinated, brominated, and mixed bromochloro aromatics, alkanes, alkenes, and alkynes; chlorinated, brominated, mixed bromochloro, alkylated, oxygenated polyaromatic hydrocarbons; and chlorinated, brominated, mixed bromochloro dibenzodioxins and furans. Of the volatile and semivolatile organic species found, less than half have been identified. Less than a quarter of those found were actual test analytes.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Wastes Incinerators Organic Compounds Kilns Analyzing	Pollution Control Stationary Sources Hazardous Waste Products of Incomplete Combustion (PICs)	13B 14G 07C 13A 14B
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS <i>(This Report)</i> Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS <i>(This page)</i> Unclassified	22. PRICE