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Research and Development

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# Project Summary

# Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators

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**Laboratory and field studies were performed to develop and evaluate a sampling and analytical technique for measuring hydrogen chloride (HCl) from stationary sources. Studies were conducted in three phases: (1) literature search and development of a candidate sampling and analysis protocol, (2) laboratory evaluation and refinement of the protocol, and (3) field evaluation. A modified Method 6 sampling train was selected for sample collection due to its ease of operation, availability, and cost. An acidified water absorbing solution was identified for collecting HCl in the impingers. The acidified water solution was selected to minimize the potential for diatomic chlorine ($Cl_2$) to interfere with the HCl determination. Ion chromatography was selected as the most suitable technique for the analysis of HCl. The laboratory phase evaluated the HCl collection efficiency of the sampling protocol and the distribution of $Cl_2$ in the sampling train. A preliminary field test was included in the laboratory phase to indicate any further protocol modifications. A ruggedness test was designed to evaluate the effect of six variables that may be encountered when employing the sampling protocol. A field evaluation was conducted to determine the precision and estimate the accuracy of the sampling and analytical protocol. The candidate method was also employed to determine the bias and precision of two HCl continuous emission monitoring systems.**

***This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment 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

The United States Environmental Protection Agency (EPA) is currently regulating emissions of HCl from hazardous waste incinerators under 40 CFR 264.343 to 4 lbs/hr or an HCl removal efficiency of at least 99%. The EPA is also currently considering regulating HCl emissions from municipal waste combustors (MWC's). Several state and local agencies have already set HCl emission limits for new MWC's and are requiring installation of HCl continuous emission monitoring systems (HCl CEMS's) at certain facilities.

To support current and future regulations on HCl emissions, a sampling

and analysis method evaluation study was conducted for the Quality Assurance Division of EPA's Atmospheric Research and Exposure Assessment Laboratory. This method, designed to measure hydrogen chloride emissions from stationary sources, was developed and then evaluated both in the laboratory and in the field. Details of the evaluations are presented including (1) laboratory assessment of the sampling protocol employing gas mixtures of HCl and $Cl_2$, the effect of variations in the sampling train and technique, and the impact of possible analytical interferents; and (2) results of co-located duplicate and quadruplicate-train sampling and continuous emissions monitoring at two municipal waste incinerators.

The study was conducted in several phases. The initial phase involved a literature search which formed the basis for development of the sampling and analytical protocol. The procedures chosen are outlined in the next section and discussed in detail in the draft method for measurement of HCl in stationary source emissions, written in Federal Register format, provided in Appendix A of the report. The remaining two phases consisted of (1) an initial laboratory evaluation, including the collection and analysis of preliminary field samples from a stationary source and a six-variable, one-blank ruggedness test; and (2) a final field evaluation which included comparison of values from the candidate protocol with continuous emissions monitoring values. Conclusions and recommendations are made regarding the application, precision, and accuracy of the proposed method.

## Procedures

The sampling and analytical protocol evaluated in this laboratory and field study was proposed based on a thorough literature search. Candidate sampling methods, absorbing solutions, and analytical methods, as well as potential interferents were reviewed. A modification of the EPA Method 6 protocol was chosen for sampling, and ion chromatography was selected for analysis based on (1) demonstrated speciation of HCl and $Cl_2$ and (2) accuracy of the analytical technique, respectively, and secondarily, the availability of equipment, and universality of sampling and analytical techniques (see Figure 1). Two impingers containing a dilute sulfuric acid solution (0.1 N $H_2SO_4$) are followed by one impinger containing a dilute caustic solution (0.1 N NaOH) to provide high HCl collection efficiency while minimizing $Cl_2$ interference.

In the first phase of the laboratory evaluation, the sampling trains were challenged with various concentrations of HCl and $Cl_2$ at different flow rates. The ability of the absorbing solution to efficiently collect and speciate one gas in the presence of low (zero) to high levels of the other was evaluated. The effect of flow rate on the absorption capacity for $Cl_2$ in the acidic impinger solution was also examined. All impinger samples were analyzed separately by ion chromatography. The concentration of the cylinder gases used were independently verified prior to the testing.

