

DEVELOPMENT OF A LABORATORY METHOD FOR
ESTIMATION OF HYDROGEN CHLORIDE EMISSION POTENTIAL
OF INCINERATOR FEED MATERIALS

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ABSTRACT

A laboratory method has been developed to provide an estimate of the amount of hydrogen chloride gas that will form during incineration of a waste. The method involves heating of a sample of the waste to 900° C in a tube furnace, removal of particles from the resulting gases by filtration, collection of hydrogen chloride gas in a water-filled impinger, and measurement of the collected HCl as chloride using ion chromatography. The original goal of this project was to develop a method which would allow accurate determination in the laboratory, of the amount of HCl formed upon full-scale incineration of a given hazardous waste feed material. Although the laboratory equipment and procedures performed as designed, the data show that results are very sensitive to materials of construction, availability of hydrogen, and probably other factors difficult to translate accurately from laboratory to full-scale equipment. In particular, the incomplete and variable conversion of inorganic chlorine compounds upon incineration makes estimation of HCl release during incineration of a real waste highly unreliable. This same variable conversion of inorganic chlorides also makes use of any so-called total organochlorine analysis results extremely undependable for estimation of HCl emissions. It is recommended that the current interim procedure of using total chlorine in the waste feed to estimate worst case emissions be carried on as the permanent procedure. As specified in the interim procedure, sampling for HCl before and after the scrubber will be required for efficiency determination.

Introduction

Permitting procedures for hazardous waste incinerators and, more recently, those for hazardous waste burning boilers and industrial furnaces (BIF), require information concerning the concentration of chlorine in waste feed streams(1,2). This information is used to estimate hydrogen chloride (HCl) emissions produced upon combustion of the waste. The estimated amount of HCl has three important uses. The first use is to compare with permissible emission limits for a decision concerning the need for control technology. The second use is to set permit limits on the concentration and feed rate of waste to keep HCl production within the operating envelope defined by the trial burn. The third use of the estimated amount is to calculate the HCl feed to the scrubber or other control device for purposes of scrubber efficiency determination, after sampling the HCl emissions on the downstream side of the device.

Previously, it was concluded that these three purposes could best be served by analyzing the waste for "total organic chlorine." The key concept inherent in this logic was that the chlorine-containing organic compounds would convert efficiently to HCl upon combustion, and that inorganic chlorine would undergo no significant conversion. With further experience and upon further consideration, it became apparent that there were two major problems with the "total organic chlorine" approach.

The first of these problems was that there was no reliable analysis method for "total organic chlorine" except in very simple or well known mixtures. Most reported, and many unpublished, methods for "total organic chlorine" depend on a preliminary extraction step to separate the "organics" into one liquid phase and the "inorganics" into an aqueous phase. Unfortunately, such a simple scheme fails in most cases. Many water soluble organic compounds apportion into the water phase, and numerous inorganic compounds and complexes extract into non-aqueous solvents with high efficiency.

The second major problem with the "total organic chlorine" approach is that a significant number of inorganic compounds and inorganic complexes can be expected to decompose or otherwise react, upon heating to typical incinerator temperatures. Many of these reactions can logically be expected to produce HCl as one of the products. Any method used for estimation of HCl production upon incineration should certainly include that produced from both organic and inorganic sources.

Thus, it was apparent that no reliable method of measuring "total organic chlorine" content was available, and that it would be an inadequate quantity for the intended use even if it could be determined. Clearly, a different approach was needed. The most nearly acceptable method available for measuring HCl emission potential was the TOX procedure used for wastewater (3,4). The method was designed for analysis of water samples, and includes sorption of the organic halides onto activated carbon for separation from inorganic salts and the water sample matrix. Following sorption and rinsing, the carbon is combusted, and the combustion products are analyzed for halides. However, the carbon sorption step is inappropriate for most waste samples, and TOX equipment operators were not

optimistic about direct waste combustion in the instrument yielding meaningful results. Major concerns were stated about capacity, heating rate, splattering of combustion materials, and possible salt carry-over.

It was then decided that a tube furnace combustion device connected to appropriate sampling equipment would be designed, constructed, and evaluated for use in estimating HCl emission potential. In the interim, it was recommended to regulators that total chlorine measurements in waste should be used for a conservative estimate of HCl production and for setting waste feed rate requirements, but not for estimating HCl on the upstream side of a scrubber. The rationale for this recommendation is explained in the conclusions section of this article.

