

Project Summary

Total Mass Emissions from a Hazardous Waste Incinerator

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Past studies of hazardous waste incinerators by the Hazardous Waste Engineering Research Laboratory have primarily examined the performance of combustion systems relative to the destruction and removal efficiency (DRE) for Resource Conservation and Recovery Act (RCRA) Appendix VIII compounds in the waste feed. These earlier studies demonstrated that in general most facilities performed quite well relative to the DRE. However, subsequent review by the Environmental Protection Agency's (EPA) Science Advisory Board raised questions about additional Appendix VIII or non-Appendix VIII constituents that were not identified in the earlier tests and might be emitted from hazardous waste combustion. The full report presents results of a characterization of incinerator effluents to the extent that the emitted compounds can be identified and quantified. Measurements were made of both Appendix VIII and non-Appendix VIII compounds in all effluents (stack, ash, water, etc.) from a full-scale incinerator. A broad array of sampling and analysis techniques were used.

Sampling methods included Modified Method 5, volatile organic sampling train (VOST), and specific techniques for compounds such as formaldehyde. Analysis techniques included gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Continuous measurements were also made for a variety of compounds including total hydrocarbons by flame ionization detection (FID).

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, 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).

Background

The Resource Conservation and Recovery Act (RCRA) was enacted in 1976 and amended in 1984 by Hazardous and Solid Waste Amendments (HSWA) to handle the present day problems of toxic and hazardous waste disposal. Commensurate with these statutes, the U.S.

Environmental Protection Agency (EPA) regards incineration as one of the principal technology candidates for the ultimate safe disposal of wastes and promulgated the following standards in the *Federal Register*, Volume 46, No. 15, on January 23, 1981.

1. An incinerator must achieve a destruction and removal efficiency (DRE) of 99.99% for each principal organic hazardous constituent (POHC) designated for each waste feed.
2. An incinerator burning hazardous waste must not emit more than 1.8 kg/hr of hydrogen chloride (HCl) or must remove 99% of the hydrogen chloride from the exhaust gas.
3. An incinerator burning hazardous waste must not emit particulate matter exceeding 180 milligrams per dry standard cubic meter (mg/dscm).

Commensurate with the regulation of hazardous waste incinerators, the EPA's Hazardous Waste Engineering Research Laboratory (HWERL) has the responsibility to provide information on the ability of these combustion systems to dispose of hazardous wastes in a manner that provides adequate protection of the public health and welfare. Past HWERL studies in this area have primarily examined the performance of combustion systems relative to the destruction removal efficiency (DRE) for RCRA Appendix VIII compounds in the waste feed. These earlier studies demonstrated that in general most facilities performed quite well when determining DRE of a specific compound.

However a detailed review of these studies raised the question of overall performance of hazardous waste incinerators, and the quantitation of the emission products of incomplete combustion (PICs). A contributing factor to questionable incinerator performance was the issue of operating conditions and the effect of an occasional upset on the production of PICs.

To address these issues, EPA initiated a project to qualitatively and quantitatively study the total mass emissions (TME) generated by testing a hazardous waste

incinerator functioning under both steady state and transient combustion conditions.

Approach

The first step in the project was to find a hazardous waste incinerator that was both operational and willing to participate in the test. Table 1 summarizes the selection criteria applied to the incinerators identified for evaluation. The unit that was selected for testing was Dow Chemical's, located in Plaquemine, Louisiana. Figure 1 shows a schematic diagram of the incinerator which includes a rotary kiln combustion chamber, secondary combustion chamber, vertical quench section, three-stage ionizing wet scrubber and emission to the atmosphere.

Three types of solid waste feeds were used during all of the runs; a substituted cellulose, polyethylene wax, and chlorinated pyridine tars. Each of the solid wastes was individually contained in plastic drums and sealed with a metal rim ring. One drum of solid waste was fed every 4 minutes with the drums of each type of waste being alternately fed through a ram feeder into the kiln.

