



Project Summary

Gaseous HCl and Chlorinated Organic Compound Emissions from Refuse Fired Waste-to-Energy Systems

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Testing of the emissions of hydrogen chloride (HCl), chlorinated dibenzo-p-dioxins, dibenzofurans, chlorobenzenes, chlorophenols, polychlorinated biphenyls, and aldehydes was conducted on a water-wall, mass-fired municipal waste incinerator and a refuse-derived fuel (RDF)-fired municipal waste incinerator. The purpose of the testing was to evaluate the measurement methods used for sampling and to determine what differences may exist in the emission characteristics of the two types of units and the effect that this difference would have on the applicability of the methods employed.

Testing of HCl emissions was performed by absorption in four midjet impingers each containing 20 ml of 0.1 N NaOH. Sampling of chlorinated organic compound emissions was conducted using a modified EPA Method 5 sampling train with a cartridge of XAD-2 resin between the third and fourth impingers. Analysis was performed using high resolution gas chromatography/mass spectroscopy.

HCl emissions from the mass-fired incinerator (Site A) exceeded the HCl emissions from the RDF-fired incinerator (Site B) by approximately 45%. Chlorinated organic compound emissions from Site A exceeded those from Site B by factors ranging from 12 to 371. Emissions from both sources exhibited a large variation from test to test; however, isomeric distributions were similar.

The majority of all organic compounds were detected in the back half of the

Method 5 sampling train with the largest overall percentage found in the impinger contents. Chlorobenzenes were the only compounds of which the majority was detected in the XAD-2 resin trap.

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

Introduction

Subsequent to reports in the late 1970's that various incineration processes give rise to emissions of chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs), the United States Environmental Protection Agency conducted preliminary investigations of a resource recovery incinerator, which further indicated the presence of these compounds. The results of this program, which included data of a qualitative rather than quantitative nature, indicated the need for further investigation of the sampling methods used and, as a result, the present program was embarked upon in early 1981.

The purpose of this program was to evaluate measurement methods used for sampling the emissions of CDDs, CDFs, chlorobenzenes, chlorophenols, polychlorinated biphenyls, and aldehydes from water-wall, mass-fired and from refuse-derived-fuel (RDF)-fired municipal waste incinerators. These compounds were of

interest not only because of the potential toxicological properties associated with each, but also because several of these groups of compounds, particularly chlorobenzenes and chlorophenols, have been implicated as precursors to the formation of CDDs, CDFs, and PCBs in the combustion process. The purpose of testing the two different types of incinerators was to determine what differences may exist in the emission characteristics of these types of units and hence the effect these differences would have on the applicability of the method. Water-wall, mass-fired, and RDF-fired incinerators were chosen for the program because they are the two most prevalent types of waste-to-energy systems currently in operation or likely to become operational in the near future. One unit of each type was tested during the program.

In addition to the chlorinated organic compounds, sampling and analysis was conducted for HCl emissions from the two units. This was conducted to evaluate the distribution in the gas stream of the chlorides released from the refuse during the combustion process and the applicability of the manual method.

Site Descriptions

This program consisted of tests conducted at two separate facilities. The first facility, Site "A", is a mass-fired, water-wall, refuse-burning incinerator-boiler that is used to generate steam for various purposes at a nearby research center. The unit burns 100% refuse with no auxiliary fuel at a rate approximately 90,000 to 135,000 kg/day (100 to 150 tons/day). The unit is operated at or near capacity at all times except when firing excessively wet trash.

The second facility that was tested, Site "B", is a Detroit Rotograte Stoker Boiler that produces steam for plant heating. The unit is designed to burn coal, on which it is usually fired. The facility operators are, however, investigating the possibility of switching to refuse-derived fuel as a fuel, and the boiler was fired on 100% RDF during testing. During testing, Site "B" was fired at a rate of approximately 205Kg (225 tons) of RDF per day.

