

## EFFECTS OF VISCOSITY AND TEMPERATURE ON APPLIANCE PERFORMANCE IN RESIDENTIAL OIL COMBUSTION

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### INTRODUCTION

A research program on combustion performance evaluation of Canadian middle distillates was carried out at the Combustion and Carbonization Research Laboratory. The program was initiated in response to the needs of the oil industry as well as the standard writing bodies for better fuel quality specifications. The combined effects of industry's effort to maximize the product yield from a crude barrel and the increasing demand on light distillates created the increased use of lower quality products for heating. In Canada, where an abundance of oil sands bitumen and heavy fuels are available, the use of distillates processed from such unconventional sources presents a practical solution to increasing energy demand and declining conventional resources. The effects of these lower quality products on appliance performance must be examined and technologies developed to ensure safe and efficient utilization of the fuels in existing appliances. The standard writing bodies require such information as well to update the existing specifications as required as the quality of the products and the equipment requirements change from time to time. Data from this program are being used to establish correlations fuel properties and combustion characteristics of various Canadian distillate fuels. This paper describes information that demonstrate the effects of fuel viscosity on particulate emissions generated during the transient operation of a residential oil burner.

### EXPERIMENTAL SECTION

#### Fuel variety

Fuel oils were contributed by various Canadian oil companies. The origin of crudes and process vary depending on the company and location. Special blends were prepared in the laboratory to include fuels with a wide range of viscosities. A particular effort was made to keep other variables at a constant value especially aromaticity. All blends contained fuels of different origin and do not necessarily represent the same fuel matrix.

## Fuel analysis

Chemical and physical properties of the fuels were determined using standard ASTM techniques. Aromaticities of the fuel were determined by the proton nuclear magnetic resonance ( $^1\text{H NMR}$ ) method. The  $^1\text{H NMR}$  spectra were obtained on a Varian model EM-390 spectrometer operated at 90 MHz. The samples were prepared by mixing the oil with chloroform- $d_1$  in a 50/50 volume ratio and a drop of  $\text{Me}_4\text{Si}$  was added as a reference. Aromaticities of the fuels were calculated from hydrogen intensities using the method of Muhl et.al (1).

## Combustion experiments

Short term combustion experiments were carried out using the procedure developed at the Combustion and Carbonization Research Laboratory (2). The experimental procedure simulated the actual usage pattern of residential oil heating in Canadian homes. A typical experimental run started with an initial burner startup (cold start) which lasted one hour (steady state), immediately followed by five consecutive 10 minutes on /10 minutes off, cyclic operations. Flue gas emissions and temperatures at specified locations of the test rig were continuously monitored over the entire run. The following experimental equipment and operating conditions were used.

Fuel temperature:	15°C
Nozzle oil temperature:	set as required
Fuel pump pressure:	100 psi
Oil nozzle:	0.75 US gph with 80 spray angle
Combustion air:	Set to obtain a No 2 smoke at steady state
Cold air return temperature:	15 ± 1 °C
Burner and retention head:	Beckett burner and Aero AFC2
Furnace:	Forced air type. Brock model LO-1M, 74,000-120,000 Btu/h, with concentric tube type heat exchanger.
Furnace draft:	1 mm (0.04 in) of water column

The fuel temperature was kept constant at 15 °C in a fuel conditioner that was cooled by a circulating coolant. A thermocouple was inserted into the centre of the nozzle adapter at a closest possible position to the nozzle tip. The oil temperature at discharge was determined using this thermocouple. That temperature was controlled by cooling the combustion chamber and burner with a blast of chilled air. The nozzle temperature was held between 17 and 19°C for all fuels. Each fuel was tested for a minimum of three times and average values were reported.

## Measurement of particulate emissions

Particulates, mainly soot, in the flue gas stream were determined using a commercial smoke opacity meter (Celesco model 107). The meter uses a light attenuation principle and is normally used for determining smoke in diesel engine exhaust gases. The instrument was installed vertically, in line with the furnace flue pipe. The opacity % reading from the meter was continuously recorded on a strip chart recorder to capture the entire soot production profile at each transient operation. Area under the peak of each operation was reported as area in square inch per transient cycle.

## RESULTS AND DISCUSSION

### Fuel variety

Several Canadian oil companies contributed fuels of different origins to this quality evaluation program. These included products from conventional crudes, both Canadian and imported, and synthetic crudes processed from oil sands bitumen and heavy oils. Several special blends had to be prepared in house to obtain fuels with specific qualities. Results have shown that fuel viscosity and aromatics show the strongest influence on oil burner performance (3). This study was dedicated to examine the fuel viscosity effects on combustion performance and required fuels with varying viscosities but with similar aromatic contents. The current CGSB requirement for No. 2 heating fuels is a minimum of 1.4 and a maximum of 3.6 centi stoke or millimetre/second at 40 °C. Fuels with a range of viscosities 1.8 to 5.1 at 38°C (100°F) were included in this study.

### Chemical and physical properties of the fuels

Each fuel was analyzed for aniline point, aromatics, aromaticity, calorific value, cloud point, density, distillation range, flash point, pour point, rambottom carbon, viscosity, water and residue, and ultimate analysis using ASTM (American Society for Testing and Materials) and CGSB (Canadian General Standards Board) standard methods. The fluorescent indicator adsorption method (FIA) presents operational problems for fuels with final boiling points higher than 315 °C and colored fuels in determining the fuel aromatic content. The <sup>1</sup>HNMR technique provides the percent ratio of the aromatic carbons to the total number of carbons present in an average molecule that represent a fuel. Table 1 reports some of the analysis data of 15 fuels included in the experimental program.

## Particulate emissions from combustion

Performance of fuels are rated in terms of several combustion characteristics including burner ignition behaviour, flame characteristics, potential burner failure, appliance efficiency, heat exchanger corrosion and gaseous and particulate emissions. Poor fuel quality is associated with poor appliance performance and excessive emissions of incomplete combustion products such as particulates, carbon monoxides, and hydrocarbons. Data indicate that carbon monoxide and hydrocarbon emissions exhibit the same trend as particulate emissions. The discussion in this paper is focused on the performance rating as reflected by the generation of particulates.

The commercial smokemeter used was found to be sensitive to particulates equivalent to or higher than smoke number 5, when tested with a commercial Bacharach smoke tester (industry's standard smoke test equipment). The meter has to be especially calibrated for this application.

Results indicate that particulates generated during the cold temperature burner start (cold start) are significantly higher than those from on/off cyclic operations (warm start). This difference is mainly due to the temperature difference at which combustion of the oil takes place. The cold start temperature was set between 17°C and 19 °C, based on the actual readings found in homes located in central Canada (17 - 24 °C). The nozzle oil temperature increased to between 45 °C and 70 °C during cyclic operations. A significant observation was made in that lower quality fuels generated excessive soot at cold start but produced near normal levels (compared to within-spec heating fuel) at warm start.

Figure 1 shows the smoke opacity profile recorded from a commercial within-spec heating fuel. The first peak represents the cold start and the peak at the end of one hour run represents the burner shutdown. It can be compared to the Figure 2 profile from combustion of a fuel with high aromatics and a viscosity higher than specifications. The duration of time taken for dissipation of soot from the furnace exit also serves as a good indicator of performance. Table 2 represents data from 15 test fuels. As indicated by data in table 1, aromaticity of fuels is reasonably similar with the exception of Fuels 14 and 15. Both have high fuel aromatics but Fuel 14 has higher viscosity (beyond maximum 3.6 c St at 40°C) than Fuel 15 (within-spec). Data in table 2 indicate an increase in both area under the smoke opacity peak and smoke dissipation time with increased fuel viscosity. Figure 3 is the graphical representation. The high value for Fuel 14 resulted from high fuel viscosity as well as high fuel aromatics. However, Fuel 15 exhibits only a higher than normal value (than those from Fuels 3,4,5), despite the fact that it has

a similarly high aromatics as in Fuel 14. It appears that higher than spec viscosity can be tolerated provided that fuel aromatics are reasonably low. There is no specific specification for fuel aromatics in place but most of the commercial furnace fuels have below 40 volume percent (about 25% aromaticity). A similar example can be demonstrated using data from Fuels 10 and 11. The fuel density also plays a partial role. Although there is a general positive trend between viscosity and density, the correlation is not always true. If higher than specifications viscosities are to be used, it is essential that both aromatics and density be kept at low levels.

Figure 4 represents the effect of oil temperature at the nozzle on particulate emissions of Fuel 15. It is similar to the viscosity - emission relation, since the oil temperature directly controls the viscosity. It can be compared to Figure 5 showing the viscosity - emission relation of a commercial furnace fuel (Fuel 3). The viscosity of Fuel 3 was determined at different temperatures and a temperature-viscosity calibration line was developed. Particulate emissions of Fuel 3 determined at different cold start combustion temperatures are shown in Figure 5. This fuel was tested to provide information on the cold start behaviour of commercial furnace fuels at cold regions of Canada. There are certain areas of area where the basement temperatures are low enough to have an oil combustion temperature of 5°C. In such cases, the viscosity of a commercial fuel suitable for an average climate could increase to its critical value at which poor combustion will result (3). Data suggests that a fuel with viscosity about 2.5 c St at 38°C could be used in locations where the coldest basement temperature is about 10°C, without any negative effects.

It can be concluded from this study that increasing fuel viscosity has a strong positive influence on incomplete combustion products. The combustion performance of lower grade fuels can be improved and manipulated to advantage if other dominating fuel properties can be controlled.

#### ACKNOWLEDGEMENT

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2. Lee, S.W. and Hayden, A.C.S. " An experimental program for evaluation of fuel quality effects on oil burner performance". ASHRAE Transactions, 1986, Volume 92, Part 1. pp 667-682.

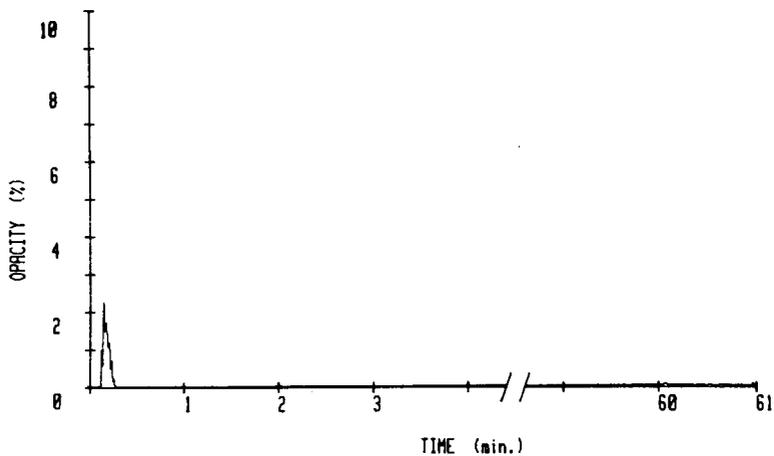


Fig. 1. Opacity profiles of cold start and shut down from a steady state furnace fuel

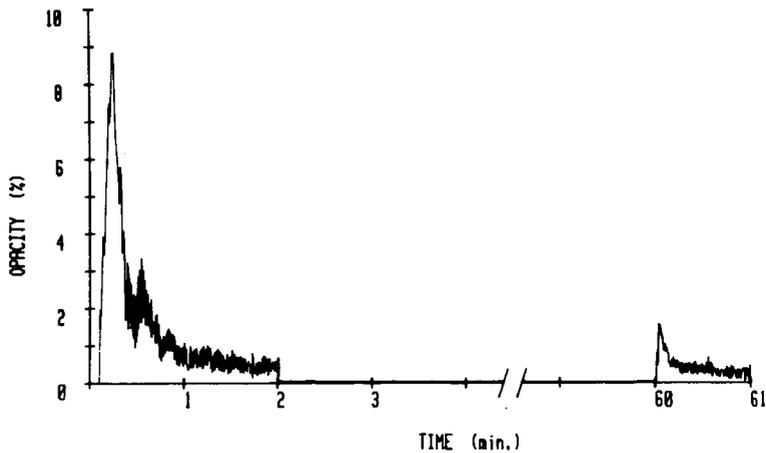


Fig. 2. Opacity profiles of cold start and shutdown from a steady state firing a high viscosity, high aromatic fuel.

3. Eng, J. and Himmelman, W.A. Engineering Journal. Feb. 1967. pp 10.

Table 1. Fuel variety and properties

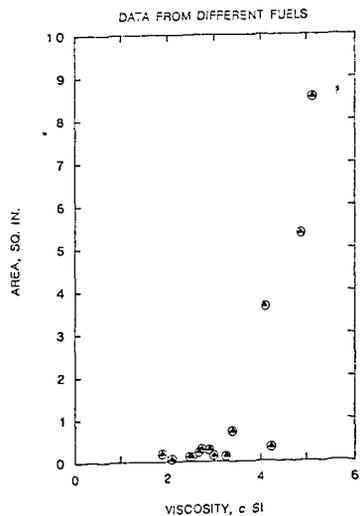
Fuel ID & type	Viscosity, c St @ 38°C	H/C ratio	Aromaticity, % by <sup>1</sup> HNMR	Density, kg/L @15°C
1. special blend	1.88	1.806	15	0.840
2. winter diesel	2.09	1.802	16	0.845
3. furnace fuel	2.48	1.782	16	0.844
4. furnace fuel	2.52	1.748	20	0.855
5. furnace fuel	2.68	1.732	21	0.864
6. special diesel	2.90	1.663	24	0.879
7. special blend	3.00	1.712	21	0.864
8. light gas oil	3.26	1.798	21	0.860
9. special blend	3.39	1.744	23	0.864
10. special blend	4.09	1.746	18	0.872
11. special blend	4.24	1.766	11	0.881
12. special blend	4.87	1.768	11	0.883
13. special blend	5.12	1.740	18	0.884
14. light cycle oil	3.60	1.378	40	0.926
15. special blend	2.74	1.406	42	0.923

Table 2. Particulate emissions from fuels with different viscosities

Fuel	Viscosity, c St @ 38°C	Area <sup>1</sup> sq.in.	Time <sup>2</sup> sec
1.	1.88	0.21	15
2.	2.09	0.08	12
3.	2.48	0.15	22
4.	2.52	0.13	24
5.	2.68	0.26	29
6.	2.90	0.31	44
7.	3.00	0.16	12
8.	3.26	0.16	42
9.	3.39	0.73	55
10.	4.09	3.65	180
11.	4.24	0.35	120
12.	4.87	5.36	325
13.	5.12	8.56	465
14.	3.60	52.30	750
15.	2.74	0.31	44

1. area under the opacity peak  
2. Time for smoke to dissipate

Fig. 3. The effects of visco on particulate emissions



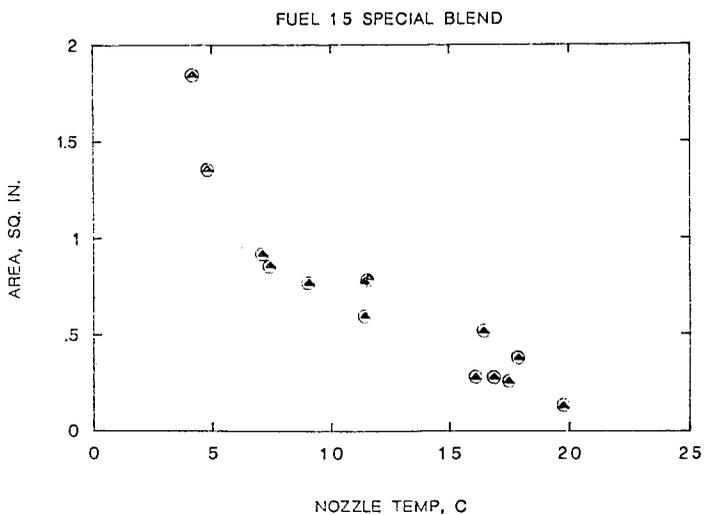


Figure 4. Effect of temperature on particulate emissions. Fuel 15.

