

**DEVELOPMENT OF MERCURY AND
HYDROGEN CHLORIDE EMISSION MONITORS
FOR COAL GASIFIERS**

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ABSTRACT

Hg and HCl CEMs for coal gasifiers were developed and tested. The CEMs employ a nonchemical gas conditioning approach using catalytic oxidation of the sample stream. Critical gas conditioning steps include the removal of NH₃, tars, aromatic hydrocarbons, and moisture. A commercially available platinum (Pt) catalyst effectively destroyed NH₃, but could not pass Hg or HCl. Using pure Pt wire as a catalyst effectively destroyed NH₃, tars, and toluene (aromatic hydrocarbon) while passing both Hg and HCl. A Nafion-based dryer removes moisture after the catalyst. Hg and HCl (in air) could be successfully transported through the dryer, although small Hg losses were observed at extremely low concentrations. The gas conditioning system needs to be simplified and sample transport issues need to be improved before routine use of the CEMs.

Atomic absorption was selected for use in the Hg CEM. Because of spectral overlaps from interfering gases, background corrections are needed. The Hg CEM, which has a detection limit of about 0.1 µg/m³, uses a deuterium (D₂) lamp for broadband background corrections. The D₂ system effectively corrected for SO₂ interferences when using Hg concentrations of 9-26 µg/m³. However, a correction factor on the D₂ absorption data was needed, and this factor changed slightly with changing SO₂ concentration for SO₂ levels greater than 0.25%. Tests with the Hg CEM using 15 µg/m³ of elemental Hg in air indicated that 50% of the elemental Hg was lost, apparently from wall losses. Additional losses were observed when HCl was added, indicating that the pyrolytic converter after the catalyst was not working properly, or that elemental Hg was reoxidizing in the presence of HCl after the converter. When using a simulated gasifier stream, background-corrected absorption readings were too erratic to get meaningful Hg signals. This was apparently related to problems associated with H₂S and/or SO₂. Sulfates deposited in the sample line between the catalyst tube and Nafion dryer. This is a likely source of Hg losses. The deposition of sulfate aerosols and the successful conversion of oxidized Hg back to elemental Hg (without reoxidation) are issues requiring further study.

Ion mobility spectroscopy (IMS) was selected for use in the HCl CEM. IMS has a detection limit of about 5 ppb and few interferences, but has a narrow dynamic range. Tests with the CEM using simulated gasifier streams with 1-10 ppm HCl were generally successful. IMS readings tracked well with changing HCl concentrations, and changes of 1 ppm in the HCl concentration could be observed. However, about 20% of the HCl appeared to be lost somewhere during sample transport and conditioning. Suitable calibration procedures require investigation, since commercially available systems were not always reliable.

EXECUTIVE SUMMARY

Integrated sampling/analysis systems for on-line monitoring of mercury (Hg) and hydrogen chloride (HCl) in advanced coal-based gasification systems were developed. Research efforts focused on 1) identifying and testing suitable analytical approaches, 2) gas conditioning techniques, 3) sample transport, 4) calibration approaches, 4) background correction approaches for Hg determinations by atomic absorption, and 5) building and testing Hg and HCl CEMs using simulated coal gasification streams. Work performed in this study is summarized below.

GAS CONDITIONING

Removal of ammonia (NH₃) is important in view of potential chloride losses during sample transport, plugging of sample lines, or coating of optical components in analytical systems. This could occur from the possible formation and deposition of ammonium chloride as the gases cool. The NH₃ can be removed at about 900°C without a catalyst, but catalytic oxidation was still used to help ensure complete removal of NH₃ under a wide variety of conditions. A commercially available platinum (Pt) catalyst on alumina effectively destroyed NH₃ when using air/nitrogen blends. However, work with that catalyst was discontinued because neither Hg or HCl could be passed through the catalyst bed. Using pure Pt wire as a catalyst effectively destroyed NH₃ while passing both Hg and HCl when using air/nitrogen carrier gases. A palladium (Pd) wire catalyst was tested because of its lower cost relative to Pt. Although the Pd wire effectively removed NH₃, complete meltdown of the catalyst occurred on several occasions. Therefore, the use of Pd catalysts was discontinued. In tests with simulated gasifier streams, white aerosols were observed exiting the catalyst tube containing Pt wire. Those aerosols appeared to be sulfuric acid mist from the oxidation of H₂S. The sulfur-bearing aerosols formed very easily in the presence of a catalyst. Also, when using simulated gasifier streams, pulsing flame fronts which migrated upstream from the catalyst (but which quickly dissipated) occurred if the preheat zone immediately upstream from the catalyst was above 700°C.