Experimental Method

Sampling Methods

Sampling for HCl concentrations in the exhaust stream was conducted by pulling a sample through a stainless steel probe, through four midjet impingers each containing 20 ml of 0.1 N NaOH, through a diaphragm pump, and finally through a

flow meter, flow control valve, and a dry gas meter.

The sample was drawn at a rate of approximately 2 L/min and sampling was conducted for 30 min, thus, a sample volume of approximately 0.06 m³ was collected. The impingers containing the absorbing solution were submerged in an ice bath during sampling. Following sampling, the impinger contents were placed in labeled sample jars where they were maintained until analyzed on site.

Organic compound sampling was conducted using a modified EPA Method 5 sampling system. This system consisted of a heated glass-lined sample probe with a stainless steel nozzle, a glass fiber filter in a heated glass filter holder with a stainless steel filter support; a Greenburg-Smith impinger containing 100 ml distilled water followed by a modified Greenburg-Smith impinger (dry for mist knockout), both containing 5 cm of 3 to 6 mm diameter glass beads and immersed in an ice bath, a resin cartridge containing 60 g of XAD-2 sorbent resin, and finally an impinger containing 200 to 300 g of silica gel. Sample flow was measured and controlled by a conventional EPA Method 5 meter box. All glassware used in the tests was annealed prior to being taken into the field.

Sampling was conducted isokinetically during all tests. Tests were conducted for 180 and 300 min time periods with sample volumes ranging from 2.5 to 6.8 m³.

Analytical Procedures

HCl analysis was performed by the mercuric nitrate (Hg(NO₃)₂) method, which involves titrating Cl⁻ with a standardized Hg(NO₃)₂ solution using a diphenylcarbazone indicator-acidifier reagent. This method is known to be subject to interference and endpoint masking by the presence of sulfite (SO₃²⁻) and cationic metals in the exhaust stream. In order to alleviate this problem, samples were treated with 3% hydrogen peroxide to eliminate the sulfite interference, and they were passed through a Rexyn 101-H column (a registered trademark of Fisher Scientific) to eliminate the cationic endpoint masking.

The procedures used to separate the halocarbons of interest from the matrices in which they were collected involved solvent extraction with the addition of internal standards of [³⁷Cl₄]-2,3,7,8-TCDD, [³⁷Cl₇]-1,2,3,4,6,7,8-H_pCDD, [³⁷Cl₆]-OCDD, [D₈]-3,3',4,4'-tetrachlorobiphenyl, [¹³C₆]-pentachlorophenyl, and [¹³C₆]-hexachlorobenzene to each sample.

Further sample preparation procedures included acid, water, basic, and further solvent extractions, macro-column elution, and mini-column liquid chromatography. If preliminary GC-MS screening analysis of a sample indicated the presence of potential interfering compounds or other sample matrix constituents that eluted from the GC at very long times, then additional sample clean up or fractionation was required using high performance liquid chromatography (HPLC). The HPLC used for this purpose was a Varian Model 5021 Microprocessor Controlled HPLC equipped with a CDS-111L Data System. Dual Dupont Zorbax ODS Columns (25 cm x 0.6 cm I.D.) were employed. Methanol was employed as the mobile phase in the isocratic mode.

The instrumentation utilized to perform the quantitative analyses for the chlorocarbons of interest was comprised of a gas chromatograph-mass spectrometer-data system (GC-MS-DS) that included a Perkin-Elmer Sigma III Gas Chromatograph coupled through a specially modified interface to a Kratos System. This analytical system falls in a class of analysis referred to as "high resolution gas chromatography/high resolution mass spectroscopy" (HRGC/HRMS). The gas chromatograph was equipped with a split/splitless injector and a wall-coated open-tubular fused-silica capillary column. The interface mentioned above included provision for both direct admission of the column effluent into the mass spectrometer source as well as admission of the column effluent via a single-stage, all-glass jet separator. The interface was modified to minimize peak broadening due to excessive dead volume and to optimize the temperature throughout the interface. The mass spectrometer was operated in the multiple ion monitoring mode under the control of the computer-based Kratos DS55SM data system. Elaborate programs for the DS55SM data system were developed that permitted rapid, automated retuning of the mass spectrometer during analysis of a sample extract and thus 20 to 30 separate ion masses were sequentially monitored during an analysis. Each of the groups of chlorocarbons of interest (CDDs, CDFs, chlorobenzenes, chlorophenols, and PCBs) were analyzed separately.