The preliminary field test was conducted primarily to identify any potential problems that might occur with the sampling and/or analytical methods when used at a typical HCl emission source. The samples were taken downstream of acid gas and particulate control equipment at a MWC where an HCl continuous emission monitor was operating concurrently. Dual-train sampling was utilized during the testing to identify the effect, if any, of using stainless steel versus glass probe tips. Comparison of HCl train values with the HCl CEMS values provided information concerning the proposed method's ability to follow trends in HCl effluent levels.

After completion of the initial laboratory and field studies, a ruggedness test was developed to assess the effect on the method of selected variables that may affect actual sampling. The variables, or deviations from standard procedure, chosen for evaluation were low reagent volume, increased impinger pH, longer sampling time, elevated impinger temperatures, higher sampling rate, and elevated $Cl_2$ levels. These six variables plus control blank were combined in an eight-run duplicate sample train test matrix, which allowed the necessary computations to identify which variable(s) had a significant effect on the results.

The final phase of the method evaluation consisted of a field test at a MWC. The objectives of the test included determination of the precision and accuracy of the draft HCl protocol and the bias and precision of HCl CEMS's. A TECO HCl CEMS and a Bran and Luebbe HCl CEMS were installed at the MWC downstream of a lime-slurry spray dryer and a three-field ESP. The bias of the CEMS's and the precision of the protocol were obtained concurrently by conducting relative error test runs using paired sampling trains. The accuracy of the combined sampling and analysis protocol was estimated emplo ing 30-minute test runs consisting dynamic spiking of the sampling trai with HCl cylinder gas. The concentrati of the HCl gas cylinders were determine by independent analysis before and aft the field test. Two additional relate experiments were conducted determine the amount of flue gas C absorbed by the alkaline imping reagent and to compare the HCl resu from the draft HCl protocol to tho obtained using a Method 5-typ sampling train employing an alkali impinger reagent.

## Results and Discussion

The HCl collection efficiency in the fi acidified midget impinger averaged 102 percent for a 442 parts per million (ppr HCl gas mixture sampled at 2 liters p minute (lpm), with the second acidifi impinger collecting only 0.4 percent. F a gas mixture of 221 ppm HCl and 1 ppm $Cl_2$ sampled at 2 lpm, the H collection efficiency for the first acidifi impinger averaged 103.0 percent, wi the second impinger collecting 3 percent. For a 393 ppm $Cl_2$ gas mixtu sampled at 2 lpm, the $Cl_2$ collecti efficiency of the first alkaline imping averaged 88.2 percent, with each of t two acidified impingers collecting 0 percent. For the same gas mixtu sampled at 0.5 lpm, the first tv acidified impingers collected an avera of 3.2 percent and 2.9 percer respectively, with the first alkali impinger collecting 76.0 percent.

There does not appear to be interaction between HCl and C affecting either the HCl collecti efficiency or the retention of $Cl_2$ by t acidified impingers. The sample flow ra appears to affect the distribution of C throughout the train with a higher fl rate reducing the amount of $Cl_2$ retain in the acidified impingers. A higher fl rate does not appear to reduce the H collection efficiency at the levels teste Based on these observations, t acidified midget impinger sampling tra operated at a sampling rate of 2 lp appears to minimize the high H measurement bias caused by $Cl_2$ to le than 5% for the conditions tested.

The preliminary field test indicated t both stainless steel and glass probe ti could be used for HCl sampling. The H emission trends indicated by an install HCl CEMS were reflected by the resu of the manual sampling. The relative high moisture level at the sour combined with extended sampling tim resulted in the first impinger becomi