Liquid waste feeds were of either organic or aqueous composition. Prior to testing, a uniform supply of the liquid organic waste, sufficient for about 100 hours of incinerator operation, was accumulated in a 15,000-gal. capacity tank. The liquid organic waste feed was spiked so as to achieve a mixture of about 10% carbon tetrachloride, with the remainder being primarily Isopar (C5-C8 saturated through the stack).

The operating conditions in the incinerator are summarized in Table 2 and indicate fairly consistent combustion conditions throughout the test. hydrocarbons).

A summary of the sampling and analysis parameters and methods employed during the test is shown in Table 3. The sampling methods, field measurement methods and analytical methods are presented in greater detail in Appendix A of the final report.

Table 1. Summary of Site Selection Criteria

	<i>Required</i>	<i>Desirable</i>
<i>Incinerator type</i>	Rotary kiln (semicontinuous feed) Secondary combustion chamber or afterburner Organic liquid feed	Aqueous liquid feed Sludge feed Dry ash collection system
<i>Air pollution control system</i>	Wet scrubber for HCl Particulate control device	Venturi scrubber Once through water
<i>Feed characteristics</i>	Amenable to spiking Volatile organic solids (e.g., paint wastes) Large storage capacity	Variety of chlorinated organics
<i>Operating and control flexibility</i>	Wide range of operating conditions Willingness to vary conditions	
<i>Sampling location</i>	Access to all effluent streams Adequate stack sampling ports and platform Space for mobile van and trailer	

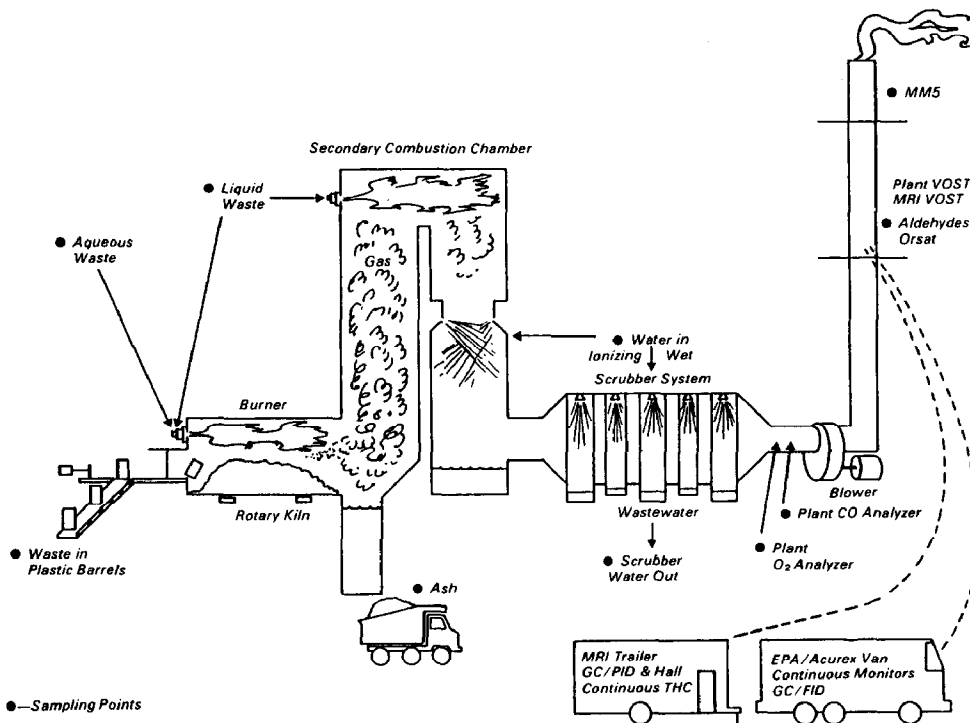


Figure 1. Process schematic.