Preliminary test results were reported previously, and an EPA report was published containing complete experimental results and detailed procedural and equipment descriptions (5,6). This paper summarizes the complete experimental work and interprets the results in light of related papers recently discovered in the combustion and process literature (7,8).

Experimental

The experimental approach consisted of heating a waste sample in a tube furnace, cooling effluent gases to 120°C, filtering the gases at 120°C to remove any chloride containing particulate matter, collecting HCl in a water-filled impinger, collecting chlorine in an impinger filled with sodium hydroxide solution, and measuring chloride ion in the impinger solution by ion chromatography with conductimetric detection.

Figure 1 is a schematic drawing of the apparatus used to carry out the experiments. Key components included a sample injection assembly, a tube furnace, a heated filter box with filter holder, and sample collectors. The injection assembly consisted of a rod with a sample boat on one end and a piece of magnetic material attached to the other end. The boat mechanism and the furnace tube were constructed of quartz for some of the experiments and Inconel 600 (Inconel is a trademark of the International Nickel Co., Inc.) for others. A small magnet was used to slide the boat into the 0.5 in. ID furnace tube, and to withdraw it after each sample had been heated. The furnace zone was inside a quartz or Inconel combustion tube that was heated in the tube furnace. Waste samples were volatilized and thermally oxidized in the furnace zone. A thermocouple was used to determine temperature profiles of the furnace zone at tube-center temperatures of 400°C and 900°C. The profiles indicate that (1) the furnace zone was maintained at the desired temperature setting for at least 1 in. on either side of the center and (2) the temperature of the gas stream at the exit of the tube furnace was greater than 100°C. The latter condition prevented condensation of water vapor during transfer of gases to the heated filter zone, which was located immediately downstream from the furnace zone. The filter apparatus consisted of a quartz-fiber filter supported by a perforated Teflon disk and was used to remove particulate material from the gas stream. The entire filter apparatus and associated connectors were housed in an insulated box and maintained at a temperature of 120°C to prevent condensation.

Sample collectors were located immediately downstream from the heated filter zone. The filtered gases were bubbled through two midget impingers connected in series. The first impinger contained deionized water to remove gaseous HCl; the

second impinger contained 0.1 N NaOH solution to remove any chlorine gas present in the gas stream.

The heating and sampling procedure for each sample consisted of eight steps: (1) the impingers were attached; (2) the air flow, which served as a sampling carrier as well as a combustion oxygen source, was turned on; (3) the gas flow path of the apparatus was tested for leaks; (4) the waste sample was injected into the boat; (5) the boat was moved into the furnace zone; (6) after 15 min., the impingers were disconnected; (7) after an additional 15 min., the boat was removed from the furnace zone; and (8) at the end of 30 additional min. (60 min. from the beginning of step 5), the air was turned off. These steps were repeated for each sample injection.

Water samples from the first impinger were diluted to 25 mL and analyzed on a Dionex Model 14 Ion Chromatograph with conductimetric detection. A quaternary ammonium resin separator column and an anion fiber (acid form) suppressor column were used for the separation. A bicarbonate/carbonate buffer solution was used as the eluent. The conductivity meter had a detection limit of 0.01 ppm Cl^- .

The compounds selected for use in synthetic wastes were methylene chloride and dichlorobenzene, both organohalogen compounds; ferric chloride, a predominantly molecular inorganic compound; and sodium chloride and potassium chloride, two very ionic inorganic compounds. Table I gives the composition and chlorine concentration of the synthetic wastes used in the study. Inorganic compounds were dissolved in water, and the organic compounds were dissolved in ethanol.

Four different test atmospheres were investigated: (1) 100% zero grade air, (2) zero grade air containing 0.5% propane, (3) zero grade air containing 2.4% water vapor, and (4) zero grade air containing 5.0% water vapor. The last three atmospheres were investigated to determine if the presence of a hydrogen-containing species would affect the recovery of inorganic chlorine as HCl.

An airflow of 200 mL/min. was used to sweep material through the furnace tube and sampling train. This flow rate gave a residence time of 3-4 sec. in the hottest part of the tube. At the 900°C setting, residence time in the region heated above 700°C was 8-10 sec. For a more detailed description of equipment and procedures, refer to the EPA report (6).

Results and Discussion

The recovery results of a preliminary set of runs is shown, along with waste composition, in Table I. The test atmosphere for this run was 100% zero grade air, and the furnace zone temperature was 900°C. Conversion efficiency to HCl was high for organic compounds and generally low for inorganic chlorides, although the KCl conversion was higher than expected.