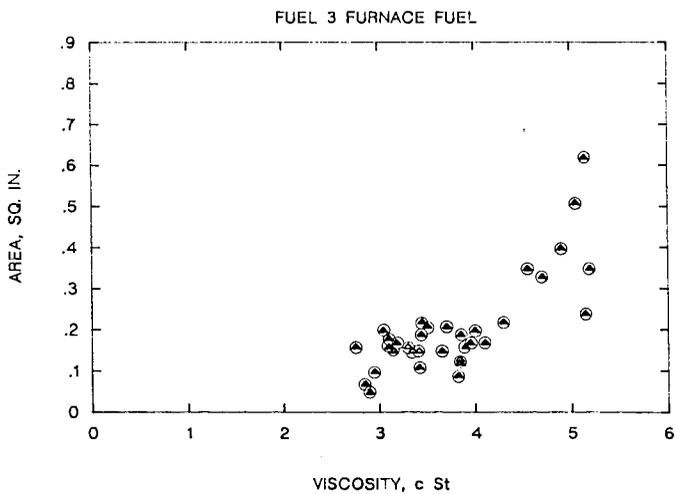


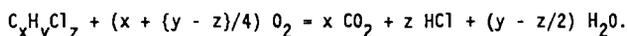
Figure 5. Effect of viscosity on particulate emissions. Fuel 3.

## HIGH TEMPERATURE PYROLYSIS OF C<sub>2</sub>-CHLOROCARBONS

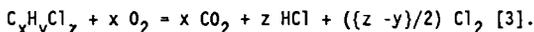
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Environmental concern over the safe disposal of toxic organic wastes has led to the emergence of the field of incineration as one of the more controversial and exciting applications of the combustion sciences [1]. A significant fraction of hazardous organic wastes are chlorinated hydrocarbons (CHCs) [2]. The presence of chlorine brings a number of complications to the understanding of the incineration process beyond that usually addressed in combustion research.

For a CHC designated by C<sub>x</sub>H<sub>y</sub>Cl<sub>z</sub>, the overall equilibrium combustion stoichiometry can be defined for y > z:



For y < z, the formation of molecular chlorine (Cl<sub>2</sub>) must be considered:



Numerous full-scale tests and thermodynamic calculations have clearly indicated that the nature and quantity of organic compound emissions from toxic waste incinerators are not thermodynamically controlled, actual emissions being greater than 10<sup>6</sup> times that predicted from equilibrium [4]. Due to their toxicity, there is particular concern over the emissions of chlorinated products of incomplete combustion (PICs).

Simple conceptual and more complex computer models suggest that kinetic factors including temperature, time at temperature, and reaction atmosphere in the post-flame, or thermal zones, of full-scale incinerators control the emission of organic compounds from such systems [5-7]. These models further indicate that hazardous wastes entering the flame zone are completely oxidized and only the small fraction that does not pass through this zone may undergo incomplete reaction. Various excursions may cause a small fraction of the waste to circumvent the flame zone [6,7]. Once in the post-flame zone, high-temperature thermal decomposition kinetics control the rate of waste destruction and the rate of formation and destruction of organic byproducts.

Emissions from full-scale incinerators are generally several orders of magnitude higher than those calculated using rate parameters obtained from laboratory-scale experiments simulating the oxidative reaction conditions in the post-flame zones of such systems [6,8]. This result suggests that oxygen-starved reaction pathways may be responsible for most organic emissions since the rate of destruction of the parent is significantly slowed and the rate of organic byproduct formation is substantially increased [8-10]. Thus, although incinerators operate under oxygen-rich conditions, oxygen-starved pockets may exist in the system due to locally poor mixing conditions. Consequently, laboratory-scale flow reactors appear to be particularly well suited for the evaluation of the fuel-rich thermal decomposition behavior of CHCs.

To build a database of the possible reaction mechanisms involved in the formation of CHC emissions under oxygen-starved reaction conditions, we have initiated a program to evaluate the high-temperature thermal decomposition behavior of different classes of CHCs using fused silica flow reactor thermal instrumentation. Our initial study involved an analysis of the simplest of CHCs, the chlorinated methanes, as pure compounds and as mixtures of varying elemental composition [11-13]. The most important finding was the observation of significant yields ( $\geq 0.1$  mole %) of higher-molecular-weight, thermally stable, unsaturated CHCs, e.g., hexachlorobenzene ( $C_6Cl_6$ ), for H:Cl ratios less than 1.0 under oxygen-starved ( $\phi = 3.0$ ) reaction conditions.

As a consequence, we have begun a study of  $C_2$ -CHCs, with particular interest on the analysis of pentachloroethane ( $C_2HCl_5$ ), hexachloroethane ( $C_2Cl_6$ ), trichloroethylene ( $C_2HCl_3$ ), tetrachloroethylene ( $C_2Cl_4$ ), and dichloroacetylene ( $C_2Cl_2$ ). These saturated and unsaturated  $C_2$ -chlorocarbons have been observed as intermediates in the high-temperature oxygen-starved decomposition of chloroform, carbon tetrachloride, and chloromethane mixtures (H:Cl = 0.2) [11,12]. The formation of these compounds has been hypothesized to be an important step in reaction channels leading to chlorinated aromatics and chlorinated polynuclear aromatic hydrocarbons (PNAHs) [11-13]. These high-molecular-weight organic compounds have been detected in stack gases of full-scale incineration systems. Such emissions are unacceptable because of their potential toxic effects on human health and the environment.

## EXPERIMENTAL

Kinetic studies were conducted using various isothermal fused silica flow reactors equipped with in-line GC and GC/MS analytical systems [14,15]. These closed continuous thermal instrumentation systems permit quantitative data to be obtained expeditiously without errors associated with batch sampling and lack of true quantitative transport. A block diagram of one such system, the System for Thermal Diagnostic Studies (STDS) is shown in Figure 1a; a cross-section view of the thermal reactor is shown in Figure 1b.

The reactor is geometrically configured as a helical tube 500 cm long with an internal diameter of 0.17 cm. The geometry of the reactor produces a laminar gaseous flow which exhibits a nearly square wave thermal pulse with a very narrow, near-Gaussian residence time distribution, thus making this reactor ideally suited for reaction kinetic studies. The thermal reactor consists of a relatively inert, high-temperature fused silica material. However, one of the compromises of the precise time/temperature control of this reactor is the corresponding large surface to volume ratio ( $23.5\text{ cm}^{-1}$ ). Using gas collision theory, we have evaluated the relative importance of heterogeneous surface decomposition as compared to homogeneous thermal decomposition for several hydrocarbons and CHCs for which experimental rate data have been previously estimated. Activation energies for heterogeneous decomposition were estimated by assuming the wall reaction rate represented 100% of the experimental reaction rate at a temperature corresponding to the onset of chemical reaction.

Ratios of rate constants and destruction efficiencies (DE) were calculated at temperatures corresponding to 50%, 90%, and 99% decomposition for 2 hydrocarbons and 6 CHCs. With the exception of benzene ( $C_6H_6$ ) and dichloromethane ( $CH_2Cl_2$ ), the results indicated that heterogeneous decomposition accounted for less than 10% of the measured decomposition at overall decomposition levels of 90 and 99%. These calculations imply that, at low temperatures, wall collisions may initiate

the radical chain processes that likely dominate CHC decomposition. However, at higher temperatures, due to the much larger activation energies for homogeneous (-55.0 to -100 kcal/mole) as compared to heterogeneous (-25.0 to 35.0 kcal/mole) decomposition, gas-phase reactions dominate initiation processes and radical chain processes in general.

Following thermal exposure, the effluent is quenched in a heated (250°C) fused silica transfer conduit which connects the reactor to the thermal trapping/gas chromatographic assembly. Leading to and from this assembly are separate, thermally programmable transfer paths designed to produce nonreactive quantitative transport of organic substances. Migrating effluent species from the reactor are then trapped at -60°C and axially focused at the head of the GC column for subsequent analysis.

In this manuscript, we report the results of two different sets of experiments. Pure  $C_2Cl_4$  thermal decomposition was studied under oxygen-starved conditions. The thermal decomposition behavior of the chlorinated ethanes and chlorinated ethenes was evaluated in multi-component organic mixtures of constant elemental composition ( $C_2H_nCl$ ) under oxygen-starved conditions. The constant elemental composition produces in an essentially invariant radical pool which allows the evaluation of stability of the CHCs under realistic conditions. The experimental approach will be presented in more detail in future publications.

## Results

The thermal stability data for the chlorinated ethane and chlorinated ethene mixture experiments are summarized in Figures 2 and 3 and Table 1. For the chlorinated ethanes, three initiation pathways are plausible: (1) concerted 4-center elimination of HCl, (except for  $C_2Cl_6$ ); (2) carbon-chlorine bond rupture; and (3) carbon-carbon bond rupture. In addition, the reactive radicals formed by the latter two mechanisms can attack the parent compound and abstract available hydrogen atoms, resulting in an apparent decomposition rate as much as 2-3 times greater than the unimolecular initiation rate. In all cases, a major product is expected to be the olefin corresponding to loss of HCl by one of these mechanisms. This is even the case for  $C_2Cl_6$ , with a hypothetical mechanism involving C-Cl  $\beta$ -bond rupture following initial C-Cl bond rupture. Our mixture studies generally result in a faster rate of decomposition compared with pure compound flow reactor and shock tube studies reported in the literature, presumably due to secondary chain reactions [16-20]. Important decomposition rate parameters which include data reported in the literature and thermochemical estimates are given in Table 2. Both theory and experiment suggest that for the homologous series, there is a trend of decreasing stability with increasing chlorination. Carbon-carbon and carbon-chlorine bond rupture become more favorable with increased chlorination due to weakening of these bonds while the rate of HCl elimination is less sensitive. When comparing isomers, (e.g., 1,1,1-trichloroethane vs 1,1,2-trichloroethane), the isomer with more chlorines on a single carbon decomposes more rapidly. This may be influenced by weaker C-Cl and C-C bonds and a greater reaction path degeneracy for HCl elimination.

The chlorinated ethylenes are 200-300°C more stable than the chlorinated ethanes. These compounds increase in stability as chlorine substitution increases (see Table 1 and Figure 3). This suggests a dominant decomposition mechanism involving hydrogen atom abstraction by reactive radicals such as Cl atoms.  $C_2Cl_4$ , which contains no H atoms, is the most stable of the series, and decomposition by the

endothermic ( $\Delta H_{298}^{\circ} = 27.5$  kcal/mole) pathway of Cl abstraction by Cl to form  $\text{Cl}_2$  is not significant at the temperatures of our experiments.

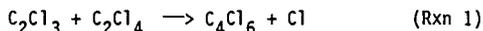
Alternative decomposition pathways for the chloroethenes include HCl elimination and chlorine displacement by hydrogen atoms. Shock tube data from the literature for  $\text{C}_2\text{H}_3\text{Cl}$  suggest that HCl elimination is too slow to account for all of the observed rate of destruction [21]. Cl<sub>2</sub> elimination for tetrachloro-ethylene seems even more unlikely due to its greater endothermicity ( $\Delta H_{298}^{\circ} = 53.5$  kcal/mole). Cl displacement by H has been experimentally demonstrated to be a viable mechanism for pyrolytic decomposition of chlorinated aromatics and is a potential destruction mechanism for chlorinated olefins [10]. However, the trend of increased stability with increasing chlorine content in our mixture studies does not support this pathway as the principal mechanism of destruction of the chloroethenes. The relative importance of H abstraction and Cl displacement mechanisms for these compounds has not yet been established.

These mixture studies have not addressed product formation; however, previous flow reactor studies of chloroform, carbon tetrachloride, and premixed flat-flame studies of trichloroethylene have shown that chlorinated olefins and olefinic radical species may be key intermediates in the formation of higher-molecular-weight chlorinated aromatic species [11-13,23]. As such, it appears important to study the chemistry of these intermediates more thoroughly.

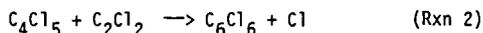
The oxygen-starved thermal decomposition profile of  $\text{C}_2\text{Cl}_4$  is presented in Figure 4. The results indicate that this compound is very stable ( $T_{99}(2) = 980^{\circ}\text{C}$ ) under the conditions studied with measurable quantities (0.007%) persisting at the highest temperatures studied ( $1050^{\circ}\text{C}$ ). Of the two compounds detected as PICs, hexachlorobenzene ( $\text{C}_6\text{Cl}_6$ ) exhibited the greatest yields (~11% at 950 and  $1050^{\circ}\text{C}$ ) and was the most thermally stable. Carbon tetrachloride ( $\text{CCl}_4$ ) was produced in lower yields and was 99.9% destroyed at  $950^{\circ}\text{C}$ . It is probable that  $\text{C}_2\text{Cl}_4$  and  $\text{Cl}_2$  were produced as well in the thermal decomposition experiments; however, mass spectral data acquisition limitations precluded the detection of these products.