Table 2. Summary of Key Process Parameters

Parameter	Average Value, Run No.					
	1	2	3	4	5	6
Total methane mass flow, lb/hr	372	414	423	552	615	532 ^a
Kiln temperature, °F (°C)	1550 (843)	1386 (752)	1438 (781)	1440 (782)	1364 (740)	1467 (797)
SCC ^b temperature, °F (°C)	1857 (1014)	1738 (948)	1708 (931)	1776 (969)	1782 (972)	1852 (1011)
Stack gas temperature, °F (°C)	163 (73)	160 (71)	154 (68)	160 (71)	165 (74)	167 (75) ^a
Stack gas flow rate, acfm x 10 ⁻³	21.8	20.1	21.2	23.4	24.9	23.4
Oxygen (% O ₂) in stack	10.1	11.1	11.5	11.2	10.6	9.9
Kiln vacuum, in. H ₂ O	-0.34	-0.33	-0.30	-0.35	-0.35	-0.35 ^a
SCC vacuum, in. H ₂ O	-0.05	-0.05	-0.05	-0.04	-0.04	-0.04
Atomization steam pressure (kiln), psig	25.0	25.0	25.5	25.0	25.0	25.0
Atomization steam pressure (SCC), psig	50.0	50.0	50.0	50.0	50.0	50.0

^a Dow Incinerator Control Center data logger was inoperable for the first 110 min of the run. Average values based on last 65 min of the run.

^b SCC = Secondary Combustion Chamber.

Table 3. Summary of Sampling and Analysis Parameters and Methods

Sample	Sampling frequency for each run	Sampling method	Sample size	Analytical parameters	Preparation method ^a	Analytical method ^a
Liquid organic waste	One grab sample every 15 min composited into one sample for each run	Tap (S004)	1 L	SV POHCs ^b Chlorides Heating value Ash Viscosity	Sample dilution NA NA NA NA	GC/MS ^c Organic halide (D4327-84 or D808-81) Calorimeter (D240-73) Ignition (D482-80) Viscometer (D-88-81)
	Once at end of run	VOA vial ^d filled from composite	40 mL	V POHC ^e	Purge and trap	GC/MS
Aqueous waste	One grab sample every 15 min composited into one sample for each run	Tap (S004)	4 L	SV POHC ^b Chlorides Heating value Ash	Solvent extraction NA NA NA	GC/MS Organic halide (D4327-84 or D808-81) Calorimeter (D240-73) Ignition (D482-80)
	One VOA vial every 15 min	Tap (S004)	40 mL per vial	V POHC	Purge and trap	GC/MS
Solid waste	One grab sample per solid charge, composited at end of test	Scoop (S007)	≈ 250 g per grab	V POHC SV POHC Chlorides Heating value Ash	Tetraglyme dispersion/purge and trap Solvent extraction NA NA NA	GC/MS GC/MS Organic halide (D4327-84) Calorimeter (D2015-77) Ignition (D482-80)
	One grab sample every 30 min composited into one sample each run	Dipper (S002)	4 L	SV POHC	Solvent extraction	GC/MS
Scrubber water inlet	One grab sample every 30 min composited into one sample each run	Dipper (S002)	4 L	SV POHC	Solvent extraction	GC/MS
	One VOA vial every 30 min	VOA vial filled from grab sample	40 mL/VOA	V POHC	Purge and trap	GC/MS
Scrubber water outlet	One grab sample every 30 min composited into one sample each run	Dipper (S002)	4 L	SV POHC	Solvent extraction	GC/MS
	One VOA vial every 30 min	VOA vial filled from grab sample	40 mL/VOA	V POHC	Purge and trap	GC/MS

Table 3. (Continued)