Catalytic oxidation is also being used for tar removal. Field studies were performed at a 800 kW biomass gasifier to confirm whether a Pt wire catalyst could effectively remove tars from a process gas slipstream. For comparative purposes, tests were also performed with α -alumina at 900°C. Although the hot alumina did not remove tars, the tars were completely removed by the Pt catalyst. Due to highly exothermic reactions, localized temperatures appeared to be near the melting point of the quartz tube holding the catalyst. Therefore, caution must be exercised when using catalytic oxidation.

Proper conditioning of coal gasification streams is very complex and does not have simple solutions. This is particularly true in view of the fact that the gas conditioning system must deal with tars, high moisture contents, and problems with NH₃ without affecting ppb levels of Hg, ppm (or lower) levels of HCl, or the successful operation of conditioner components and analytical systems. Trying to develop a non-chemical system for gas conditioning was an ambitious task in view of the difficult sampling environment and unique problems associated with coal gasification streams.

MERCURY STUDIES

The complexities of sample transport were shown by tests with elemental Hg injections into stainless steel and Teflon lines. Full Hg recoveries were obtained using air in stainless steel sample lines at room temperature, but recoveries gradually decreased to 20% as the sample line was heated to 200°C. When dry, simulated gasifier streams were used in steel lines, no Hg was detected between 25 and 200°C. After using the simulated gasifier streams in the steel lines, poor Hg recoveries were obtained when switching back to dry air and testing at room temperature. Full recoveries could be restored by adding humidity or by purging the lines for several days. The presence of sulfur-containing gases inhibited the transport of elemental Hg vapors, even in Teflon sample lines. These tests are important because Teflon lines can not be used for much of the sample transport due to the high sampling temperatures anticipated.

Elemental Hg could not be successfully passed over a commercially available Pt catalyst (on alumina) being used for gas stream oxidation. However, low levels of elemental Hg in air could be passed over a hot plug of Pt wire. Full Hg recoveries were still obtained when using a simulated gasifier stream, but 25% of the Hg was in the oxidized form when HCl was present, even when a pyrolytic converter was used after the catalyst. Because an oxidation catalyst is used, there are concerns regarding the Hg analyses, since the detection system responds to only elemental Hg. Although a high-temperature pyrolysis zone is used downstream from the catalyst, the potential recombination of Hg and chloride after the pyrolyzer requires further study.

Because of the high moisture content of coal gasifier streams, a Nafion-based dryer is being used. Low levels of elemental Hg (in air) could be successfully transported through a laboratory-scale Nafion dryer. When using a large Nafion-based dryer intended for process gas streams, elemental Hg (in air) recoveries of only 80-95% were obtained. The sample gas flow rate was a very important variable. Tests with the laboratory-scale dryer were also performed with HgCl₂ streams. Substantial losses of HgCl₂ were observed, but additional work is required to determine the source of the losses. Studies are also required regarding Hg transport using Nafion in the presence of simulated gasifier streams.

Because of concerns regarding transport of HgCl₂ during sampling and the effective conversion of that Hg species to elemental Hg (required for detection by atomic absorption), tests were performed on the transport of HgCl₂ and on the pyrolytic conversion of HgCl₂ to elemental Hg. When using HgCl₂ streams in air, the HgCl₂ was effectively transported and converted to elemental Hg without any recombination of the Hg and Cl atoms. However, thermodynamic calculations indicated that recombination might be of concern in gas streams with elevated levels of HCl. Testing of this possible problem using mixtures of elemental Hg, HCl, and air flowing over a pyrolyzer at 900°C indicated that this could be an area of concern.