Comparison of the results of this pure compound study with previous flow reactor mixture experiments under fuel-rich conditions provides insight into possible  $\text{C}_2\text{Cl}_4$  decomposition pathways. Under hydrogen-rich mixture conditions, the formation of high yields of  $\text{C}_2\text{HCl}_3$  was observed indicating the importance of a mechanism involving H displacement of Cl atoms. Under pure compound conditions, the absence of hydrogen precludes such a mechanism. The types of products shown in Figure 4 suggest that C-Cl bond fission followed by reactions of  $\text{C}_2\text{Cl}_3$  radicals plays important roles in destruction of  $\text{C}_2\text{Cl}_4$ .

We have previously proposed a mechanism for formation of  $\text{C}_6\text{Cl}_6$  from chloroform, which involves Cl displacement from  $\text{C}_2\text{Cl}_4$  (formed as an intermediate from chloroform) via reaction 1 [11-13]:

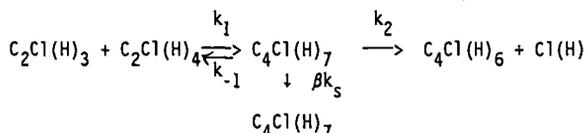


Hexachlorobutadiene ( $\text{C}_6\text{Cl}_6$ ) has been shown in our lab to rapidly decompose via C-Cl bond rupture to form the resonance stabilized pentachlorobutadienyl radical ( $\text{C}_5\text{Cl}_5$ ) which can then react with dichloroacetylene ( $\text{C}_2\text{Cl}_2$ ) to form  $\text{C}_6\text{Cl}_6$  via reaction 2.

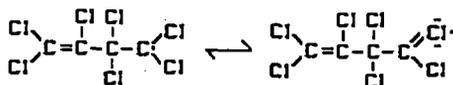


A possible route of formation of  $\text{CCl}_4$  is chlorine addition to  $\text{C}_2\text{Cl}_4$  to form  $\text{C}_2\text{Cl}_5$ , followed by  $\alpha$ -bond fission to form  $\text{CCl}_3$  and  $\text{CCl}_2$ , which can subsequently recombine with Cl atoms to form  $\text{CCl}_4$ .  $\beta$ -bond fission of  $\text{C}_2\text{Cl}_5$  to reform  $\text{C}_2\text{Cl}_4$  is likely a faster reaction, and indeed there is evidence for reformation of  $\text{C}_2\text{Cl}_4$ , as indicated by the knee in the decomposition curve at  $950^\circ\text{C}$  (see Figure 4).

We were intrigued by the possibility that reaction 1 may be faster than its hydrocarbon analogue which has been proposed as a key reaction in soot and PNA formation in fuel-rich hydrocarbon flames. [24] The general scheme for activated complex reactions was used to perform a Quantum RRK (QRRK) calculation [25]:



If  $k_2$  is rate-limiting, the stabilization reaction involving the chlorinated species may be facilitated by the following resonance structure



which is not possible for the hydrocarbon analogue. If  $k_2$  is rate-limiting, the chlorocarbon reaction is facilitated by the displacement of chlorine which has a lower bond energy ( $D_0(\text{C}-\text{Cl}) \sim 85 \text{ kcal/mole}$ ) than hydrogen in the hydrocarbon ( $D_0(\text{C}-\text{H}) = 108 \text{ kcal/mole}$ ).

Rate constants for the hydrocarbon reaction were estimated from the literature [25]. The rates for  $k_1$  and  $k_{-1}$  were assumed to be the same for both hydrocarbon and chlorocarbon analogues.  $A_2$  was estimated via transition state theory for the chlorocarbon reaction and  $E_2$  was estimated by assuming a linear relationship between activation energy and bond dissociation energy. Using the same rate for  $k_1$  and  $k_{-1}$  for the chlorocarbon and hydrocarbon was considered a conservative method of evaluating the effect of chlorine substitution in displacement reactions. One could argue that the chlorocarbon addition step,  $k_1$ , is slower due to the inductive destabilizing effect of chlorine; however, since radicals are not charged species, they do not respond to inductive effects as fully as to electrophilic attack by cations. Thus, we feel that resonance stabilization effects of chlorine may dominate. The results in Figure 5 confirm that the displacement reaction is faster at all temperatures for the chlorocarbon system. This is consistent with our findings in the chloromethanes, where relatively large yields of  $\text{C}_4$  and aromatic products were seen from chloroform ( $\text{CHCl}_3$ ) and  $\text{CCl}_4$ , but not observed at all from chloromethane ( $\text{CH}_3\text{Cl}$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ).

The experimental and theoretical studies presented in this manuscript suggest that chlorinated hydrocarbons may be particularly prone to formation of complex, potentially toxic, reaction byproducts. A systematic, detailed kinetic and mechanistic study of the reactions of these compounds, particularly the  $\text{C}_2$ -olefins and acetylenic compounds is indicated.

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TABLE 1

Temperature for 99% Destruction of Chlorinated Ethanes and Chlorinated Olefins in Mixtures at  $\bar{t}_r = 2.0$  s,  $\phi = 3.0$ , H:Cl = 3.0

Chlorinated Ethanes		Chlorinated Olefins	
Compound	$T_{99}(2)$ (C°)	Compound	$T_{99}(2)$ (C°)
Chloroethane	620	Chloroethene	770
1,1-Dichloroethane	610	1,1-Dichloroethene	860
1,2-Dichloroethane	680	1,2-Dichloroethene	835
1,1,1-Trichloroethane	545	Trichloroethene	865
1,1,2-Trichloroethane	635	Tetrachloroethene	890
1,1,1,2-Tetrachloroethane	560		
1,1,2,2-Tetrachloroethane	690		
Pentachloroethane	640		
Hexachloroethane	580		

Table 2a. Decomposition Rate Parameters—Chloroethanes

Compound	$\Delta H^{\circ}300$ (kcal/mole) [b]						log k 300					
	C-Ci	C-C	HCl	Elim.	H abst.	(Ci)	C-Ci (1/s) [c]	C-C (1/s) [c]	HCl elim. (1/s) [d]	H abst. by Cl [e]	(cm <sup>3</sup> /mol-s)	
C2H5Cl	82.1	89.3	17.2	-	-	-	15.1-81.8/2.3RT	17.2-89.0/2.3RT	13.5-56.6/2.3RT	13.6-1.5/2.3RT	[29]	
1,1-C2H4Cl2	-	89.5	17.5	-	-	-	16.1-80.0/2.3RT	17.3-89.2/2.3RT	13.5-53.5/2.3RT	13.0-1.9/2.3RT	[29]	
1,2-C2H4Cl2	-	87.6	17.4	-	-	-	16.0-81.5/2.3RT	17.2-87.3/2.3RT	13.6-58.0/2.3RT	13.8-3.1/2.3RT	[29,30]	
1,1,1-C2H3Cl3	-	85.9	12.1	-	-	-	16.4-78.5/2.3RT	17.4-85.6/2.3RT	14.1-54.2/2.3RT	12.4-3.6/2.3RT	[30]	
1,1,2-C2H3Cl3	-	85.5	12.1	-	-	-	16.4-79.7/2.3RT	17.3-85.2/2.3RT	13.1-57.0/2.3RT	13.0-3.1/2.3RT	[29]	
1,1,2-C2H3Cl3 [f]	-	83.3	13.1	-	-	-	16.6-78.2/2.3RT	17.4-83.0/2.3RT	14.1-54.0/2.3RT	12.2-2.5/2.3RT	[29]	
1,1,1,2-C2H2Cl4	-	84.7	10.6	-	-	-	16.6-78.5/2.3RT	17.3-84.4/2.3RT	14.1-58.0/2.3RT	12.6-2.5/2.3RT	[29]	
1,1,2,2-C2H2Cl4	68.3	76.6	6.7	-11.5	-	-	16.7-68.0/2.3RT	17.5-76.3/2.3RT	14.1-59.7/2.3RT	12.7-3.6/2.3RT	[29]	
C2Cl6	70.0	69.1	NA	NA	NA	NA	16.8-69.7/2.3RT	17.5-68.8/2.3RT	NA	NA	NA	

Table 2b. Decomposition Rate Parameters—Chloroethanes

Compound	$\Delta H^{\circ}300$ (kcal/mole) [b]						log k 300					
	C-Ci	HCl	Elim.	Cl Disp.	H abst.	(Ci)	C-Ci (1/s) [c]	HCl elim. (1/s) [d]	Cl disp. by H	H abst. by Cl	(cm <sup>3</sup> /mol-s)	
C2H3Cl	89.5	23.8	-19.1	-	-	-	14.9-89.2/2.3RT	14.0-69.3/2.3RT	[21]	-	-	
1,1-C2H2Cl2	-	28.8	-15.8	-	-	-	15.7-85.0/2.3RT	14.3-75.0/2.3RT	-	-	-	
1,2-C2H2Cl2	-	28.1	-15.1	-	-	-	15.6-85.0/2.3RT	14.0-75.0/2.3RT	-	-	-	
C2HCl3	-	27.6	-21.5	3.5	-	-	15.9-84.0/2.3RT	14.0-75.0/2.3RT	-	-	-	
C2Cl4	85.3	NA	-21.2	NA	NA	NA	14.7-80.0/2.3RT	[22]	-	-	NA	

Legend:

- [a] Decomposition pathways from left to right are unimolecular C-Cl bond fission, C-C bond fission (chloroethanes only), 4-center HCl elimination, and bimolecular H abstraction by OH, and Cl displacement by H (for the chloroethanes only).
- [b] Thermodynamic data were obtained from one of the following sources:
  1. Reference 27
  2. Reference 20
  3. Reference 28.
- [c] Except where noted, Arrhenius A factors were calculated by transition state theory. Arrhenius Ea's were calculated by subtracting 0.5RT from the reaction enthalpy. In the absence of reaction enthalpies, Ea's were estimated by comparison with similar compounds. For 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, and pentachloroethane, Arrhenius parameters reflect fission of the weaker C-Cl bonds.
- [d] Except where noted, Arrhenius A factors were calculated by transition state theory. Ea's were estimated by comparison with similar compounds.
- [e] Rate coefficients reflect H abstraction from highest chlorinated carbon unless otherwise noted.
- [f] 4-center HCl elimination from 1,1,2-trichloroethane can occur by two pathways, with different reaction enthalpies.
- [g] Beta-H abstraction.

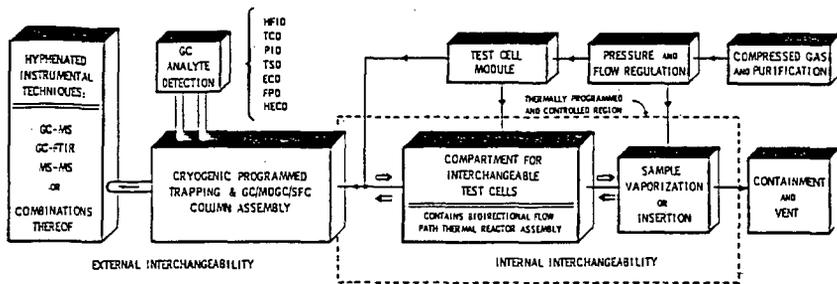


Figure 1a. Schematic Diagram of the System for Thermal Diagnostic Studies.

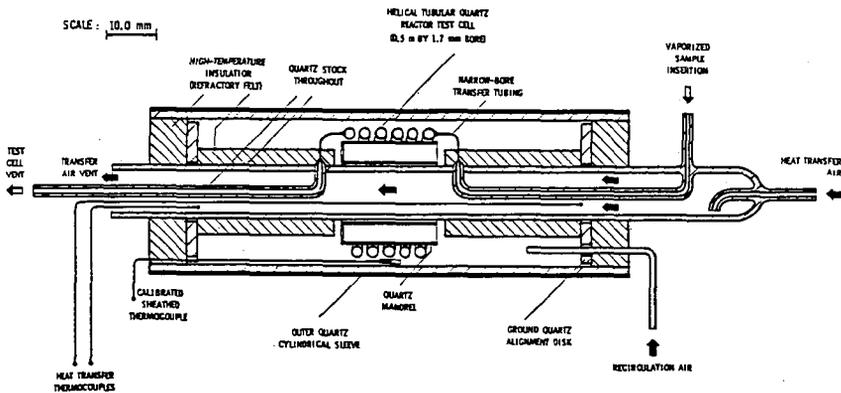


Figure 1b. Cross-sectional schematic of helical tubular reactor.

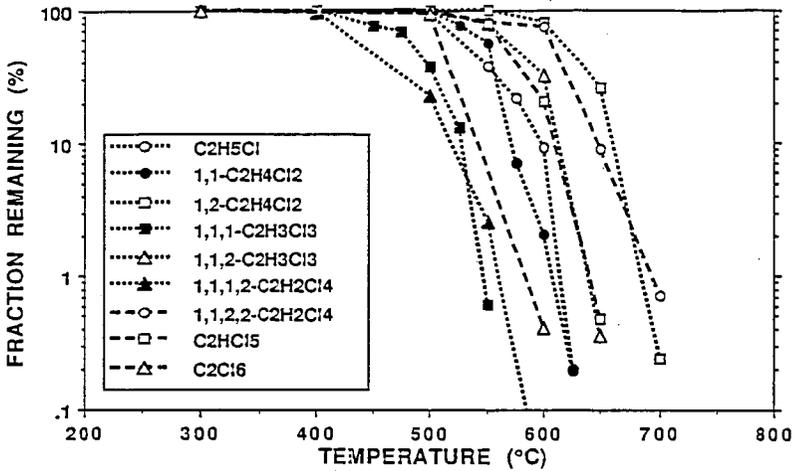


Figure 2. Thermal decomposition curves for the chlorinated ethanes. Fuel/oxygen equivalence ratio = 3.0, mixture elemental composition =  $C_2H_3Cl$ ,  $t_r = 2.0$  s, total organic concentration =  $4 \times 10^{-5}$  moles/ $l_3H_3Cl$ .