Sample	Sampling frequency for each run	Sampling method	Sample size	Analytical parameters	Preparation method ^a	Analytical method ^a
Ash	One grab sample per run	Scoop (S007)	500 g	SV POHC	Solvent extraction	GC/MS
Stack gas	2-hr composite per run	MM5 ^f	~ 60-100 ft ^{3g}	Particulate HCl	Desiccation NA	Gravimetric (EPA RM5) Colorimetric (EPA 325.2)
				Moisture Temperature Velocity	NA NA NA	Gravimetric Thermocouple Pitot tube
				SV POHC Moisture Temperature Velocity	Solvent extraction NA NA NA	GC/MS Gravimetric Thermocouple Pitot tube
	Three trap pairs at 40 min per pair per run	VOST (S012) ^h	20 L per trap pair	Method 624 compounds	Purge and trap	GC/MS
	One composite sample per run	EPA Reference Method 3	~ 20 L	Oxygen, carbon dioxide	NA	Orsat
	One composite sample per run 1 min averages	Midget impinger Continuous	~ 100 L NA	Aldehydes CO, CO ₂	NA NA	HPLC NDIR
	1 min averages	Continuous	NA	O ₂	NA	Paramagnetic
	1 min averages	Continuous	NA	NO _x	NA	Chemiluminescent
	1 min averages	Continuous	NA	THC	NA	FID
	~ once/5 min	Gas sampling valve	NA	THC	NA	GC/FID
	~ once/30 min ⁱ	Gas sampling valve	NA	C ₁ to C ₃ hydrocarbons	NA	GC/FID
	~ once/30 min ⁱ	Gas sampling valve	NA	Aromatics	NA	GC/PID
	~ once/30 min ⁱ	Gas sampling valve or syringe	NA	Halogenated organics	NA	GC/Hall or PID

Note: Sampling method numbers (e.g., S004) refer to methods published in "Sampling and Analysis Methods for Hazardous Waste Combustion," December 1983; analytical methods beginning with prefix D and E refer to ASTM methods.

^a Sample preparation and analytical methods are described in detail in Appendix A referencing the A. D. Little, EPA 600, and SW-846 methods.

^b Semivolatile principal organic hazardous constituents.

^c Gas chromatography/mass spectroscopy.

^d Volatile organic analysis vial.

^e Volatile principal organic hazardous constituents.

^f MM5 = Modified Method 5.

^g Exact volume of gas sampled will be dependent on isokinetic sampling rate.

^h VOST = Volatile organic sampling train.

ⁱ Maximum rate permitted by analysis time.

Discussion of Results

The combustion of organic materials in an incinerator and the resultant formation of products of incomplete combustion (PICs) are always in a dynamic state. Regardless of the degree of control over the incinerator operating parameters, the products resulting from the combustion may not be identical from one time period to another; concentrations of specific compounds will vary with time. Table 4 shows the identification and concentration of the volatile organic compounds identi-

fied in the tests that were conducted under steady state conditions. In general, the volatile organic constituents found in the incinerator stack gas during the steady state conditions were aromatic and aliphatic hydrocarbons and halogenated hydrocarbons, primarily chlorinated aliphatic hydrocarbons. Acetonitrile and dichloroacetonitrile were the only volatile nitrogen-containing compounds identified. The presence of the hydrocarbons and the chlorinated hydrocarbons as the principal organic emissions was not surprising considering the composition

Table 4. Stack Concentrations of Volatile Constituents During Steady State Conditions