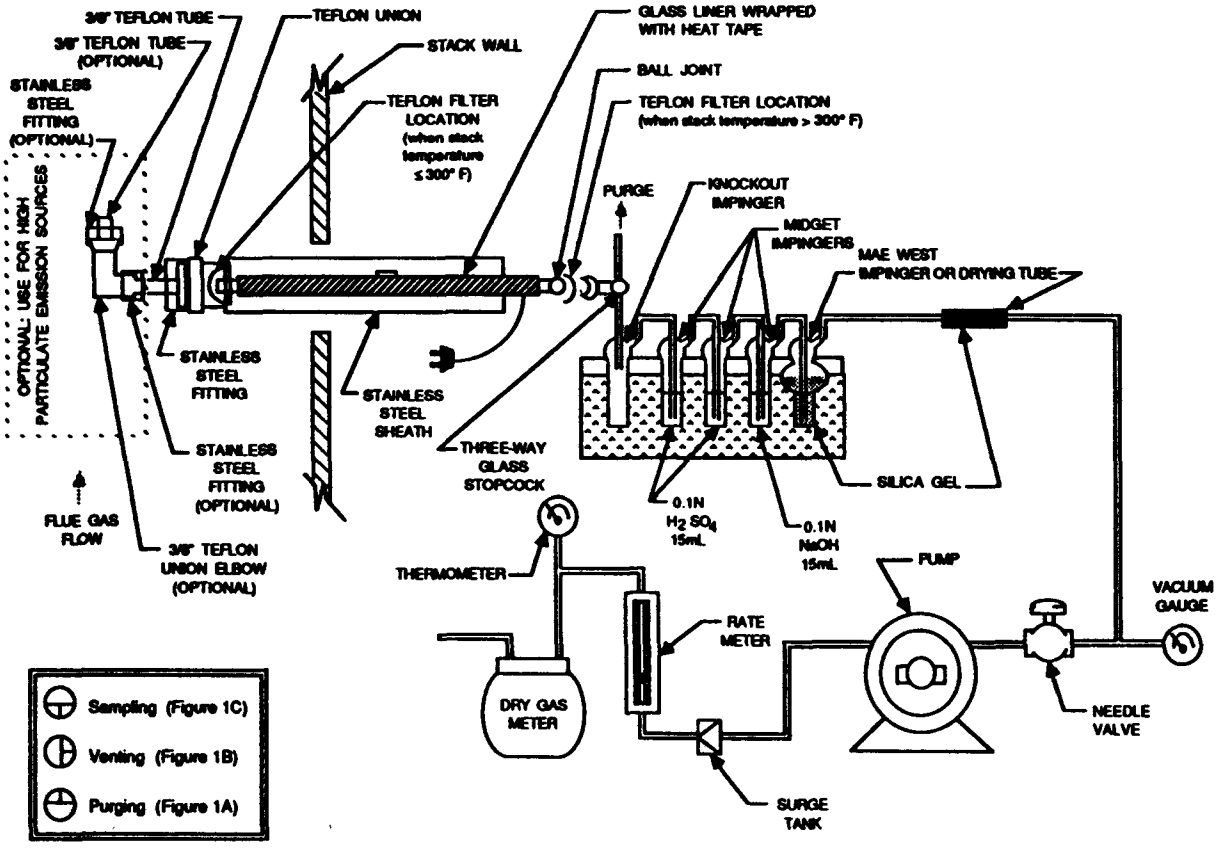


***Figure 1.*** *HCl Sampling Train*

full of condensed flue gas moisture. A water knockout impinger was incorporated into the sampling train for the field evaluation test.

The ruggedness test was used to assess the sensitivity of the method to selected variables which may affect sampling. The results showed percent differences for the six variables of less than ± 2.5%, indicating that the method was insensitive to the selected variables: low reagent volume, increased impinger pH, longer sampling time, elevated impinger temperature, higher sampling rate, and elevated $Cl_2$ levels. These results, in conjunction with the earlier laboratory evaluation, indicated that at $Cl_2$ levels up to 50 ppm, the measurement of HCl is not biased significantly.

The field test involved paired midget impinger train sampling using the sampling train shown in Figure 1. As indicated in Figures 2 and 3, flue gas HCl levels determined by the manual method were in good agreement with the levels indicated by the TECO HCl CEMS. The Bran and Luebbe HCl CEMS was able to follow the changes in the HCl flue gas levels, but was biased low by approximately 60 percent (4 ppm). The specific results of the field test are as follows:

- The average precision (expressed as the relative standard deviation) of the HCl sampling and analysis protocol was 6.2% at an average flue gas HCl concentration of 3.9 ppm and 3.2% at an average concentration of 15.3 ppm. The average relative standard deviation for the moisture determination employing the midget impinger train was 4.5% and 3.2%, respectively, at the same concentrations.
- The average relative error of the HCl sampling and analysis protocol, established by dynamic spiking, was 5.5% and 7.1% for HCl gas mixtures of 9.7 and 34.3 ppm, respectively
- The relative errors and biases relative to the manual HCl method for the TECO® HCl CEMS were 1.6% and 6.8%, and 0.07 ± 0.79 ppm and 0.68 ± 1.58 ppm, at average flue gas HCl levels of 3.9 and 9.9 ppm, respectively.
- The relative errors and biases relative to the manual HCl method for the Bran and Luebbe® CEMS were 69% and 58%, and -2.66 ± 0.90 ppm and -5.7 ± 2.35 ppm, at average flue gas HCl levels of 3.9 and 9.9, respectively.
- The precisions (standard deviations) for the TECO CEMS were 0.75 ppm and 1.50 ppm at average flue gas HCl levels of 3.9 and 9.9 ppm, respectively. The precisions (standard deviations) for the Bran and Luebbe CEMS were 0.87 ppm and 2.30 ppm at the same flue gas HCl levels.
- Flue gas $CO_2$ absorbed by alkaline impinger reagents was not found to be significant in either the midget impinger train and the Method 5-type train.
- The midget impinger train and the Method 5-type train produced similar HCl results at a flue gas HCl concentration of 21.2 ppm. However, the Method 5-type train produced significantly lower HCl results than the midget impinger train at a flue gas concentration of 4.8 ppm. The low bias may have been a result of unreacted lime collected on the filter or the glass-fiber filter itself absorbing gaseous HCl from the sample

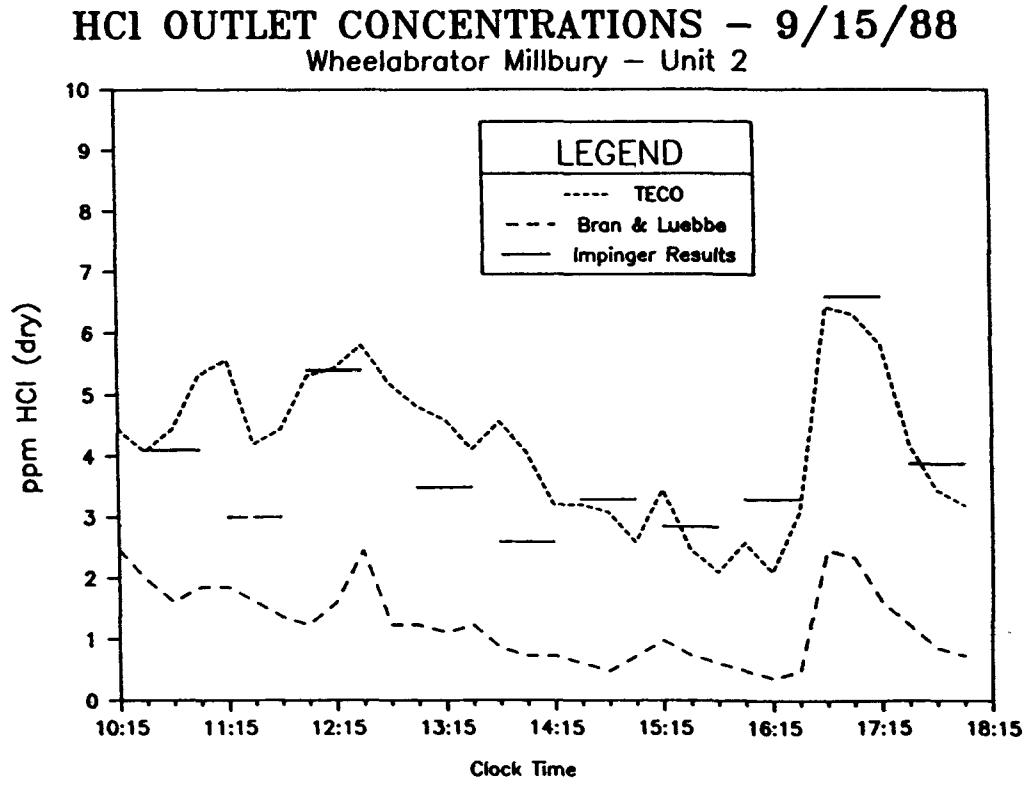


***Figure 2*** *Flue Gas HCl trends indicated by HCl CEMS's under normal acid gas conditions*

## Conclusions and Recommendations

A midget impinger train employing an acidified impinger reagent and operated at a sampling rate of 2 lpm provides acceptable HCl collection efficiency at HCl levels up to 500 ppm and is not susceptible to significant $Cl_2$ interference at $Cl_2$ levels less than 50 ppm. The method, as described, may also be suitable for determining $Cl_2$ emissions. The method is insensitive to slight changes in reagent volume, impinger pH, sampling time, impinger temperatures, and sampling rate that may occur during actual use.