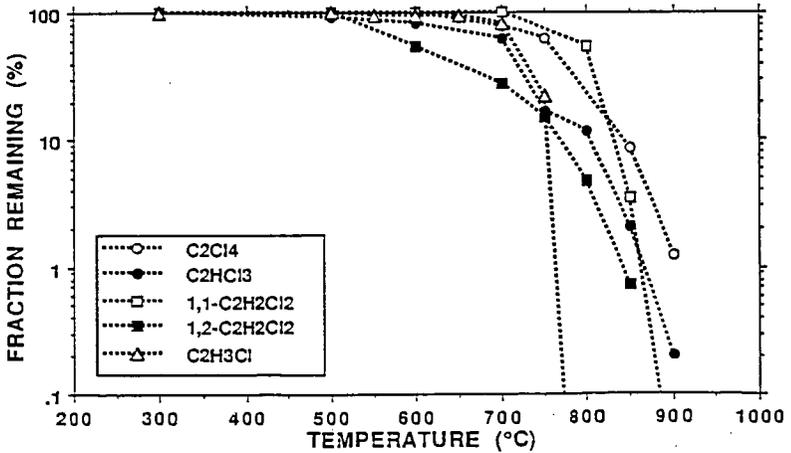


Figure 3. Thermal decomposition curves for the chlorinated ethenes. Fuel/oxygen equivalence ratio = 3.0, mixture elemental composition =  $C_2H_2Cl$ ,  $t_r = 2.0$  s, total organic concentration =  $4 \times 10^{-5}$  moles/L.

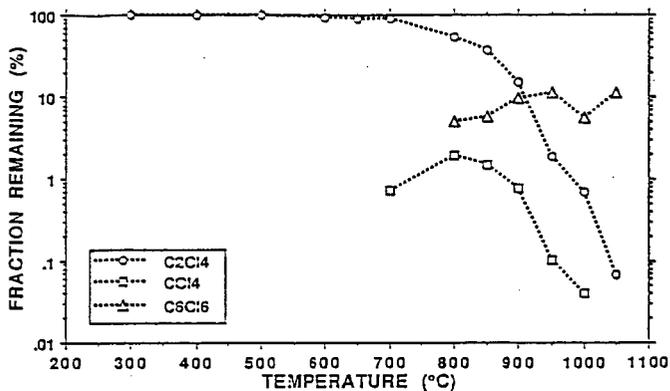


Figure 4. Thermal decomposition profile for tetrachloroethene. Fuel/oxygen equivalence ratio = 3.0,  $t_r = 2.0$  s,  $[C_2Cl_4] = 4 \times 10^{-5}$  moles/L.

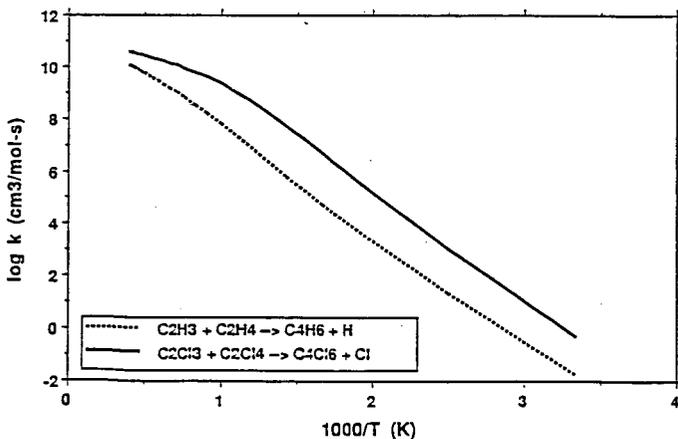


Figure 5. Predicted effect of temperature upon reaction 1 for both hydrogen and chlorine analogues.  $P = 1$  atm,  $\log A(H) = \log A(Cl) = 11.2$ ,  $E_1(H) = E_1(Cl) = 7.3$ ,  $\log A_1(H) = \log A_1(Cl) = 12.7$ ,  $E_2(H) = E_2(Cl) = 27.8$ ,  $\log A_2(H) = \log A_2(Cl) = 13.1$ ,  $E_2(H) = 38.4$ ,  $\log A_2(H) = 14.5$ ,  $E_2(Cl) = 29.7$ ; units for rate parameters are  $cm^3$ , mole, s, kcal.  $V_{C_4H_7} = 1500$   $cm^{-1}$ ,  $V_{C_4Cl_7} = 250$   $cm^{-1}$ . Energy transfer media: air (21%  $O_2$ , 79%  $N_2$ ).

SOLVENT EFFECTS ON THE THERMAL  
DECOMPOSITION OF 1,2-DICHLOROBENZENE

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ABSTRACT

The incineration of hazardous wastes is emerging as a positive solution to the management of hazardous organic containing wastes. To better understand the formation of products of incomplete combustion (PICs), a study of the thermal decomposition of dichlorobenzene in the presence of several organic solvents was studied. Experiments have been conducted in a laboratory scale test system using a steady state combustion environment to study the effects of co-solvents on product distribution. The introduction of chlorinated solvents resulted in an increase in the number and concentration of chlorinated compounds being formed. Conversely, the introduction of chlorophenol into the system had little effect on the product distribution. The introduction of methanol, hexane, and water into the system lowered the number of chlorinated compounds being formed.

INTRODUCTION

The incineration of hazardous organic wastes is gaining acceptance as a technique for the management of these materials. The placement of wastes containing hazardous organic chemicals in landfills represents a potential hazard to the water supplies of future generations. For this reason, landfilling of wastes is meeting with greater resistance from the public and tighter restrictions from regulating agencies.

Incineration offers a more permanent solution to handling organic compounds. During the combustion process, organic compounds are converted to carbon dioxide, water, and acid gases. A public concern to incineration is the survival of compounds from the combustion environment and the products of incomplete combustion (PICs) that are formed during the combustion reaction. This study was undertaken to define the parameters that affect the formation of PICs during combustion.

Dichlorobenzene (DCB) was selected for this study as a model of a typical industrial organic compound found in hazardous

wastes. The thermal decomposition of DCB was reported earlier.<sup>1</sup> The present study expands the previous work by investigating the effect of solvents on the decomposition products from DCB.

#### PIC Formation in Mixtures.

Others have reported that thermal treatment of mixtures of organic compounds produce more PICs than when these compounds are treated individually. The University of Dayton Research Institute has done extensive work on the thermal stability of organic compounds. They tested a six-component mixture and found that the relative thermal stability of compounds changed when they were present in mixtures as compared to testing the individual compounds.<sup>2</sup> The compounds studied were divided into two classes. One class was the compounds whose decomposition was independent of the reaction atmosphere. The other class of compounds were those species that increased in stability with decreasing oxygen concentration. From the thermal treatment of these compounds, the Dayton group identified 58 different PICs. This testing was done in different atmospheres and at different temperatures. Not all 58 compounds were present in any of the individual tests. The PICs ranged from benzene to polynuclear aromatic (PNA) compounds and from chloroform to chlorinated benzenes and naphthalenes. Many of these compounds were seen primarily from oxygen deficient conditions. It was proposed that a substantial portion of these products were formed in the initial reaction, but they are destroyed by oxidative pathways when they are available leaving only the compounds insensitive to oxidative pathways. Under oxygen deficient conditions, the competing oxidative pathways are no longer available and the PNAs show up as PICs.<sup>2</sup>

Taylor and Dellinger<sup>3</sup> reported on a study conducted on the thermal decomposition of chloromethane mixtures. They studied the decomposition of  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{Cl}$ . This group reported that the thermal stability of these compounds was dependent on the oxygen concentration and the other compounds present in the feed to the system. The evaluation of the decomposition of mixtures indicated that the degradation of  $\text{CHCl}_3$  initiated the generation of a radical pool that lead to the decomposition of the other compounds.

### EXPERIMENTAL

#### Test Apparatus

The test combustion apparatus has a sample introduction system, a preheater section, the high temperature reaction section, and the absorber section. The sample introduction device is composed of a pump, gas flow meters, and a spray nozzle. The pump delivers the test compounds to the introduction system at a set rate that can be adjusted to the desired level

using a fine metering valve. The tests that added water to the system used a second pump and a spray nozzle with two tubes for delivering compounds to the system. The gas flow meters were two sets of gas proportioning valves for adjusting flows of oxygen and nitrogen to achieve the desired atmosphere for testing. The spray nozzle atomized the test compounds into the preheater section to assist evaporation of the compounds. The preheater and reaction sections were tubes packed with an aluminosilicate fire brick material. The reaction tube had a coiled tube following the packed bed section which can be adjusted in length to change the reaction time. The temperatures of the two heated zones were controlled separately. The absorber unit was a series of impingers containing methanol to condense and absorb organic compounds as they exit the heated zones.

#### Analysis Methods

The solvent used in the impingers for these tests was methanol. The absorbing solutions were analyzed directly using GC/MS. In addition, the solutions from the first impinger were also concentrated by extraction into methylene chloride. The methylene chloride was then evaporated to a small volume and analyzed by GC/MS for the detection of compounds present at lower concentrations.

#### RESULTS

The tests conducted had only two variables: the oxygen concentration and the feed mixture composition fed to the system. The oxygen concentration caused a large variation in the number and concentrations of compounds formed. The type of compounds added to the system also affected the product distribution and the concentrations of PICs. The presence of a highly chlorinated solvent in the system led to the formation of more chlorinated compounds. The presence of a non-halogenated solvent in the system tended to suppress the formation of chlorinated species.

Solvents were tested with DCB alone or in combination with other solvents. The other solvents tested were hexane, methanol, chloroform, carbon tetrachloride, chlorophenol, and water. The chlorinated solvent tests were performed to determine if their decomposition would increase the available chlorinating species and increase the number of chlorinated compounds formed. The non-halogenated solvent tests allowed determination of their effect on the chlorinating species produced by the decomposition of DCB.

The multi-solvent combinations studied were DCB/chloroform/methanol, DCB/chloroform/water, and DCB/carbon tetrachloride/water. Tests with the non-halogenated solvents mixed with the halogenated solvents were conducted to determine if the chlorination caused by the halogenated solvents could be suppressed by a hydrogen donor solvent. The results of the tests

indicated that fewer highly chlorinated compounds were formed when a hydrogen donor solvent was present.

The tests with hexane present were complicated by the low autoignition temperature of hexane. The temperature of the reaction chamber was set at 750°C, which caused auto ignition of the hexane. The flame front was observed to move back into the preheater section where it turned the last 1.5 inches of the bed bright red. This resulted in a non-controlled temperature for the tests with hexane.

The comparison of the results of DCB alone, DCB with hexane and DCB with methanol are shown in Table I. These results show a marked decrease in the amount of DCB remaining for those tests where a non-halogenated solvent was added to the system. The introduction of methanol into the feed resulted in the largest decrease in the number and concentration of chlorinated compounds formed. The test with hexane reduced the concentration of chlorobenzene, DCB, and hexachlorobenzene. It also reduced the number of compounds formed from 10 to 6. The tests with methanol reduced the concentration of DCB two orders of magnitude and reduced the number of compounds formed to 4.

Table II lists the product distribution of PICs formed for the tests of DCB, DCB/chloroform and DCB/carbon tetrachloride. The PICs were largely chlorinated compounds of various chemical classes. The chlorinated benzenes and chlorinated phenols show a general trend of increasing concentration with increasing number of chlorine atoms on the molecule. The compounds having the highest concentrations after combustion in the tests with the chlorinated solvents are the tetra- to hexachlorobenzenes. These compounds were three orders of magnitude higher in concentration than with DCB alone. The concentration of DCB remaining decreased in the tests with the chlorinated solvents, but this effect was overwhelmed by the much higher concentrations of the higher chlorinated benzenes. The tests with CCl<sub>4</sub> converted about 1 % of the dichlorobenzene to hexachlorobenzene. Crystals of hexachlorobenzene were also noted between the preheater and the reaction chamber indicating that some chlorination was taking place at the preheater temperatures of around 400°C.

The thermal decomposition of DCB in the presence of chlorophenol was studied to determine if this combination would lead to the formation of fused ring heterocyclic compounds. The excess oxygen test produced very few compounds and resulted in low levels of DCB or chlorophenol surviving the thermal decomposition. The compounds identified were similar to the thermal decomposition products of DCB by itself. The chlorophenol tests did follow the trends of other tests in that the decrease in the oxygen concentration produced a marked increase in the number of compounds formed and the amount of DCB remaining. The amount of chlorophenol did not necessarily follow this trend. Only small amounts of chlorophenol remained in any

of the tests. No fused ring heterocycles were formed except in the oxygen deficient test.

The studies conducted to this point had shown that increasing the chlorine content of the feed increased the number of chlorinated compounds formed. The addition of a non-halogenated solvent decreased the number of chlorinated compounds. The next investigations were designed to determine if the addition of a non-halogenated solvent to the feed could reduce the number of chlorinated compounds produced by acting as a scavenger for the chlorinating species present.

The use of methanol as a non-halogenated solvent was chosen to avoid the temperature increases caused by the ignition and burning of hexane with a flame front. To test this theory, DCB was mixed with chloroform and methanol in two different ratios. The methanol concentration was doubled in the second set of tests. Table III summarizes the results of these tests as compared to the DCB/chloroform test. The methanol showed some effectiveness at reducing the amount of chlorination with the largest reductions being in the amount of hexachlorobenzene being produced.

The addition of water into the system had a similar effect of reducing the amount of chlorination that takes place in the system. Table IV summarizes the data from the tests where water was added as a separate feed to the system. The water clearly reduced the concentrations of higher chlorinated compounds, but increased the amount of DCB that remained in the system.

#### CONCLUSION

The formation of products of incomplete combustion are influenced by the compounds in the combustion feed system, the temperature of the oxidizing system, and the oxygen available for combustion. The presence of highly chlorinated solvents in the feed can result in a chlorinating environment that leads to the production of more highly chlorinated PICs. The presence of non-halogenated solvents in the system produces an environment that suppresses the chlorination processes. When both types of solvents are introduced into the feed system, there is a moderate suppression of the chlorination. One possible explanation of this phenomena is that the hydrocarbon solvents produce water during combustion which acts as a hydrogen source for scavenging the chlorinating species present. Commercial scale incineration systems that use hydrocarbon fuels for maintaining combustion temperatures can actually lead to environments that suppress the formation of PICs by providing a pool of hydrogen donors to react with the released chlorine from the combustion of chlorinated compounds.