To provide more favorable conditions for inorganic chloride conversion, water or propane was added to the gas stream in a test series summarized in Table II. All runs were carried out at furnace temperature of both 900°C and 1000°C. The concentrations of propane and water vapor for this series gave approximately the same concentration of hydrogen in the test atmosphere and resulted in very similar recoveries of HCl. Increasing the water vapor concentration to 5.0% had no appreciable effect on recovery of HCl.

Conversion of NaCl to HCl at the efficiencies shown in Table II was surprising, since NaCl was assumed to be the most thermodynamically stable form for the thermally activated chlorine to assume upon cooling to room temperature. One possible explanation for this behavior was that a reaction was occurring in the hot zone, which removed major portions of the activated sodium atoms from the material balance. That, in turn, would favor HCl formation when sufficient hydrogen was present.

Further support for this hypothesis was observed in the form of degradation of quartz components when water vapor was present. The tube and boat took on a frosted appearance, and a white crust formed on the inside of the tube. The boat was brownish-red at the end of the ferric chloride runs, presumably because of the presence of iron in the degraded quartz. The evidence suggests that sodium and iron ions remained, perhaps as silicates, on the walls of the tube and boat following conversion of chlorides to HCl.

The presence of significant amounts of HCl gas in the sample stream during this series was confirmed with an HCl monitor based on gas-filter correlation infrared spectroscopy. This evidence, plus a 14:1 ratio of chloride to sodium ions found in the sample collector liquid, eliminated any concern that the chloride found in the sample collectors was caused by NaCl migration through the entire experimental apparatus.

Since degradation of the quartz apparatus was more severe at 1000°C than at 900°C, and HCl recoveries were similar at the two temperatures, all subsequent experiments were carried out at 900°C.

It was observed that the quartz was involved in some form of chemical reaction during the experiments, and it was suspected that the reaction played a key role in promoting HCl formation. Therefore, a series of runs was conducted using a furnace tube and sample boat constructed of Inconel 600 to observe any differences in recovery caused by the change in construction materials. Inconel 600 contains 76.0% nickel, 15.5% chromium, and 8.0% iron.

The Inconel tube withstood the 900°C temperatures of the furnace without sagging; however, the interior of the tube became discolored after several runs. The surface of the Inconel boat mechanism slowly deteriorated during the study. The boat eventually became pitted and cracked, and material resembling iron filings collected in the tube. This material was attracted to a magnet, while the Inconel components were not.

Table III presents the results of experimental runs conducted at 900°C with quartz components and with Inconel components, with and without water vapor present. The test solutions are the same as those shown in Table I. The following observations may be made about the results in Table III.

1. In all cases, hydrogen deficient compounds gave higher conversion to HCl when water vapor was added and, except for FeCl₃, gave very little recovery when water vapor was not added. Water in which the KCl and NaCl were dissolved and injected was thought to evaporate or boil so early in the test sequence that it was not available as a hydrogen source for critical stages of the test. Perhaps the small recoveries that were achieved in the zero air tests were the result of a small portion of this solution water still being available.

2. Even without added water vapor, the FeCl_3 was converted to HCl with 76.8% efficiency. Since it is not possible to form HCl without a hydrogen source, some form of hydrogen capture was operative in the FeCl_3 conversion that was absent during NaCl and KCl tests. One possibility is that the hygroscopic nature of FeCl_3 and its ability to form a hexahydrate might delay test solution water loss just enough for a higher concentration of the water to participate in conversion than in the NaCl and KCl tests.
3. Methylene chloride conversion was lower with water vapor present in the quartz test equipment, but was higher in the Inconel apparatus. It is possible to speculate somewhat about reasons for the Inconel results, but the lower yield in quartz is puzzling. The 75.0% value given is the result of six injections which produced a data set with only a 3% relative standard deviation.

In the absence of unexpected effects, a recovery of very close to 100% would be expected when methylene chloride is combusted, whether in quartz or Inconel. Obviously, some unexpected effects were at work during the test series. Since the methylene chloride in Inconel series showed recovery patterns similar to NaCl or KCl in quartz, perhaps some undefined reaction caused a hydrogen deficiency. Since CH_2Cl_2 only contains the minimum amount of hydrogen for HCl formation, the effect would be more critical than during combustion of a more hydrogen-rich compound. What the hydrogen consuming mechanism might be is not apparent, although the degradation of the Inconel equipment certainly shows that chemical reaction of some sort had occurred.