The precision and bias demonstrated for the HCl method are acceptable, and the method can also be used for moisture determination. The agreement between the manual method and the TECO HCl CEMS, calibrated with HCl cylinder gases, was acceptable at relatively low flue gas HCl levels.

A nozzle oriented opposite the gas flow and a Teflon filter can be used with the manual method probe assembly to avoid collection of particulate matter and loss of gaseous HCl through reaction with glass surfaces and alkaline particulate matter. A glass wool plug or a glass fiber filter should not be used to prevent particulate matter from entering the train, since this will increase loss of HCl due to reaction with alkaline particulate matter. A 1-hour sampling time is recommended to decrease any bias introduced by the reaction of HCl with glass surfaces and alkaline particulate matter.

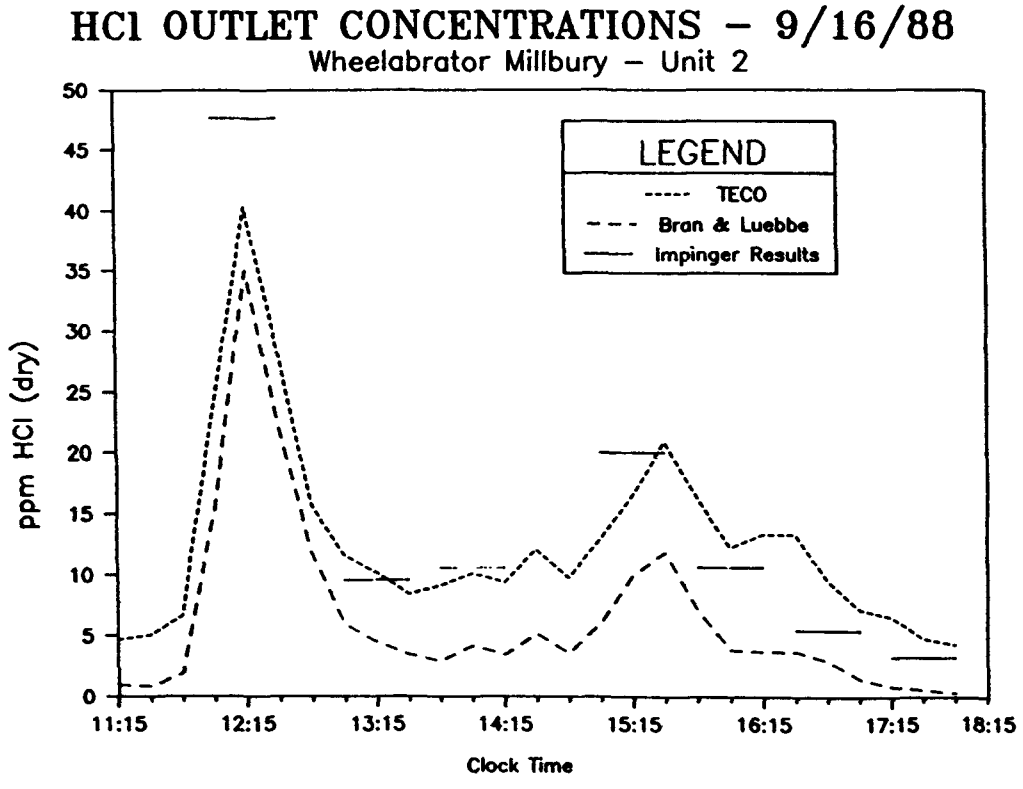


***Figure 3.*** *Flue Gas trends indicated by HCl CSMS's under elevated acid gas conditions*

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*The complete report, entitled "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," (Order No. PB 89-220 586/AS; Cost: $15.95, subject to change) will be available only from:*

*National Technical Information Service*
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