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Table I  
EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C  
Hydrocarbon Solvents

<u>Compound Present</u>	<u>Solvent System Additions</u>		
	<u>None</u>	<u>Hexane</u>	<u>Methanol</u>
Chlorobenzene	18	7.7	1.1
Dichlorobenzene	372	137	1.5
Trichlorobenzene	0.8	1.4	<0.1
Tetrachlorobenzene	0.3	1.8	<0.1
Pentachlorobenzene	1.4	0.3	3.0
Hexachlorobenzene	7.5	<0.5	1.5
Additional Compounds	4	1	0

\* Concentrations are in ug/gram of Mixture input.

Table II  
EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C  
Chlorinated Solvents

<u>Compound Present</u>	<u>Solvent System Additions</u>		
	<u>None</u>	<u>CHCl<sub>3</sub></u>	<u>CCl<sub>4</sub></u>
Chlorobenzene	18	<10	3.17 mg
Dichlorobenzene	372	40	12
Trichlorobenzene	0.8	40	1.4
Tetrachlorobenzene	0.3	1.42 mg	3.1
Pentachlorobenzene	1.4	1.24 mg	130
Hexachlorobenzene	7.5	1.67 mg	11.3 mg
Chlorophenol	<0.1	<0.1	4.0
Dichlorophenol	<0.1	0.7	0.9
Trichlorophenol	<0.1	0.4	1.5
Tetrachlorophenol	<0.1	6.9	<0.1
Pentachlorophenol	<0.1	5.3	<0.1
Additional Compounds	4	23	23

\* Concentrations are in ug/gram of Mixture input, unless noted.

Table III  
EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C  
Chlorinated Solvents with Methanol

<u>Compound Present</u>	<u>Solvent System Additions</u>		
	<u>CHCl<sub>3</sub></u>	<u>Ratio #1</u>	<u>Ratio #2</u>
Chlorobenzene	<10	14	167
Dichlorobenzene	40	806	589
Trichlorobenzene	40	850	748
Tetrachlorobenzene	1.42 mg	1.15 mg	1.19 mg
Pentachlorobenzene	1.24 mg	869	748
Hexachlorobenzene	1.67 mg	212	261
Chlorophenol	<0.1	1.2	0.4
Dichlorophenol	0.7	8.4	1.1
Trichlorophenol	0.4	8.9	0.6
Tetrachlorophenol	6.9	15	0.7
Pentachlorophenol	5.3	5.4	0.9
Additional Compounds	23	50	30

\* Concentrations are in ug/gram of Mixture input, unless noted.

Table IV  
EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C  
Chlorinated Solvents with Water

<u>Compound Present</u>	<u>Solvent System Additions</u>		
	<u>None</u>	<u>CHCl<sub>3</sub></u>	<u>CCl<sub>4</sub></u>
Chlorobenzene	6.61 mg	88	214
Dichlorobenzene	51.1 mg	1.76 mg	5.07 mg
Trichlorobenzene	334	1.37 mg	1.11 mg
Tetrachlorobenzene	0.7	2.49 mg	3.61 mg
Pentachlorobenzene	0.9	2.02 mg	4.18 mg
Hexachlorobenzene	2.1	2.44 mg	4.72 mg
Chlorophenol	694	0.4	13
Dichlorophenol	381	6.0	8.6
Trichlorophenol	1.2	4.0	0.9
Tetrachlorophenol	0.9	6.6	1.7
Pentachlorophenol	6.3	3.8	4.5
Additional Compounds	4	18	38

\* Concentrations are in ug/gram of Mixture input, unless noted.

MONITORING THE EVOLUTION OF ORGANIC COMPOUNDS FROM THE THERMAL TREATMENT  
OF CONTAMINATED SOIL SAMPLES USING SHORT COLUMN GC/MS

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INTRODUCTION

Incineration is an effective technology for the remediation of organic chemical contaminated wastes. For solid wastes, such as contaminated soils, processes involving separate stages of a primary desorber and secondary afterburner are particularly useful. The desorption stage is currently being modeled using a particle-characterization reactor (PCR, 0-500 g capacity), a bed-characterization reactor (BCR, 0.5-5 kg), and a rotary kiln simulator (2-15 kg) to study fundamental processes such as mass transfer, heat transfer, and volatilization of contaminants [1,2]. This paper describes the analytical methods and preliminary results from monitoring the evolution of organic compounds in these and smaller reactors.

The samples are soil contaminated with a broad range of polynuclear aromatic (PNA) hydrocarbons such as those derived from coal tars. The analytical methods primarily involve mass spectrometry (MS) with a variety of sample introduction techniques. The on-going analyses include solvent and thermal extractions of soil before and after various thermal treatments as well as on-line monitoring of vapors during desorption.

EXPERIMENTAL

Samples - Contaminated and uncontaminated clay soil samples were obtained from an undisclosed site. The samples were received air dried and simply designated as "soil A" and "soil B". The soils were analyzed for approximate mineral content by Fourier Transform Infrared (FTIR) spectroscopy of standard KBr pellets. Extracts were prepared from mg to g size samples by ultrasonification with repetitive aliquots of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ). Further, standard solutions of PNA's from naphthalene through dibenzoanthracenes were prepared for calibration purposes at 1, 23 ng/ $\mu\text{l}$  and 200 ng/ $\mu\text{l}$  in methylene chloride.

Extract Gas Chromatography/Mass Spectrometry (GC/MS) - GC/MS analyses of the extracts (procedure described above) were performed using a Hewlett-Packard 5890 chromatograph with a 15 m x 0.25 mm i.d. x 0.25  $\mu\text{m}$  film thickness DB-5 column (J&W Scientific). Extracts were injected either by split injection or by flash vaporization in a Curie-point pyrolysis GC inlet [3] using 358 C Curie-point wires in an inlet set at 250 C. For the Curie-point injection, 2 to 10  $\mu\text{l}$  of  $\text{CH}_2\text{Cl}_2$  extract were concentrated on the pyrolysis wire with only limited loss of the smaller PNA's. The column was temperature programmed from 40 to 300 C at 15 C/min. An Ion Trap Detector (ITD, Finnigan MAT) was scanned from m/z 50 to 350 at 2 scans/sec.

Solids Probe MS - Soil samples were analyzed directly by use of a solids probe on a Ion Trap Mass Spectrometer (ITMS, Finnigan MAT). 1-3 mg samples were

placed in aluminum vials with 0.1 mm diameter holes in the press fit caps. The probe tip was then heated from 40 to 500 C at 60 C/min to desorb the organics directly into the ion trap maintained at 120 C. The mass spectrometer was scanned from m/z 50 to 350 at 2 scans/sec. PNA standards were deposited from CH<sub>2</sub>Cl<sub>2</sub> solutions into the vials with and without soil substrate. Both uncontaminated and previously desorbed soils were used as substrates for the standards in separate experiments.

On Line Short Column GC/MS - The desorbing organic vapors were monitored during thermal treatment using a newly designed vapor sampling inlet with short column GC on a miniaturized ITMS (MINITMASS) all of which is described in detail elsewhere [4,5,6]. The system used a 1 m x 0.18 mm i.d. x 0.4 μm film thickness DB-5 column (J&W Scientific) in the standard ITD transfer line for isothermal operation. For these analyses the MINITMASS was operated in electron ionization mode with software features for enhanced sensitivity [6,7]. Retention time standards for various PNA's were acquired by direct injection of micro liter volumes of PNA standard solutions. Various inlet and column temperatures were used.

Thermal Treatment Reactors - Preliminary micro scale heat treatments (5-60 mg) were performed by thermogravimetry (TG) (Perkin Elmer TGA 7). In initial vapor sampling tests, 1 μg each of naphthalene and acenaphthylene were added to 10 mg of clean soil and then heated at 50 C/min to 600 C while the 125 or 200 C vapor inlet sampled the TG furnace outlet at 30 s intervals. In other tests, 50-60 mg portions of soil A were heated at 100 C/min to 250, 350 or 450 C, held for 5 min and then cooled at 50 C/min under He. The thermal treated soils were then analyzed by the extraction GC/MS and solids probe MS techniques.

The laboratory-scale reactors for particle and bed characterization, and the rotary-kiln simulator are described in detail elsewhere [1,2]. At the time of this writing, vapor sampling of test soils A and B was not completed. However, these results will be included in the oral presentation. A set of preliminary experiments in the bed-characterization reactor (BCR) have been conducted where "clean" clay soils were loaded with 0.5 wt% of either toluene, ethylbenzene, isopropylbenzene, or t-butylbenzene. In these runs, the tray of organic-loaded soil was placed beneath radiant heaters directly in the 536 C preheated air stream. The evolved gases were sampled at 60 s intervals for repetitive short column GC/MS analysis. The vapor inlet was operated at 160-175 C and the transfer line at 30 C isothermal.

## RESULTS AND DISCUSSION

Extract GC/MS - Figure 1 shows a series of ion chromatograms from the flash vaporization GC/MS of the soil A extract. The total ion chromatogram is shown for the complete run (Figure 1a) and as an expanded short segment (Figure 1b). Single ion chromatograms are shown for m/z 228 (Figure 1c), 252 (Figure 1d) and 276 (Figure 1e). This data demonstrates the complexity of the chemical contaminants and the wealth of detailed qualitative and quantitative data that are available through this technique using a high resolution capillary column of normal length. Note that 5 or more isomers of benzofluoranthenes and benzopyrenes are distinguishable in the trace of m/z 252. The concentrations of compounds smaller than phenanthrene are underestimated in this chromatogram due to premature evaporation from the Curie-point wire.

Solids Probe MS - Figure 2 shows the solids probe MS analysis of soil A. The single ion chromatograms indicate that the PNA's were desorbed from the soil

into the MS high vacuum over a broad temperature range of 100 to 400 C when heated at 60 C/min. These ion traces suggest the strong interaction of the PNA's with the clay soil surface since these same compounds completely evaporate from a sample vial without the soil at temperatures less than 200 C. Note that there is no separation of the various isomers as was seen with the chromatography in Figure 1.

Vapor Sampling GC/MS - Figure 3 is a set of ion chromatograms from the vapor inlet short column GC/MS analysis of PNA standard solution. This figure illustrates how compounds eluting in the 9 min to 18 min portion of the chromatogram shown in Figure 1 are compressed into a 1 min analysis on the isothermal short column at 250 C. Although the chromatographic resolution is greatly reduced from that of Figure 1, there is still a clear separation of the benzofluoranthenes from the benzopyrenes as seen in the m/z 252 trace. The significant advantage is that the partial GC/MS analysis can be repeated each 60 sec versus the 20 min in Figure 1 and this analysis still gives some isomer information beyond that which can be obtained in direct MS methods such as seen in Figure 2.

Thermal Treatment Analyses - Figure 4 illustrates the monitoring of PNA evolution from thermal treatment of the soil using the short column GC/MS system on-line. In this analysis, the 4 min to 7 min portion of the chromatogram in Figure 1 has been compressed into a 30 sec segment of Figure 3. For this preliminary test, naphthalene and acenaphthylene were repetitively analyzed each 30 sec as they were evolved from 10 mg of soil in a thermogravimetry (TG) crucible. Note that the profiles of consecutive naphthalene (m/z 128) and acenaphthylene (m/z 152) peaks trace the evolution of these compounds from the soil at the TG temperatures indicated. The naphthalene is desorbed from the soil at higher temperatures than the higher boiling acenaphthylene possibly due to the fact that it was the first one coated on the soil and thus had first access to the strongest adsorption sites. Although equal amounts of each compound were placed on the soil, recondensing of the acenaphthylene in cold regions of the TG oven greatly attenuated its signal.

Samples of soil A were heated in the TG to 250, 350, or 450 C (without on-line vapor analysis) and then analyzed by extraction GC/MS and solids probe MS. Preliminary analysis of these data indicate that there were virtually no PNA's left on the soil heated to 450 C in helium. The solids probe MS data on selected PNA's in the original soil and the 250 and 350 C thermal treated soils are listed in Table 1. Although these data show the expected reduction of these compounds from the heated soils, the actual solids probe ion profiles indicate that the remaining amounts are more tightly bound than the major portions of the original contamination. This result is readily explained if one simply assumes that the first monolayer of PNA's on the clay surface is more strongly adsorbed than additional layers. Further, a layer of black char began to form at 350 C (in helium), which might be a secondary binding site. At present it is unclear to what extent this char was formed from the PNA contaminants versus native soil humic substances.

Evolution profiles of selected compounds from .5 wt % toluene loading on a clay soil are presented in Figure 5. 600 g of soil was heated to 536 C in the BCR. Three secondary products are shown at concentrations of 1 ppb to 1 ppm (in air). In addition to the reaction products shown in the figure, the following were also detected at similar concentrations: benzylalcohol, bromotoluene, bromobenzene, quinone, benzonitrile, xylene, ethylbenzene, chlorotoluene, and dichlorobenzene. The benzaldehyde and benzylalcohol are expected as partial oxidation products. The exact sources of the other compounds are as yet

uncertain although it can be stated that these were not impurities in the original solvent and there was approximately 15 ppm chlorine found in the original soil. The quantity and diversity of these products gives some idea of possible secondary reactions and desorption characteristics expected with the PNA's.

#### CONCLUSIONS

These preliminary results clearly demonstrate the potential of mass spectral techniques for studying the effectiveness of thermal treatment in contaminated soil remediation. Solvent extraction followed by high resolution GC/MS is the method of choice for detailed examination of soils before and after treatment. Solids probe MS is a rapid technique for screening soils and can offer additional information on how the contaminant is bound to the soil. The vapor sampling short column GC/MS system is a powerful tool for on-line monitoring of the desorbed gas phase products which are important to identify for desorber optimization and afterburner design. Isothermal operation of the short column is a major limitation to the boiling point range of compounds which can currently be analyzed on a rapid repetitive basis and plans are underway for making it temperature programmable.