One obvious, but probably incorrect, explanation for low HCl recoveries from the Inconel equipment would be reaction of the HCl with the metallic surface. This seems unlikely, since the NaCl runs show an increased recovery in metal equipment rather than a decrease.

4. NaCl conversion to HCl was higher in Inconel equipment, especially with water present. Two of the three runs yielded recoveries of better than 83%, but one was only slightly higher than the quartz run.

Approximately a year after the EPA report(6) summarizing this project had been published, two earlier papers by Uchida, et. al.(7,8) were discovered. These papers report that production of HCl from inorganic chlorides during combustion in municipal incinerators is thermodynamically possible, and give results of tube furnace experiments similar to those reported in this article. Their experiments were carried out in alumina equipment, but various materials including silica, alumina, and iron oxide were added to the NaCl in the reaction boat. Residual HCl formation when the boat contained only NaCl was explained by reaction with alumina surfaces of the tube and boat. Conjugate reactions were hypothesized to explain the interaction of the various metal oxides with the basic HCl formation reaction.

It is not possible to make direct quantitative comparisons between the data reported here and that of Uchida without considerably more effort than is warranted, but the trends in the data are very consistent between the two studies which tend to strongly support each other.

The effect of increased water in the vapor phase in the current work levels off

at lower water concentrations than reported by Uchida, probably because much smaller amounts of NaCl were injected into the furnace in the EPA study. Uchida clearly shows that the presence of silica or alumina greatly increases HCl production from NaCl compared to that when no metal oxides are available. He hypothesizes formation of complex silicates which effectively remove the sodium ion from the material balance and promote HCl formation. This interpretation is in complete agreement with the explanation and data given earlier in this article.

Conclusions

The results of this study have shown that the formation of hydrogen chloride from waste incineration depends on the nature of the waste, the presence of hydrogen in the gas stream, and the composition of the walls and other surfaces in the furnace zone. Reasonable explanations have been discussed for some of the increases and decreases in conversion efficiency observed under different conditions, but other observed effects remain unexplained.

From a practical standpoint, these data show that the incomplete and variable conversion of inorganic chlorine compounds upon incineration makes estimation of HCl release during incineration of a real waste highly unreliable. A complex system of reactions and interactions with waste feed, fuel, materials of construction of the hot zone, temperature, and probably residence time makes any simulation likely to be undependable.

Because of the unreliable nature of any waste test method-based HCl emission estimates, the interim procedure described in the introduction is recommended as permanent. That is, a total chlorine measurement should be used for a conservative estimate of HCl production for setting waste feed rates and approximating uncontrolled emissions, but not for estimation of HCl levels on the upstream side of a control device. The latter situation differs from the other two since the HCl value is used in the denominator of the efficiency calculation. A high estimate for HCl thus makes control device efficiency appear higher than the correct value.

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Disclaimer

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Table I. Synthetic Wastes and Recoveries

<u>Chlorine Source</u>	<u>Chlorine Content, %</u>	<u>Chlorine Recovery, %</u>
NaCl	5.8	0.6
KCl	5.6	8.4
FeCl ₃	4.1	*
C ₆ H ₄ Cl ₂	6.6	85.5
CH ₂ Cl ₂	5.5	103.5

*Not determined in preliminary test.

Table II. Recovery from Sodium Chloride

<u>Zero Grade Air Containing</u>		<u>Recovery, %</u>	
<u>Propane</u>	<u>Water</u>	<u>900°C</u>	<u>1000°C</u>
No	No	0.6	5.1
0.5%	No	30.7	48.5
No	2.4%	38.5	38.5

Table III. Recovery of Chlorine as HCl at 900°C

<u>Chlorine Source</u>	<u>Water Vapor Conc., %</u>	<u>Quartz: Recovery, %</u>	<u>Inconel: Recovery, %</u>
CH ₂ Cl ₂	0	103	2.6 1.0
	2.4	75.0	35.6
			40.6 64.1
NaCl	0	2.0 0.55	5.0
	2.4	38.5	45.4
			83.1 83.4
KCl	0	0.56	1.8
	2.4	23.7	18.6
FeCl ₃	0	76.8	5.2
	2.4	92.8	68.1