Based on available information at the start of the project, the analytical methods considered for our Hg CEM were cold vapor atomic absorption (AA) and cold vapor atomic fluorescence (AF). Two Hg detectors (one each based on AA and AF) were tested in the laboratory. Both instruments were highly sensitive and had minimal base line noise, while the AF detector

exhibited lower levels of base line drift. The extent of signal quenching from most of the major matrix gases in gasifier streams precluded the possibility of direct gas analysis using AF. The determination of Hg in gasifier streams by AF is still possible if collection and preconcentration on gold is used. However, because of possible poisoning of the gold amalgamation devices in gasifier streams, AA was selected for use in our Hg CEM and no gold traps were used.

Because of spectral interferences in AA, background corrections are needed for direct, real-time analyses of Hg if interfering gases are not removed. Interferences include sulfur-containing gases and aromatic hydrocarbons. The sulfur-containing gases could potentially produce a signal equivalent to that observed for a 100 ppb_w Hg stream or more, which stresses the importance of the background correction. The assumption was made that aromatic hydrocarbons would be destroyed by the Pt catalyst. Tests indicated that a hot Pt wire catalyst effectively destroyed 2% toluene (an aromatic hydrocarbon) in air while passing low levels of elemental Hg. Although toluene was not intended to be a model compound for coal gasifiers, it at least provides some data on the removal of aromatic hydrocarbons by the catalyst. For background corrections, the Ames Laboratory Hg CEM uses a broadband background correction technique employing a deuterium (D₂) lamp. That approach has not been used previously for Hg CEMs.

The initial design of the D₂ module was formulated, assembled on an optical breadboard, and tested. After coupling a commercially available Hg detector to the D₂ unit, the D₂ module successfully corrected for background interferences when using Hg concentrations of 2 to 11 µg/m³ in the presence of up to 0.5% SO₂. However, a correction factor on the D₂ channel of the system was needed. In view of those encouraging results, a prototype Hg CEM containing a Hg detector and D₂ correction system in a single, compact, fully integrated analyzer was built. The prototype Hg analyzer weighs 50 pounds and is housed in a 26" by 9" by 18" case. Up to 48 hours of data can be stored in nonvolatile internal memory. The analyzer can also be operated with an external computer for extended data collection and storage. The analyzer contains tools for data processing, data acquisition, and optical alignments.

The prototype Hg analyzer was evaluated in the laboratory using streams of air, SO₂, and Hg. Levels of base line noise and drift were acceptable. With the Hg channel of the analyzer, excellent calibration curves were obtained, and a detection limit of about 0.1 µg/m³ was calculated. Design modifications can improve this considerably. High levels (50 µg/m³) of Hg had no effect on the D₂ base line, which is of critical importance for the proper operation of the monitor. As was the case with the optical breadboard system, a D₂ correction factor was needed. The correction factor was affected slightly by the SO₂ concentration. The D₂ system effectively corrected for SO₂ interferences when using Hg concentrations of 9-26 µg/m³ and SO₂ concentrations up to 0.44%. However, a "sliding" D₂ correction factor dependent on the SO₂ concentration was needed for SO₂ concentrations greater than 0.25%. Background corrected absorbance readings were within 10% of the theoretical values in 85% of all cases and were within 5% of the theoretical values in 50% of all cases. Modifications in the optics changed the numerical value of the correction factor significantly, but the SO₂ concentration still affected the correction factor. Heating the sample cell decreased instrument sensitivity, apparently from defocusing of the optics. However, it is not yet known whether a heated sample cell will be required. The Hg analyzer with a D₂ background correction system is promising, but is not yet fully developed. The primary complicating factor at this time is the fact that the required

correction factor on the D₂ channel of the instrument changes slightly with changing levels of interfering gases. Additional work is required to resolve that issue. Since this analyzer is the first of its kind, it is very probable that the analyzer can be improved substantially.