Constituent	Concentration (ppb)											
	Run 1			Run 2			Run 3			Avg. 1-3		
	MRI (VOST)	MRI (GC)	Dow (VOST)	MRI (VOST)	MRI (GC)	Dow (VOST)	MRI (VOST)	MRI (GC)	Dow (VOST)	MRI (VOST)	MRI (GC)	Dow (VOST)
Priority Pollutants												
Methyl chloride	4.4	226.0	29.6	NA	309.9	3.7	1.7	102.8	0.0	3.1	212.9	11.1
Methyl bromide	0.0	0.0	0.0	NA	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0
Vinyl chloride	0.9	1.9	2.1	NA	2.8	0.0	0.6	6.6	0.0	0.8	3.8	0.7
Dichloromethane	2.4	4.7	0.9	NA	1.1	0.7	1.0	1.2	0.0	1.7	2.3	0.8
Trichlorofluoromethane	4.1		0.0	NA		0.0	0.1		0.0	2.1	0.0	0.0
1,1-Dichloromethylene	1.0	0.0	0.0	NA	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0
Chloroform	62.2	15.4	16.3	NA	37.5	30.7	64.2	36.1	26.2	63.2	29.6	24.4
1,2-Dichloroethane	2.6		1.2	NA		1.3	0.2		0.2	1.4	0.0	0.9
1,1,1-Trichloroethane	0.2	0.0	0.2	NA	0.4	1.5	1.2	0.0	0.8	0.7	0.1	0.8
Carbon tetrachloride	3.8	0.3	2.0	NA	0.6	0.8	1.3	1.0	0.6	2.5	0.6	1.1
Dichlorobromomethane	14.0	4.4	4.4	NA	7.8	5.6	13.4	6.0	5.7	13.7	6.1	5.2
1,2-Dichloropropane	1.2	0.0	0.0	NA	0.0	0.0	0.0	0.1	0.0	0.6	0.0	0.0
Trichloroethylene	0.1	0.0	NA	NA	2.3	NA	0.1	0.0	NA	0.1	0.8	NA
Benzene	4.6	3.0	8.0	NA	6.4	11.4	1.7	3.0	3.4	3.1	4.1	7.6
Chlorodibromomethane	2.3		1.3	NA		0.9	1.7		0.8	2.0	0.0	1.0
2-Chloromethyl vinyl ether	1.8		0.0	NA		0.0	0.2		0.0	1.0	0.0	0.0
Bromoform	0.1		1.2	NA		0.1	0.0		0.0	0.1	0.0	0.4
1,1,2,2-Tetrachloroethylene	1.2		0.4	NA		0.3	0.4		0.3	0.8	0.0	0.3
Toluene	7.9	0.0	7.3	NA	0.0	2.4	0.9	0.0	4.7	4.4	0.0	4.8
Chlorobenzene	0.1	0.0	0.1	NA	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1
Ethylbenzene	1.0	0.0	0.7	NA	0.0	0.2	0.1	0.0	0.1	0.6	0.0	0.3
Total	116.0	255.7	NA	NA	368.8	NA	89.1	156.7	NA	102.6	260.4	NA
Nonpriority Pollutants												
C ₂ H ₄	0.0			NA			0.0			0.0		
Dimethyl ether	18.8			NA			0.3			9.6		
Dichlorodifluoromethane	0.2			NA			0.2			0.2		
Acetonitrile	0.0			NA			0.1			0.1		
C ₆ H ₁₀	0.0			NA			0.2			0.1		
C ₆ H ₆ /Acetone	4.1	0.0		NA	3.4		3.4	9.4		3.7		
Chloropropene	0.0			NA			0.2			0.1		
Bromochloromethane	0.0			NA			0.0			0.0		
Tetrahydrofuran/C ₂ H ₁₂	0.4			NA			0.1			0.2		
C ₆ H ₆ /C ₈ H ₁₀	0.0			NA			0.2			0.1		
C ₂ H ₁₂ /C ₆ H ₁₂	0.8			NA			0.2			0.5		
C ₆ H ₁₂ /C ₆ H ₁₄	1.8			NA			0.1			0.9		
C ₂ H ₁₂ O ₂	0.0			NA			0.0			0.0		
C ₆ H ₁₂	0.2			NA			0.0			0.1		

Table 4. (Continued)

Constituent	Concentration (ppb)											
	Run 4			Run 5			Run 6			Avg. 4-6		
	MRI (VOST)	MRI (GC)	Dow (VOST)	MRI (VOST)	MRI (GC)	Dow (VOST)	MRI (VOST)	MRI (GC)	Dow (VOST)	MRI (VOST)	MRI (GC)	Dow (VOST)
Nonpriority Pollutants (continued)												
Dichloroacetonitrile	0.6			0.3			0.0			0.3		
C ₇ H ₁₄ /C ₈ H ₁₂	0.0			0.2			0.0			0.1		
C ₇ H ₁₄ /C ₇ H ₁₅	0.0			0.0			0.1			0.0		
C ₆ H ₁₂	0.0			0.1			0.5			0.2		
C ₇ H ₁₄ /C ₇ H ₁₆	1.4			0.2			0.2			0.6		
Hydrocarbon	0.1			0.1			0.0			0.1		
C ₆ H ₁₂	0.4			0.4			0.3			0.3		
Isooctane	44.0			3.7			0.0			15.9		
Hydrocarbon	1.1			0.0			0.0			0.4		
Total	58.9	0.0		14.2	11.5		16.8	2.9		30.0	4.8	