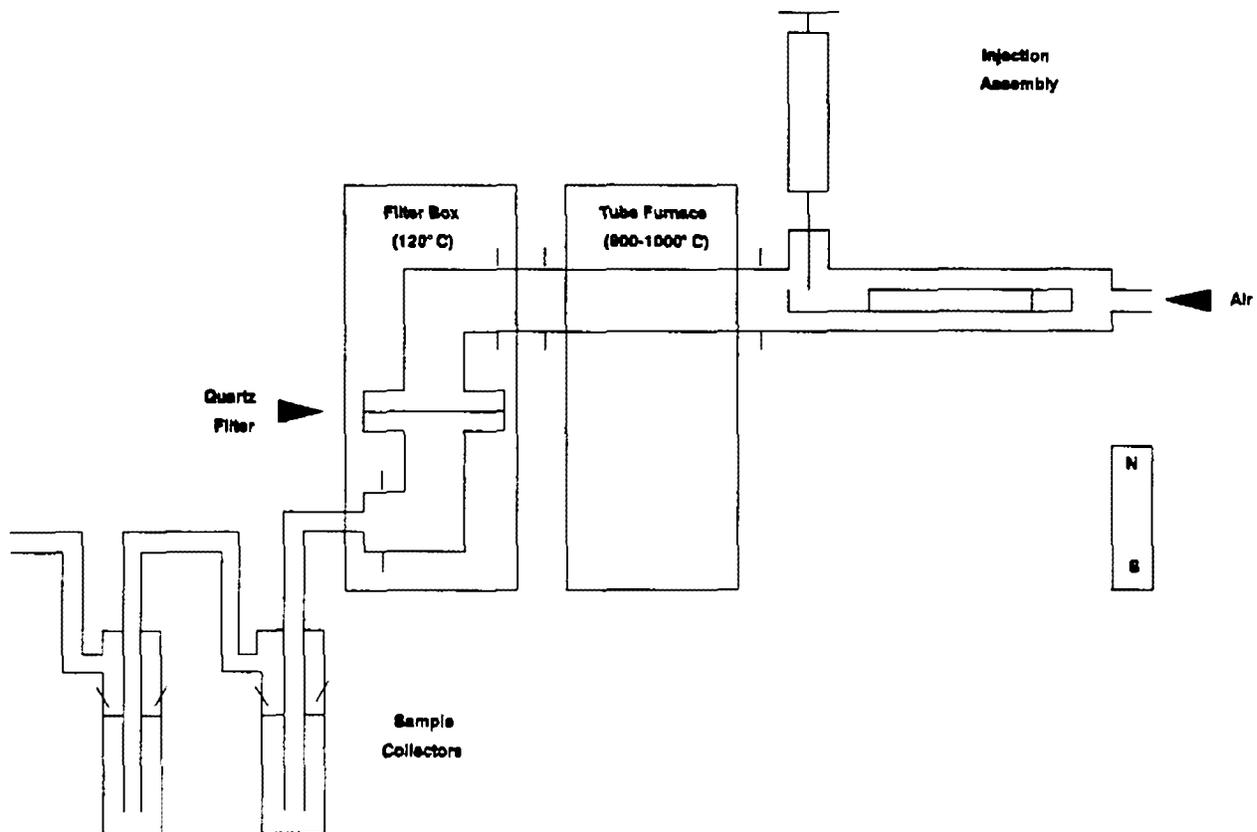


Figure 1. Laboratory apparatus used in the study.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

A laboratory method has been developed to provide an estimate of the amount of hydrogen chloride gas that will form during incineration of a waste. The method involves heating of a sample of the waste to 900° C in a tube furnace, removal of particles from the resulting gases by filtration, collection of hydrogen chloride gas in a water-filled impinger, and measurement of the collected HCl as chloride using ion chromatography. The original goal of this project was to develop a method which would allow accurate determination in the laboratory, of the amount of HCl formed upon full-scale incineration of a given hazardous waste feed material. Although the laboratory equipment and procedures performed as designed, the data show that results are very sensitive to materials of construction, availability of hydrogen, and probably other factors difficult to translate accurately from laboratory to full-scale equipment. In particular, the incomplete and variable conversion of inorganic chlorine compounds upon incineration makes estimation of HCl release during incineration of a real waste highly unreliable. This same variable conversion of inorganic chlorides also makes use of any so-called total organochlorine analysis results extremely undependable for estimation of HCl emissions. It is recommended that the current interim procedure of using total chlorine in the waste feed to estimate worst case emissions be carried on as the permanent procedure. As specified in the interim procedure, sampling for HCl before and after the scrubber will be required for efficiency determination.

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