Tests with the Hg analyzer and gas conditioning system were performed using a simulated gasifier stream containing 15 µg/m³ of elemental Hg. For comparative purposes, Hg streams in air and nitrogen were passed directly (bypassing the gas conditioner) into the Hg analyzer. Similarly, tests were performed whereby Hg in either air or nitrogen was passed through the entire heated gas conditioning system. When using streams of Hg in air (at room temperature) and bypassing the conditioner, rapid instrument response was observed, and the addition of 50 ppm HCl resulted in little or no Hg oxidation. When Hg in N₂ was passed through the heated gas conditioning system, Hg readings were about 50% below expected values. Since little or no Hg oxidation would be anticipated in the N₂ stream, this suggests that wall losses in the gas conditioner were substantial. The presence of 50 ppm HCl in the N₂ stream had little effect on the Hg signals. Similar results were obtained while using streams of air and Hg without HCl. However, when the air stream contained 50 ppm HCl, the Hg signals decreased substantially and were only about 15% of those obtained while bypassing the gas conditioning system. Apparently, either the pyrolyzer is not effectively converting oxidized Hg (formed when passing over the oxidation catalyst) back to the elemental form, or the pyrolyzer is working as expected, but elemental Hg is reoxidizing in the presence of chloride as the gases cool.

Attempts were made to pass elemental Hg in a simulated gasifier stream through the gas conditioning system. When using a simulated gasifier stream and adding oxidation air prior to the catalyst, the background-corrected base line readings from the Hg detector were too erratic to get meaningful Hg signals. A variety of possibilities could account for this observation. After using the simulated gasifier stream, the gas stream was switched back to only N₂ (no oxidation air) and Hg. However, the Hg signals were much lower than previously observed when using only N₂ to transport the Hg through the conditioner. Thus, something apparently "poisoned" part of the sample transport and/or gas conditioning system. Sulfur-containing gases are the most likely cause.

After completing the tests, the heat tracing was taken off the Teflon sample line connecting the catalyst tube to the gas dryer. The tube contained numerous spots on the interior walls and was heavily fogged. The spots were crystalline and highly enriched in oxygen and sulfur, and possibly lesser amounts of nitrogen. The spots are apparently sulfate compounds, such as ammonium sulfates and/or ammonium thiosulfates. The presence of the latter compounds was previously shown to exist if NH₃ was not completely removed from the gas stream. It is very likely that these sulfur-containing deposits were responsible for at least some of the Hg losses observed during sample transport. Additional effort would be required to elucidate the mechanisms responsible for the Hg losses.

Passing low levels of elemental Hg successfully through the gas conditioning system is very complex. Additional work is required to address sample transport issues through the gas conditioner. Also, the formation and deposition of sulfate aerosols and the successful conversion of oxidized Hg (formed while passing over the oxidation catalyst) back to the elemental form are

issues that still require further study. The overall gas conditioning system needs to be simplified to allow for more routine use.

HYDROGEN CHLORIDE STUDIES

When air streams containing 100 ppm HCl were passed through a Nafion-based dryer, HCl recoveries of 80-100% were obtained, and no HCl was generally detected in the countercurrent purge gas stream used with the Nafion dryer. However, more work on HCl transport through Nafion dryers is needed. Tests were also performed on passing HCl streams through oxidation catalysts. HCl could not be successfully passed through a commercially available catalyst (Pt on an alumina substrate), but low levels (10 ppm) of HCl could be passed successfully over a catalyst consisting of pure Pt wire, even when using simulated gasifier streams.

A variety of commercially available HCl calibration devices were investigated with respect to accuracy and response times while using gas streams containing about 1 ppm HCl. The devices examined included aqueous and anhydrous HCl permeation tubes, an anhydrous HCl permeation wafer, and an aqueous HCl diffusion vial. Each of the calibration devices was used in conjunction with a corresponding calibrator from the respective companies participating in this study. Direct analysis (using IMS) of the span gases from the calibrators indicated that the time required to reach maximum span gas concentrations differed significantly between calibrators, but was reached within several minutes in all cases. In addition, span gases were bubbled into absorbing solutions and analyzed by ion chromatography to calculate actual HCl emission rates from the calibrators. Actual HCl emission rates from the calibrators were significantly different from the levels expected based on the certified emission values for the calibration devices. In some cases, minor procedural variables significantly affected HCl concentrations in the span gases. In follow-up tests with one of the calibration devices, the temperature of the permeation chamber was found to be an important factor. Specifically, HCl recoveries were 40%, 80%, and 90% of theoretical values at temperatures of 30°, 35°, and 70°C, respectively. It is not known whether this is due primarily to temperature effects or to the elevated HCl concentrations at higher temperatures (or both). Caution must be exercised if commercially available calibration systems are used, and verification of the HCl output from such systems at the HCl concentrations of interest is vital.