of the liquid organic waste. In terms of specific volatile organic constituents, the principal constituent found by MRI was methane at an average level of approximately 1,400 ppb. Two other compounds present in major quantities were chloroform at an average concentration of 213 ppb (based on field GC data) and chloroform with an average level of 63

ppb (based on VOST data). The data obtained by Dow showed chloroform to be a major volatile organic constituent of the stack gas at an average level of 24 ppb.

Data similar to that presented in Table 4 is also shown in the final report for the semivolatile organic compounds derived under steady state and transient operating conditions, plus the volatile organic

Table 5. Total Hydrocarbon Response and Total Mass (Organic) Emissions

Run No.	THC	Methane	Ethylene	Organics			Fraction of total (%)
				Other volatiles	Semi-volatiles	Total organics	
1	7.6	1.7	ND	0.6	2.5	4.7	62
2	6.8	1.2	ND	0.8	1.6	3.6	53
3	6.2	1.3	ND	0.2	1.9	3.3	54
4	8.8	4.3	1.1	1.1	1.6	8.0	91
5	145	93	1.3	0.5	2.0	96.8	67
6	106	51	0.6	0.7	1.5	53.7	50

Note: All values are ppm methane (FID) equivalent, dry gas basis.
 ND = not detected.

Table 6. Particulate and HCl Emissions

Run	Particulate (mg/m ³)	HCl emissions ^a (kg/hr)	HCl efficiency ^a
1	15.9	0.022	0.99993
2	14.2	0.016	0.99989
3	9.0	0.016	0.99990
4	11.1	0.028	0.99978
5	23.6	0.030	0.99985
6	35.5	0.038	0.99984

^a Average of two values.

compounds produced under transient operating conditions. The differences between the two sets of operating conditions produced few if any changes in the resulting combustion products produced or their concentrations. This was true for both volatile and semivolatile compounds.

The total mass (organic) emissions from the stack are summarized in the report and the various measurements of organics have been converted into a common basis of dry methane equivalent using FID. Table 5 sums up all the contributing factors and compares it with the values collected on the total Hydrocarbon Analyzer. The data show that for the steady state tests the closure on the hydrocarbon material balance was 56.3 ± 5% while on the transient conditions it was 69.3 ± 21%.

Table 6 presents the particulate and HCl emissions and the HCl removal efficiency for each run. The range of particulate emissions was 9.0 to 35

mg/m³. The range of HCl emissions was 0.016 to 0.038 kg/hr. HCl removal efficiencies averaged 99.98%. These rates are all very low compared to the regulatory limits and to typical results from other hazardous waste incinerator tests. No levels of cyanide ion were found in the analysis of any of the runs.

Conclusions

1. The transient upsets during Runs 4 to 6 did not cause significant increases in concentrations of semi-volatile compounds or most volatile compounds. The three volatile compounds that did increase were methane, methylene chloride, and benzene. Methane increased the most dramatically.
2. The percent of the total hydrocarbon (THC) emissions that were detected as specific compounds ranged from 50 to 67% for five of the six test runs; 91% was detected in one run.
3. Methane accounted for the largest fraction of the THC.
4. Oxygenated aliphatic compounds were the largest class of compounds among the semivolatiles, both in total mass and number of compounds.
5. Particulate and HCl emissions were low and did not change between the steady state and transient test runs.

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Robert C. Thurnau is the EPA Project Officer (see below).

The complete report, entitled "Total Mass Emissions from a Hazardous Waste Incinerator," (Order No. PB 87-228 508/AS; Cost: \$24.95, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

The EPA Officer can be contacted at:

*Hazardous Waste Engineering Research Laboratory
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