#### ACKNOWLEDGEMENTS

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TABLE 1  
 Approximate Concentrations in ng/mg (ppm) of Selected PNA's  
 on "As Received" and TG Thermally Treated Soil A

Compound m.w.	Concentration (ppm)		
	Soil A	250 C	350 C
128	600	66	19
202	200	17	1
278	16	14	0

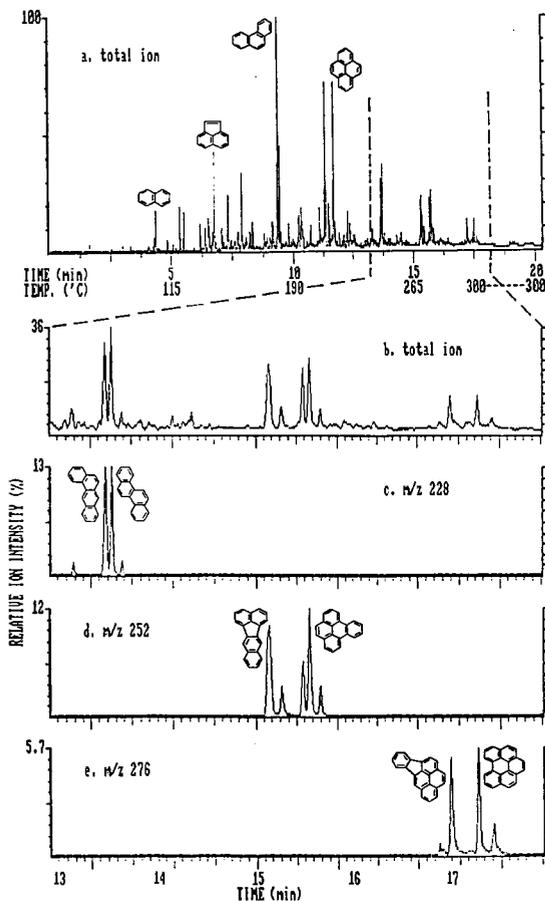


Figure 1. GC/MS ion chromatograms from the analysis of the soil A extract on a 15 m column.

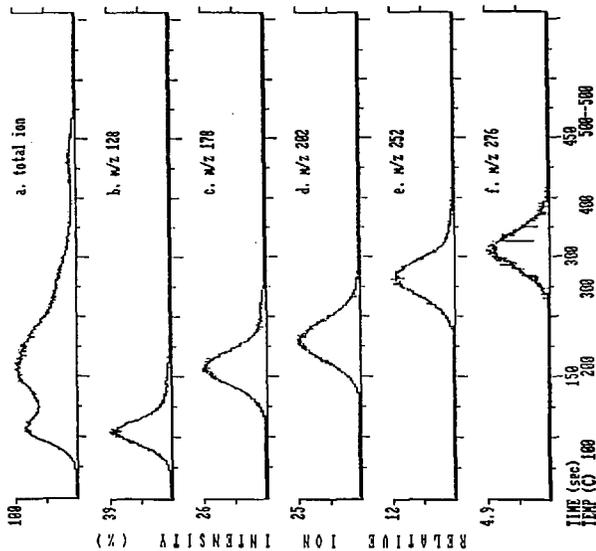


Figure 2. Solids probe MS ion chromatograms from the thermal desorption of soil A directly into the mass spectrometer high vacuum.

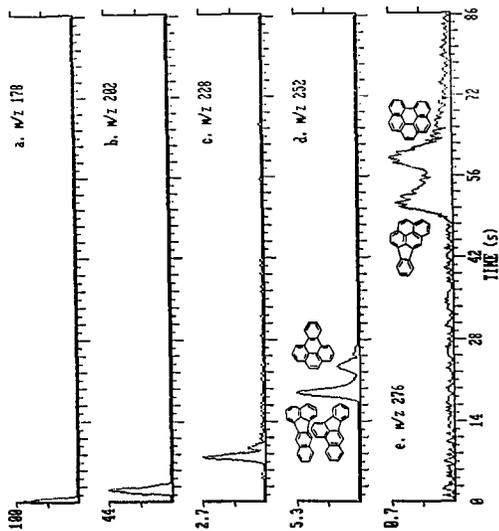


Figure 3. Selected ion chromatograms from the vapor sampling GC/MS analysis of a PNA standard solution.

Repetitive vapor samples taken at 30 second intervals

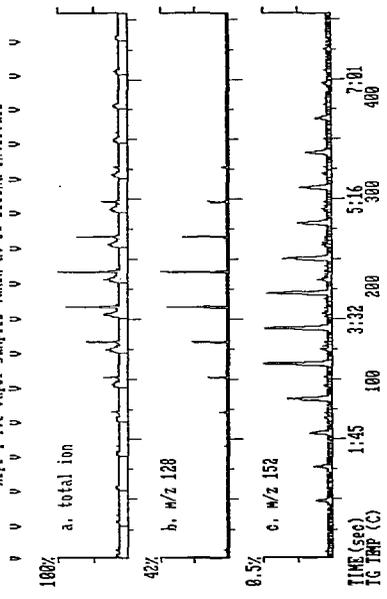


Figure 4. Ion chromatograms for repetitive on-line sampling using vapor inlet short column GC/MS during a TG soil desorption.

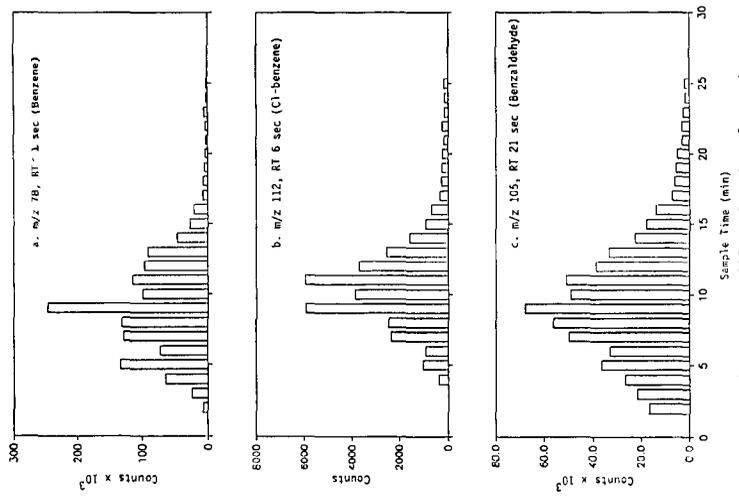


Figure 5. Peak area profiles for 3 selected reaction products produced from toluene desorption.

**NEWSPAPERS - A MAJOR CONTRIBUTOR TO THE MUNICIPAL  
SOLID WASTE STREAM**

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Each year Americans must deal with over 160 million tons of municipal solid waste. This material (the stuff we throw away with very little concern as to where it goes) is a pollutant in itself and no matter how well managed, will have some measure of environmental impact. Integrated solid waste management techniques reduce the adverse impact and minimize the risk that may be incurred by relying on only one disposal alternative.

In order to manage heterogeneous garbage in a safe and sane manner, local governments must use all solid waste management options available. They include: waste reduction (volume or toxicity); recycling or reuse; treatment for volume reduction, organic destruction, and recovery of energy; and land disposal. While each option can be used to manage a different materials in the municipal waste stream, none can do the job alone. All have the potential for causing environmental harm and must be performed carefully to minimize the adverse impact. For example, reducing the volume of food packaging could increase the potential for bacterial and viral exposure; recycling uses energy and releases waste products into the environment that could contaminate ground and surface waters and contribute to regional air pollution; waste-to-energy plants must control air emissions to safe levels and ensure proper management of ash so as not to endanger water supplies.

Landfills, which have the greatest potential for contamination, must control disease vectors, air emissions (fugitive dust and organic vapors) and leachates generated during the decomposition of the waste.

Ogden Projects, Inc., (OPI) is involved with integrating all solid waste management options. Although the company's primary focus is designing, building, and operating waste-to-energy facilities, it also operates landfills and manages recycling programs. Since the most important aspect of municipal solid waste (MSW) management is public health protection, non-management of waste is as much a cause for concern as the AIDS epidemic. If MSW is not collected or just dumped at the edge of town, there will be health incidents arising from the bacteria and virus contained in the trash that is spread by wind, rain, and rodents. While integrated solid waste management will mitigate these kinds of adverse health incidents, no one method will eliminate all potential problems.

One of the most controversial problems with MSW management is the trace toxic constituents of everyday, short-lived, consumer products. From a management perspective, decreasing the large volume of material is a priority. However, from the perspective of long-term environmental impact, toxicity is much more important.

Keeping this in mind, OPI studied the potential impact of newspapers, an item that is discarded daily. Newspapers represent the single largest item in the daily waste stream, accounting for 10-20 percent of municipal waste. In New York City, newspapers account for 15 percent of all municipal solid waste. One daily newspaper admitted that it was responsible for 20 percent of municipal waste generated on Long Island.

Newspapers are the most readily recycled commodity in municipal solid waste. They have the potential to release about 8,000 British Thermal Units (BTUs) per pound if burned in a waste-to-energy facility. Unfortunately, when placed in a landfill, they biodegrade very slowly, producing organic acids that have the potential of carrying toxic constituents to water supplies. By performing a simple chemical analysis, it is evident that the amount and the type of toxics released into the environment from this short-lived product is alarming.

OPI chose a major metropolitan newspaper with one of the 10 largest circulations in the United States. In January 1988, newspapers were purchased at a convenience store for a one-week period and sent to two separate laboratories for chemical analysis. The daily newspapers were shredded, composited, and subjected to a series of organic and inorganic analyses. Likewise, the Sunday edition was treated and processed and, additionally, a second Sunday edition was analyzed for dioxin. Versar, Inc., of Columbia, Maryland (metals, organics, EP Tox, etc.), and Triangle Labs, Research Triangle Park, North Carolina (dioxin, furan), participated in the analyses.

The newspaper reported that it used eight percent recycled "fiber". Although it was assumed that each roll of newsprint contains eight percent recycled fiber, this could also be taken to mean the eight percent of the time the paper is printed on recycled newsprint. The chemical analysis showed that the newspaper contained a number of toxic, carcinogenic, mutagenic and teratogenic elements and chemical compounds. While the presence of these trace constituents is low, the amount of toxics flowing into the ecosystem is noteworthy.

Circulation data is as follows:

	<u>DAILIES</u>	<u>SUNDAY</u>
Circulation	641,000 per issue	682,000
Weight	5.87 lbs.	3.16 lbs. *
Tons/Year	97,829.42	56,033.12

\* A Sunday issue published in December 1987 weighed 4.98 lbs. That equates to 88,174.88 tons of Sunday issues per year. This number, however, is somewhat high given the extraordinary amount of advertising in holiday editions.

The following generation rates (rounded to the nearest 1,000) were used to calculate the flow into the ecosystem annually: 100,000 tons/year for dailies; 70,000 tons/year for Sunday; 170,000 tons/year total.

#### **Organics**

The trace organic compounds found in the newspapers are listed in the following table. The majority (5) of these compounds are solvents and are most likely associated with the inks as vehicles and/or press cleaners. Hexachlorocyclohexane is a pesticide and is probably a residual from the papermaking process. The phenol is also a probable residual. The data is quantified in parts per billion and pounds per year.

<u>Organics</u>	<u>Daily*</u>	<u>Sunday*</u>	<u>Daily</u>	<u>Sunday</u>	<u>Total</u>
Methylene Chloride	94	69	18.8	9.66	28.46
Acetone	230	630	46	88.2	134.2
Toluene	130	1800	26	252	278
Ethylbenzene	22	480	4.4	67.2	71.4
Xylenes	130	2300	26	322	348
Hexachlorocyclohexane	23	23	4.6	3.22	7.82
Phenols	1100	1000	220	140	<u>360</u>
					1,227.88

\* PPB. All other - pounds per year.

#### **Dioxins**

Because of the high cost of analysis, only one dioxin/furan analysis was performed on the Sunday edition. The analysis showed the presence of dioxin/furan at the same levels, and with the same isomer profile, as many other paper products analyzed. Therefore, it was assumed that the dailies also contained the same levels. The dioxin/furan releases to the ecosystem are based on the 170,000 tons/year figure.

Interestingly, paper contains the most toxic isomers of

dioxin/furan in the highest concentrations. In comparison, ash and air emissions from resource recovery facilities have low relative concentrations of the most toxic isomers.

The total concentration of dioxin/furan in the newspaper was 248.49 parts per trillion (ppt). Converted to a 2,3,7,8 TCDD toxic equivalent basis (US EPA method), the amount is 11.158 ppt. This results in more than a gram (.004 lbs) of 2,3,7,8 TCDD equivalents entering the ecosystem each year. By comparison, Ogden Martin's Marion County facility, which burns an equivalent tonnage of waste each year (170,000), emits 20 times less dioxin/furan to the environment.

#### PCDD/PCDF ANALYSIS

##### Concentration and Toxic Equivalents (EPA Method) (ppt)

<u>NAME</u>	<u>CONCENTRATION</u>	<u>MULTIPLIER</u>	<u>TOXIC EQUIVALENT</u>
2378-TCDD	3.915	1.0	3.915
Other-TCDD	ND	0.01	-
2378-Sub-H <sub>x</sub> CDD	ND	0.04	-
Other-H <sub>x</sub> CDD	2.181	0.0004	0.00087
1234678-HpCDD	12.841	0.001	0.0128
Other-HpCDD	25.747	0.00001	0.000257
2378-TCDF	69.504	0.1	6.95
Other-TCDF	131.381	0.001	0.131
23478-PCDF	1.472	0.1	0.147
Other-PCDF	<u>1.449</u>	0.001	<u>0.00145</u>
ppt	248.49		11.158

#### **Heavy metals**

Two types of heavy metals analyses were conducted. The EP Toxicity test, which was the first, is a leaching test that attempts to simulate what occurs in a landfill. It indicated the newspaper did not exhibit hazardous waste characteristics and metals did not leach out at levels above the regulatory threshold. There are, nevertheless, heavy metals present in the newspaper that were detected as a result of a chemical analysis procedure. The following table lists the metals detected in parts per million and in pounds/year to the ecosystem.

<u>HEAVY METALS</u>	<u>DAILY*</u>	<u>SUNDAY*</u>	<u>DAILY</u>	<u>SUNDAY</u>	<u>TOTAL</u>
Barium	14.0	17.0	2800	2380	5180
Cadmium	0.021	0.1	4.2	14	18.2
Chromium	0.68	0.94	136	131.6	267.6
Copper	4.9	13.0	980	1820	2800
Iron	7.10	44.0	1420	6160	7580
Lead	0.43	1.8	86	252	338
Manganese	38.0	50.0	7600	7000	14,600
Mercury	<0.0014	0.0066	0.28	0.924	1.204
Silver	0.032	0.14	6.4	19.6	26
Zinc	2.8	11.0	560	1540	2100
					<u>34,113.8</u>

\* PPM All other - pounds per year.