Commercially available analyzers employing gas filter correlation IR (GFCIR), dry colorimetry, and ion mobility spectroscopy (IMS) were selected for evaluation in our laboratories. The GFCIR analyzer had extremely stable HCl readings with base line fluctuations of no more than 0.2 ppm HCl. When using compressed gas cylinders for span gases, calibration curves were linear above 25 ppm HCl, but were somewhat erratic below that. However, when using HCl permeation tubes to generate gas streams containing 0.2 to 2 ppm, linear instrument responses were observed. Methane was a severe interference, but should not be a problem if gas stream oxidation is used.

The dry colorimetric analyzer was based on using continuous, color-indicating detection tapes in the form of "chemcassettes". Chemcassettes for both high and low levels of HCl were tested. For the high level chemcassettes, a calculated detection limit of less than 1 ppm was obtained, and calibration curves were generally linear in the HCl concentration range studied (0-

25 ppm). HF and HCN were minor interferences. With the low-level chemcassette, the measured detection limit was about 50 ppb HCl. Good linearity in the calibration curves was observed in the range of 75-400 ppb, but suspected wall effects caused some anomalous readings at lower concentrations. A substantial part of the problem appeared to be due to memory effects within the calibration system itself. HF was a major interference when using the low-level chemcassette, but should not be a problem if the HCl levels are much greater than the HF levels in the sample gases. HCN was not a significant interference with the low-level chemcassette.

IMS (an atmospheric-pressure, time-of-flight technique) was selected as the analytical method of choice for our HCl CEM. The detection system for the HCl CEM is a commercially available analyzer having programmable high and low alarms, built-in diagnostics, and two analysis ranges (0-20 ppm and 0-200 ppb) which are obtained by changing an internal membrane. Advantages of IMS include minimal zero drift, high sensitivity, little sensitivity to relative humidity, few occurrences of false positives, and real time monitoring capability. However, it has a fairly narrow dynamic range (factor of 200), which would necessitate a dilution system to cover HCl concentrations in the range of 0 to 100 ppm. IMS is sensitive to pulsations in the sample gas flow and the sample gas must be at atmospheric pressure, but those issues are easily dealt with. Evaluation of an IMS analyzer in our laboratories indicated that the instrument response was linear for HCl concentrations of 1 to 25 ppm and 1 to 200 ppb (after changing membranes). Substantial memory effects were noted when using ppb levels of HCl, but this appeared to be due primarily to the HCl calibrator. The detection limit was about 5 ppb. HCN, HF, and H₂S were not significant analytical interferences. However, HF could be of concern if HF levels are at or above the HCl concentration, which is not expected to be the case.

Laboratory testing was performed with the entire integrated HCl CEM. Tests were performed with 10 ppm HCl in air as well as simulated coal gasification streams. When passing those streams through the entire CEM, the IMS readings tracked well with changing HCl concentrations in the range of 1-10 ppm, and small changes (e.g., 1 ppm or less) in the HCl concentration could be observed. However, the HCl concentrations reported by the IMS analyzer were about 20% lower than those obtained while bypassing the conditioner. A variety of reasons could account for this observation. Unlike the tests with dry air streams through the gas conditioner, rapid response times were observed with the simulated flue gas streams when going from zero air to span gases, which is probably related to a “flushing” effect from the high moisture content of the simulated gasifier stream. Complete removal of NH₃ by the oxidation catalyst appeared to be important in order to avoid the formation of ammonium chloride, which in turn can result in decreases in the IMS reading. The tests with HCl using simulated gasifier streams were successful, but it is clear that additional development is needed before it is ready for field use. As with Hg, additional work on transporting HCl through the gas conditioning system is required, and the overall gas conditioning system should be simplified.