Results

The testing conducted on the two systems revealed considerable differences in the emission characteristics of the mass-fired, water-wall incinerator and

the RDF-fired incinerator with the emissions from the mass-fired unit higher in all cases. A summary of the emissions from each unit tested is presented in Table 1.

HCl emissions from the mass-fired incinerator (Site A) exceeded the HCl emissions from the RDF-fired incinerator (Site B) by approximately 45%. Chlorinated organic compound emissions from Site A exceeded those from Site B, however, by factors ranging from 12 to 371. The overall distribution of chlorides in the gas streams, which is presented in Table 2, shows that a higher percentage of total chlorides was emitted as HCl from Site B than from Site A thus indicating that combustion was more efficient for the RDF-fired incinerator. This difference may be due to differing moisture contents of the two types of fuel. The RDF was stored in silos, and was never exposed to moisture thus it was very dry when combusted. The fuel for Site A, on the other hand, was often quite wet as it was stored in open areas where it was exposed to rainfall prior to delivery to the plant site where it was stored in a covered pit.

Conclusions

1. The sampling and analytical methodologies used for this project performed well.
2. Chlorinated organic compound emissions were higher from the mass-fired incinerator than from the RDF-fired incinerator.
3. The majority of the CDDs emitted from both units were heptachlorinated dibenzo-p-dioxins.
4. Chlorophenols were detected in the highest concentrations of all types of chlorinated organic compounds evaluated.

Table 1. Summary of Emissions Data

Compound	Site A Emission Rate* (mg/h)	Site B Emission Rate* (mg/h)
HCl	61**	76**
T ₂ CDD	15.3	0.1
P ₂ CDD	19.7	0.1
H ₄ CDD	31.5	0.2
H ₆ CDD	35.4	1.5
OCDD	9.2	0.8
T ₂ CDF	76.5	1.3
P ₂ CDF	35.0	0.5
H ₄ CDF	41.2	0.9
H ₆ CDF	36.5	3.2
OCDF	2.6	0.4
DCLB	56.3	0.3
T ₁ CIB	228.0	5.8
T ₂ CIB	355.0	8.0
P ₂ CIB	551.0	39.9
H ₄ CIB	165.0	21.6
T ₁ CP	2,444.0	149.0
T ₂ CP	1,127.0	215.0
P ₂ CP	588.0	352.0
T ₁ CB	14.6	--
T ₂ CB	8.4	--
P ₂ CB	1.7	--
H ₄ CB	0.9	--
Aldehydes	166.0	9.4

* Average of all tests at each site

**HCl in kg/h

Table 2. Chloride Distribution in Gas Stream

Compounds	Percent of Total Chlorides in Gas Stream (%)	
	Site A	Site B
HCl	99.92237	99.992178
Chlorophenols	0.05233	0.007650
Chlorobenzenes	0.02136	0.000079
Chlorinated Dibenzo furans	0.00235	0.000064
Chlorinated Dibenzo-p-Dioxins	0.00140	0.000029
Polychlorinated Biphenyls	0.00019	0.000000
	100.0	100.0

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The complete report, entitled "Gaseous HCl and Chlorinated Organic Compound Emissions from Refuse Fired Waste-to-Energy Systems," (Order No. PB 86-145 661/AS, Cost: \$11.95, subject to change) will be available only from:

National Technical Information Service
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Springfield, VA 22161
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