Newspaper disposal results in seventeen plus tons of heavy metals, for which primary and secondary drinking water standards have been established, being released into the environment each year. In comparison, Ogden Martin's Bristol, Connecticut, facility, which burns an equivalent amount of trash each year, emits only one sixth as much lead.

#### Additional Impacts

If all of these newspapers were placed in landfills, there would be the potential for generating 699,125 (350 tons) of toxic hydrogen sulfide gas from the biological decomposition of the sulfur contained in the paper each year. On the other hand, if all were burned, 658 tons of sulfur dioxide, 105 tons of hydrogen chloride gas, and 127.5 tons of nitrogen oxide would be produced.

Newspaper (newsprint) is a readily recycled material. When recycled, the organic solvents and metals in the inks become waste. This particular newspaper prints their product on ninety-two percent virgin stock and eight percent recycled paper stock. During the recycling operation, in order to produce 13,600 tons of recycled newsprint, at least 1,360 tons of waste are generated. This waste consists of short unusable fibers and ink.

If any paper other than newsprint is used to produce recycled news, additional waste in the form of fillers and coatings is generated. All of this waste is contained in the pulping liquids and removed as a sludge in a complex wastewater treatment system. This sludge is often managed as a RCRA hazardous waste under Subtitle C of the Resource Conservation and Recovery Act.

Most volatile organics contained in the incoming paper flow into the receiving body of water. While the levels of organic compounds and metals detected in the newspaper do not represent an imminent threat to public health, their presence is of concern.

Because all of these compounds contribute to the environmental loading of toxic compounds, the toxicity of newspapers should be reduced. There are less toxic inks, vehicles, and solvents available for substitution.

The American Newspaper Publishers Association (ANPA), which represents approximately 1,400 daily and weekly newspapers in the US and Canada, established a set of voluntary standards for inks containing no lead, chromium, or cadmium.

ANPA has also developed standards for black ink, which has very low levels of aromatic hydrocarbons, and uses only carbon black as the pigment. In addition, ANPA has developed a water-based ink printing process. Approximately 40 newspapers have started using this new low environmental impact process. Although ANPA's efforts represent a significant first step, they are non-enforceable and address the newspaper printing process only, and not the "slick" advertising and weekend supplement inserts.

Heavy-metal based pigments are often used to produce these "slick" supplements as well as the colored ads that appear on newsprint. This fact raises questions regarding newspaper advertising. Given our free enterprise system, it is highly unlikely that newspaper publishers would eliminate advertising. If such a revolutionary idea were implemented, it would result in a weight reduction of as much as ninety-five percent, and a significant reduction to the flow of toxic compounds into the environment.

Because a newspaper is dependent on advertising revenue to continue publication and maintain high circulation, eliminating advertising in Sunday or daily editions is not highly likely in the near future.

Although it is unrealistic to expect newspapers to totally eliminate advertising, they could contribute to solving America's solid waste crisis by taking steps to reduce the toxicity of their product, and exercising discretion with respect to "slick" advertising supplements.

MUNICIPAL WASTE COMBUSTION ASH: TESTING METHODS,  
CONSTITUENTS AND POTENTIAL USES

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INTRODUCTION

This paper focuses on the content of combined ash, which represents the non-combustible portion of municipal solid waste. The term "ash" refers to all the solid residue streams of a municipal solid waste combustion system. This included: the bottom ash (approximately 85 to 95 percent of the total), also referred to as "clinker"; ash that collects on boiler, superheater and economizer tubes often referred to as "soot"; ash that is removed from the flue gas via the boiler passes, and the fly ash collected by the air pollution control equipment. The last type of ash is a combination of the solid material, as well as the reacted and unspent reagent from the acid gas scrubbers, that is collected after reaction in the scrubbers by the particulate collection equipment (e.g., the fabric filter or electrostatic precipitator). Bottom ash mainly comprises bottles, cans, auto parts, broken appliances and a myriad of other things that do not lend themselves to complete combustion. Fly ash originates from the ever-present fraction of inorganic compounds in paper, wood, plastic, rubber and food wastes. For example, there are clays in papers, stabilizers in plastics, pigments in printing, inks and mineral salts in vegetables and other products. In other words, the constituents that comprise the two types of ash represent the unavoidable, inorganic, by-products of everything that is thrown away.

By volume, the ash is approximately one-tenth to one-twentieth of the original incoming municipal solid waste. By weight, it represents approximately one-fourth of the original amount. It is much denser than raw solid waste and takes up much less space for ultimate disposal.

ENVIRONMENTAL BENEFITS OF COMBUSTING SOLID WASTE

Volume reduction, converting large amounts of solid waste material into smaller volumes, is a basic environmental protection practice that has been used for thousands of years. Many federal solid waste regulations are based on this premise and it has been a preferred solid waste management option for more than a century. Unfortunately, despite successful reduction and recycling programs, the United States will still need to combust the remainder of the waste stream.

Combusting municipal solid waste and converting it into energy has three basic purposes. First and foremost, the high temperatures accomplish sterilization and deny food and habitat

to disease vectors such as rats and flies. Secondly, volume reduction is successfully accomplished. And, thirdly, useful energy is captured. Throughout history, municipal solid waste was combusted to control disease and reduce volume. Up until the 1960s, open dumps were often set afire as a method of disease (vector) control and to make room for more garbage. Adverse repercussions such as brush fires, rat migration, air pollution, and worker fatalities led to public health problems that made open burning unsafe. However, burning municipal solid waste in a carefully-controlled furnace and managing ash efficiently can satisfy the original objectives without causing environmental harm. While volume reduction to reduce the burden of final waste disposal is essential, combustion can also convert municipal solid waste into energy that can be recovered.

The conversion of raw, unprocessed municipal solid waste into a smaller volume of ash results in long-term land preservation because ash disposal requires less space. There are many differences between disposing of raw municipal solid waste and landfilling ash.

Many environmental problems associated with municipal solid waste disposal can be reduced, mitigated, or eliminated with combustion. Landfilling of raw municipal solid waste generates odors, methane gas, and many other toxic and reactive gases. All these gases originate from the biological decomposition of organic matter. While odors are more annoying than dangerous, methane gas migration from poorly-designed and/or operated landfills has caused explosions in structures located nearby, resulting in millions of dollars of property damage and loss of life. By contrast, waste-to-energy ash is biologically inactive, generating no odors or explosive, toxic, or reactive gases from the landfill.

Potential ground water contamination can occur from any material disposed of in a landfill. This contamination is the result of moisture contained in the material, or rain, or surface water, infiltrating the material and leaching out toxic contaminants. Because organics predominate raw municipal waste, leachate from a landfill is also highly organic. In addition, it is acidic because of the biological activity within the landfill. The organic acids have a much greater potential to carry toxic compounds and elements into groundwater than the leachate from an ash landfill. In contrast, ash leachate that forms in small amounts (since infiltration through dense ash is very slight) contains only inorganic compounds -- salts and metals -- that do not easily travel through soil. By locating the landfill in the proper hydrogeological setting and/or by using liners and leachate collection systems, both leachates can be prevented from entering groundwater. Because ash leachate is predominantly inorganic, it can be contained with a simple lining system, and is not difficult to treat. Subsequently, the potential for groundwater contamination is much less than from a raw municipal solid waste landfill.

This has already been demonstrated in other parts of the world: Wurzburg, Germany; Marion County, Oregon; Denmark and

Sweden. In addition, the United States Environmental Protection Agency (EPA) is investigating ash leachate in a joint study with Marion County at the county's Woodburn monofill.

Dust represents another problem at landfills that can be reduced with combustion. Municipal solid waste is a very dusty material. When it is deposited in a landfill, without adequate controls, bits and pieces blow around. The compaction process requires driving large bulldozer-type vehicles over the municipal solid waste until it is compacted, which may increase dust generation. On the other hand, the semi-wet ash is delivered to the landfill and does not result in any fugitive dust. Since wet ash is so dense, it does not require much compaction. Consequently, very little airborne material is released into the environment during ash disposal.

Unlike ash residue, raw waste undergoes biological decomposition during the many years it remains placed in the landfill, volume reduction occurs gradually over time; it is an ongoing, slowly-evolving process. This continuous shrinkage causes the surface of the landfill to subside and requires extensive reworking of the soil. The subsidence also results in increased infiltration of rain water, which in turn produces more leachate. An ash landfill, however, becomes a stable mass within days of initial placement and requires only simple maintenance of the final cover. No subsidence whatever occurs. Modern waste-to-energy facilities reduce the volume of material and mitigate the potential public health problems associated with the ongoing land disposal of municipal solid waste.

#### PHYSICAL AND CHEMICAL PROPERTIES OF ASH

Unprocessed municipal solid waste contains varying percentages of inert materials that eventually become the ash or solid residues upon combustion in a resource recovery facility.

The volume reduction achieved by combustion increases the concentration of the metals in the ash versus the unburned municipal solid waste. The total amount of metals, however, have not increased. The increase in concentration cannot be any higher than the weight reduction (that is a 4-to-1 weight reduction of waste to ash, or 80 percent, increases concentration by a factor of five). Regardless of whether it is municipal solid waste that is landfilled, or ash from a resource recovery facility, the total amount of metals going in will remain the same. No data is available to suggest that the combustion process changes the properties of the metals to make them any more dangerous. On the contrary, leachate data from raw solid waste landfills suggests higher metal mobility because of biological activity and the presence of organic acids. From the available data on ash collected by Ogden Martin, the following list shows average metal concentrations in categories of major, minor and trace constituents:

### METALLIC ASH CONSTITUENTS

<u>MAJOR</u>	<u>%</u>	<u>MINOR</u>	<u>%</u>	<u>TRACE</u>	<u>%</u>
Aluminum	3	Copper	0.1	Arsenic	0.003
Calcium	8	Lead	0.2	Barium	0.05
Iron	10	Manganese	0.6	Cadmium	0.003
Sodium	6	Molybdenum	0.1	Chromium	0.02
Silica	30	Potassium	0.4	Mercury	0.0006
		Titanium	0.7	Selenium	0.004
		Zinc	0.3	Silver	0.0006

In addition to the metals listed above, ash contains many other elemental compounds that make up the bulk of the material. Oxygen, sulfur, chlorine, which occur as oxides and sulfates, and chlorides account for more than 30 percent of the ash. There are also trace elements that can be detected at the lowest detection levels of modern analytical chemistry. This is also true of organic compounds, other than unburned or fixed carbon.

Based on an average of available data, the physical properties of ash can be tabulated as follows:

<u>Density</u>	one or two tons per cubic yard
<u>Specific gravity</u>	approximately one to three
<u>Moisture</u>	15% to 25%
<u>Grain Size</u>	10% similar to clay 40% similar to sand 30% similar to gravel 20% larger than gravel
<u>Permeability</u>	$10^{-3}$ to $10^{-4}$ cm/sec as landfilled
<u>Texture</u>	Wet concrete-like or wet sand and gravel-like

### ASH MANAGEMENT AT AN OPERATING FACILITY

The Martin GmbH mass-burn design encompasses the closed-system concept to handle the process residue streams so that no employees, visitors or nearby residents will be exposed to airborne dust. All hoppers from the boiler to the air pollution control device have sealed, air-locked valves that transfer the fly ashes and/or dry scrubber reagent and reaction products to sealed screw or drag conveyors. In turn, these conveyors deliver all of the combined fly/bottom ash stream to the sealed discharger at the lower end of the furnace; just below the level where the bottom ash drops off the stoker grate.

As the bottom ash falls down the ash discharger chute into the quench water bath, the fly ash is captured, moistened and combined with the bottom ash before it is hydraulically discharged by a ram. The ram extrudes and dewateres the ash prior to dropping it on the conveyor system. At this point, the ash has the consistency of wet concrete.

As it moves outside the boiler building, an enclosed conveyor transfers it to the ash storage building or another area to await transfer to covered, water-tight trucks or containers for eventual utilization or landfill burial. At any point, where the

employees or the public may be exposed, the ash system is either sealed or the ash moistened and enclosed in a building or conveyor.

#### ASH CHARACTERIZATION

Since the state environmental regulatory agencies have difficulty accurately predicting the potential adverse effects of burying waste, these governmental agencies typically have a two-pronged approach to the problem. Specific types of wastes, with high potential for causing environmental harm, are listed as "hazardous".

Secondly, regarding other wastes including ash, these agencies have established four broad characteristics to use in identifying waste that must be managed as "hazardous waste". The characteristics include ignitability, corrosivity, reactivity, and extraction procedure toxicity. This last characteristic is often applied to municipal waste combustion ash. The EP toxicity characteristic is determined by a devised laboratory test that attempts to mimic the landfill environment and disposal scenario of five percent unknown waste and 95 percent raw municipal waste in an unlined landfill.

Many problems occur with tests that take a small sample of waste, subject it to a laboratory analysis and then use the results to predict how larger quantities of hypothetical waste will really behave. For example:

- o How do you obtain representative samples?
- o How do you prepare these samples for laboratory analysis?
- o What type of test is most appropriate for the manner in which the waste will be managed?
- o How should varying results be interpreted?

Researchers in the waste management field have proposed additional tests that may be more appropriate. Currently, however, the ultimate test is one of sampling the actual leachate/groundwater from the managed (or mismanaged) land disposal unit.

The EP Toxicity test is the current test method employed by the EPA to determine if an unknown waste that may be subject to leaching in a landfill should be managed as a "hazardous waste". The Toxic Characteristics Leaching Procedure (TCLP) and other tests have also been proposed (published in the Federal Register and implemented for certain regulations as the land ban for certain hazardous wastes). Indeed, after much consideration, some agencies have eliminated or exempted waste-to-energy ash from laboratory testing.

Before considering what test should be used for regulatory or research purposes, a method must be available to obtain a representative sample. One cannot obtain an accurate sample by simply "grabbing" a small portion of the ash residue from a resource recovery facility, test it and declare that it is "hazardous". There is a very deliberate and detailed sampling procedure mandated by Section 1 of SW-846 (Test Methods for

Evaluating Solid Waste: Physical/Chemical Methods, U.S. EPA, Publication #SW 846, July 1982 as amended). Only by following these guidelines can one attempt to obtain representative ash samples and conclude within a certain degree of confidence, that the ash does or does not exhibit the characteristic of EP Toxicity, that it is hazardous by the TCLP, or by any other leaching procedure.

Even when Section 1 is closely followed and an extensive sampling program is performed, it may not necessarily provide representative samples. To adequately state the results within a 90 percent confidence limit, the number of samples cannot be determined until all the results of the samples are analyzed statistically. After following the sampling guidelines in SW-846, a difficult task of sample preparation must be applied.

The preparation methods in SW-846 result in the collection of many samples each weighing 50 to 100 pounds. These must be reduced in size to pass through a nine millimeter sieve. Typically, this step has been omitted in most ash sampling programs. The samples are usually screened and the subset of the sample, which passes through the nine millimeter screen, is the portion subjected to laboratory analysis. This, however, results in an unrepresentative sample in violation of the procedures in SW-846. Furthermore, some laboratories have failed to maintain the sample's moisture content or have completely dried the samples to ease preparation.

Once a representative sample is obtained, there are many laboratory tests that can be performed to collect data about it. This data is then used to determine leaching characteristics. Different official procedures require different tests for various characteristics that the ash exhibits. These tests include:

1. Percent Moisture
2. Particle Size and Structural Integrity
3. pH
4. Selected Anions (negatively-charged ions) and Cations (positively-charged ions)
5. Total Metals
6. Organic and Carbonaceous Material
7. Leaching or Extraction Tests, such as the EP Toxicity Test, the TCLP Test, a De-Ionized Water Leaching Test, a Solid Waste Leaching Procedure Test or Column or Lysimeter Tests

The extraction fluids are analyzed by atomic absorption or inductively-coupled argon plasma (ICAP). The analytical data are then examined for quality assurance/quality control and treated statistically to determine the results and confidence limits.

As rigorously as possible, OMS has followed the procedures in Volume 40 C.F.R. 261.24 and SW-846 in sampling and analyzing the ash from its operating facilities located in: Tulsa, Oklahoma; Marion County, Oregon; Hillsborough County, Florida; Bristol, Connecticut and Alexandria, Virginia. The ash did not exhibit the characteristic of hazardous waste in any instance.

The TCLP which is under development appears to be more consistent in yielding results. Sample collection and preparation problems are the same as with the EP (grinding portions of the ash that will not break down in the landfill). Consequently, like the EP, the results never represent behavior in the real environment because acid is poured through the ash, rather than dripped through it, over an extended period of time. Although the consistency of the data resulting from leachate procedures in the EP toxicity test have been improved with the TCLP, neither test produces data that simplifies what actually leaches from ash. A more accurate procedure for determining leaching characteristics would involve testing the actual leachate from an ash fill, especially a monofill that contains only waste-to-energy ash residue.

Test data for ash residue from OMS plants has been submitted to the EPA and state regulatory agencies. Lead and cadmium represent the only metals that occasionally show levels higher than the regulatory threshold in some limited samples. To simplify the following discussion, only lead will be addressed. When presenting the EP Toxicity or TCLP data, the value that is important is the upper limit of the confidence level. It is this value that is compared to the regulatory threshold and not individual sample values, even if they exceed the regulatory threshold. The most recent testing of the ash at Tulsa shows the following results for the upper band of the confidence limit on three separate analyses for EP toxicity and are for TCLP:

	<u>EP Toxicity</u>	<u>TCLP</u>	<u>Regulatory Threshold</u>
Lead (mg/l)	2.8	3.0	5.0

for the upper bound of the confidence limit. Of course, this means the average values were actually less.

For Marion County, a comprehensive testing program was performed in November 1986 during the facility's energy and capacity tests. The Marion County data is particularly significant because this facility is the first in the United States using a dry scrubber and high efficiency particulate control equipment (fabric filter baghouse) on a resource recovery facility. The data from Marion County's ash yielded the following results for the upper bound of the confidence limit on three separate analyses for EP toxicity and one for TCLP:

	<u>EP Toxicity</u>	<u>TCLP</u>	<u>Regulatory Threshold</u>
Lead (mg/l)	3.4 to 4.9	0.9	5.0

The tests conducted on the Bristol, Connecticut, facility, which has the same air pollution control configuration as the Marion plant, yielded similar test results. The upper bound of the confidence limit for lead was 2.5 mg/l.

OMS has performed, or has cooperatively studied with regulatory agencies, other tests on the ash from its facilities. With regard to the EP Toxicity organic substances, the levels are below the detection limit. Portions of the ash (i.e., the fly

ash) were analyzed by the EPA and determined to contain among the lowest levels of dioxin ever found in fly ash. These extremely low levels correspond to the very low levels of dioxin emissions achieved from the Martin GmbH stoker combustion system without any back-end pollution control, as well as from the stack gases with pollution control.

Limited leachate data is available from existing ashfills and sanitary landfills. The lead levels are lower for ash monofills, but results from both are far below the regulatory threshold of 5 mg/l. The data are as follows:

	<u>Lead (mg/l)</u>
Sanitary Landfill Leachate (Malcolm Pirnie)	0.2 to 1.0
Ashfill Leachate (Malcolm Pirnie)	<0.05 to 0.13
Wurzburg Ash Monofill Leachate	0.002 to 0.05
Sanitary Landfill Leachate (Malcolm Pirnie)	0.2 to 1.0
Ashfill Leachate (Malcolm Pirnie)	<0.05 to 0.13
Wurzburg Ash Monofill Leachate	0.002 to 0.05
*Marion, Ore. Ash Monofill Leachate	0.1 to 0.6
Scandinavian Monofill Leachates	0.001 to 0.1
**EPA Data (Four Sites)	<0.005 to 2.92

\*Oregon Department of Environmental Quality

\*\*U.S. Environmental Protection Agency data for Four Anonymous Sites

Measurements for lead and the seven other heavy metals in leachate from a landfill, in which both ash and raw solid waste have been placed (co-disposal), are well below the regulatory threshold(s), and have remained low over time. These lead levels were measured for the 1983-1987 testing of this co-disposal landfill leachate (in mg/10.10, 0.19, 0.06, 0.33 and 0.12). When ash is buried with unprocessed municipal solid waste, the collected leachate still has a very low lead level.

More importantly, data recently collected by the U.S. EPA indicate that proper monofilling of ash has a negligible impact on the environment. The EPA has initiated a long-term study at the Marion County, Oregon, ash monofill. The first year's data show the leachate contained from 0.011 to 0.025 mg/l of lead. To determine if fugitive ash is a problem, soil samples were taken from around the monofill. The lead content of the soil both upwind and downwind of the facility contained 0.01 ppm of lead. Fifty-three (53) ppm lead was detected in the soil along Interstate 5, a few hundred meters east of the site. Background sample of soil east of the Interstate and far west of the facility showed levels of lead in the range of 0.014 to 0.017 ppm.

The EPA also tested for dioxins and furans in the soil around the monofill. The results were similar to tests conducted for lead. No differences between upwind, downwind, and background. The highest levels detected were along Interstate 5.

#### THE REGULATORY STATUS OF ASH

Because of the changing definition of "hazardous" waste, the regulatory status of municipal solid waste combustion ash has

been subject to debate over the past ten years. Prior to the Resource Conservation and Recovery Act of 1976 (RCRA), ash was primarily regulated by individual states or local jurisdictions as municipal solid waste. It was often approved as cover material for municipal solid waste sanitary landfills.

With the implementation of RCRA and the development of the federal hazardous waste management program, waste classification took on a new meaning. Congress and EPA split up the universe of waste into two categories. Those wastes, subject to management under Subtitle C of RCRA (hazardous wastes), and wastes subject to management under Subtitle D (non-hazardous wastes). Household waste and the ash residue from processing household waste were specifically excluded from Subtitle C.

This meant that household waste and incinerator ash was non-hazardous by definition. Since municipal solid waste, designated for a resource recovery facility, represents a combination of household waste and non-hazardous commercial and industrial waste, exclusion under the federal hazardous waste rules (Subtitle C) was thought to be unnecessary and therefore unavailable. Consequently, it became a requirement for the owners/operators of municipal solid waste combustion facilities to determine if their ash exhibited a hazardous waste characteristic by this difficult and onerous testing method.

When Congress enacted the Hazardous and Solid Waste Amendments of 1984, this regulatory difference between household waste and municipal solid waste ash was clarified. In this law, the ambiguous definition of "household waste" was clarified. The law states that, if a facility takes only household and non-hazardous commercial and industrial waste and has a program to prevent Subtitle C hazardous waste from being accepted, it is not deemed to be generating, treating or otherwise managing hazardous waste. In other words, the ash would not be subject to management as a hazardous waste, and testing to determine its regulatory status would not be required.

When EPA placed the law into the Code of Federal Regulations (CFR), they did not interpret it in the same way as Congress intended. EPA stated that, if the ash was tested and exhibited the characteristic of a hazardous waste, it had to be managed as such. This position has caused a great deal of confusion. If it exhibits a characteristic of hazardous waste, is the ash exempt from requirements to be managed as hazardous since it represents the by-product of municipal household waste? Or, is it to be managed as a solid waste in all cases? EPA is presently re-evaluating its decision, developing a new series of characterization tests to determine the regulatory status of ash, and developing environmentally-sound design criteria for ash burial.

Numerous states have taken similar positions. New York, Massachusetts, Tennessee and others have stated publicly that they believe the congressional clarification applies to the combined ash. The state of Oregon, well-known for some of the toughest environmental standards in the United States, believes the present testing requirements in 40 CFR 261 (which stipulates

performance of the EP Toxicity test and other leaching procedures for hazardous wastes) are invalid for determining ash characteristics and should not be used to determine regulatory status. Other states are taking the same position. All state and federal regulatory agencies that are addressing this subject believe that efficient ash management is essential regardless of the outcome of various characterization tests.

There is no environmental exclusion from testing ash, but what is considered "efficient management" varies across the board nationwide. Consequently, regulators are developing proper ash management criteria for compliance. These criteria focus on prevention of groundwater contamination through the use of lined landfills. While monofilling ash is the most desirable option, it is probably an overly stringent requirement considering that it is unlikely that co-disposal leachate would penetrate a well-designed system, particularly one which incorporates a leachate collecting system as well as the required linings.

Both Congress and the EPA are in the process of further clarifying the regulatory status of ash and developing management standards. In numerous proposed bills, Congress has clearly stated that ash should be managed as a Subtitle D (non-hazardous) waste. In addition, all the bills require some type of lining, leachate collection, and groundwater monitoring systems for ash disposal. It is doubtful that these bills will be voted into law this session of Congress, but legislation as important as this should move in the spring of 1989.

EPA has released draft guidance on the handling, transport, storage, and disposal of ash. This guidance includes recommendations that ash containers and transport vehicles be leakproof and provided with tight coverings; that groundwater monitoring be performed at all ash disposal facilities. These liners and disposal recommendations are as follows:

- For fly ash disposed separately, disposal should be at a monofill with a double liner system.
- For combined ash or bottom ash, disposed of in a monofill, either a composite liner or a clay liner with special environmental or operating features should be used.
- For combined ash or bottom ash codisposed with garbage, a double liner or a composite liner, with pre-disposal ash treatment or source separation to reduce metals content prior to combustion is the preferred method.

#### ASH UTILIZATION

As discussed previously, ash contains many valuable metals and the non-metallic fraction has properties very similar to sand and gravel. These characteristics lend themselves to potential economic benefits. Ferrous and non-ferrous metal recovery using magnets, screens and other mechanical processes is used at many municipal solid waste combustion facilities worldwide. The techniques for recovery of the larger metallic components (e.g., greater than one inch) are well developed. Metals are not recovered on an industry-wide scale in the United States because

of depressed scrap metal markets (i.e., installation and operation of metal recovery equipment is dependent on local scrap metal markets). OMS investigates the local scrap markets to determine the economic viability of metals recovery from all its facilities as they enter commercial operation.

There are many metals in the ash that could only be recovered through complex and laborious processes. Metals such as cadmium, lead, zinc, copper, silver and gold are recoverable by using chemical techniques similar to those used in the minerals industry. OMS is currently investigating the feasibility of recovering these metals from the ash with various industrial concerns and research laboratories.

The major component in the ash is the inert, non-metallic fraction. Because the properties are similar to traditional aggregates, ash is commonly used as a substitute for conventional aggregate in Europe. In the mid-1970s, the Department of Transportation (DOT) researched the potential for use in the construction and maintenance of highways. Today, Marion County is pursuing the same option. In Europe, bottom ash is often used in asphaltic paving material and combined bottom and fly ash in concrete. Screened bottom ash is also used as road bed and common fill material. Perhaps, the best use of ash is as aggregate in Portland cement concrete. Municipal solid waste combustion ash has excellent properties for use in concrete itself; it is pozzolanic, which is to say it forms a weak cement-like matrix. This inherent property could be of interest to concrete block manufacturers. OMS is working with two universities to develop proper screening techniques and mixture proportions for cement blocks. Leachability of metals from the blocks will be an important issue that will require resolution before they are widely manufactured. In addition, OMS and one university are determining the likelihood of leachability of metals from the completed blocks.

There are many potentials for the use of combined ash. While the technical problems associated with the various utilization scenarios can be resolved, the institutional problems are more difficult to address (i.e., markets for the metals and public acceptance of the ash as aggregate). Lessons can be learned from Europe and Japan and other waste product utilization programs. In Japan, ash residue is used to make artificial reefs and man-made islands. Thus far, metals have not entered the food chain and subsequently pose no significant risk to aquatic life or human beings. While the United States may not necessarily need ash islands or reefs, there are many other potential uses that would fulfill material needs in the construction, manufacturing or chemical industries.

#### SUMMARY

Ash is the remaining incombustible residue representing five to ten percent by volume and 15-20 percent by weight of the municipal solid waste stream. It is a biologically inert, dense material that can be managed in a more environmentally sound manner than raw solid waste. Present testing methods do not

adequately simulate what occurs when ash is placed into a controlled landfill unit. As indicated by leachate data from actual ash fills, potential ground or surface water contamination from well-managed ash disposal units does not appear to be a problem. Before uses of combined ash can reach their fullest potential, public awareness and a better understanding of resource recovery ash characteristics is necessary. This can only be achieved through governmental leadership at state and local levels, where community education is most effective.