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INTRODUCTION

OBJECTIVES

The goal of this work was to develop integrated sampling and analysis systems suitable for on-line monitoring of mercury (Hg) and hydrogen chloride (HCl) in advanced coal-based gasification systems. Specific objectives of the study were to 1) identify and test analytical approaches which may be suitable for determining Hg and HCl in high-temperature, high-pressure process gas streams, 2) study the necessary gas conditioning and sample transport considerations, and 3) produce reliable on-line monitors which are adaptable to plant-scale diagnostics and process control applications. Although the focus of this work involved developing Hg and HCl continuous emission monitors (CEMs) for coal gasification applications, much of this work is also applicable to coal combustion units and waste incinerators. Sampling combustors and incinerators is less problematic than sampling gasifiers because the gas matrices and sampling environments at such facilities are more conducive to sampling with available analytical instrumentation.

BACKGROUND

In the 1990 Amendments to the Clean Air Act, 189 compounds and elements are listed as hazardous air pollutants (i.e., air toxics). Among those air toxics, Hg and HCl are produced during coal combustion or gasification. In coal gasifiers, concentrations of Hg are anticipated to be in the range of 0.1-100 $\mu\text{g}/\text{m}^3$ in the raw gas streams. Concentrations of HCl are anticipated to be in the range of 50 - 500 ppm_v in the raw gas and less than 1 ppm after the flue gas is treated to remove acid vapors (1-3). For fuel cell applications, there is interest in monitoring HCl levels in the ppb range, since HCl can lead to catalyst poisoning in such systems. On-line monitoring for Hg and HCl in high-temperature, high-pressure power-producing systems is of interest in view of environmental and technological considerations. However, instrumentation designed for performing those analyses in the specified environments have not been available. Although commercially available CEMs were not available for such applications, we believed that suitable detection systems existed that could potentially be adapted, with proper gas stream conditioning, for analyzing the gas streams of interest.

Even in conventional combustion systems, difficulties are often encountered in sampling and analysis of those compounds because of uncertainties pertaining to collection efficiencies, chemical interferences, and maintaining sample integrity. This is particularly true for Hg. Sampling and analysis of gasifier streams is even more problematic due to the high-temperature (up to 500°C) and high-pressure (up to 300 psi) streams that are present, as well as the unique gas chemistry and high moisture contents involved. However, by devising an integrated sampling and analysis system for the analytes of interest (i.e., Hg and HCl), process control for coal gasifiers can be improved and concentrations of air toxics in the effluent streams can be minimized.

APPROACH

Initial work in this project involved reviewing and evaluating commercially available instrumentation suitable for the monitoring applications of interest. About 150 companies who market air emission monitoring and sampling equipment were contacted to determine the availability of equipment suitable for monitoring Hg or HCl in hot gases from NETL power producing systems. In addition, pertinent literature was assessed to obtain additional information on analytical methodologies that could potentially be used. The relevant literature items were obtained after performing computerized on-line searches of appropriate technical databases.

After reviewing the pertinent literature, analytical approaches which appeared to have the most potential for our monitoring applications were identified. Using this as a basis for our work, we decided to modify existing analytical methodologies rather than try to devise new analytical technologies, since this was viewed by Ames Laboratory and NETL personnel as being the most economical approach overall. In order to help attain our end goal, extensive studies were performed in a variety of critical areas. These were 1) testing and evaluation of commercially available detectors and monitors, 2) calibration approaches, 3) sample conditioning, and 4) background correction approaches for determining Hg by atomic absorption (AA).

Testing of commercially available instrumentation was necessary for this work in order to confirm vendor claims and to gain operating experience with instruments that were candidates for use in the CEMs. This avoided purchasing expensive instrumentation that would be unsuitable for the end task. Also, because of the unique sampling environments, instrument manufacturers were often uncertain about the suitability of their instruments for our application. As an integral part of our development of Hg and HCl CEMs, commercially available calibration devices were also examined. This was considered to be a crucial part of our work since accurate CEMs require accurate calibration systems. Sample conditioning is a critical step in the development of Hg and HCl CEMs, and a major thrust of our development work was performed in this area. The most crucial areas of gas stream conditioning are the removal of moisture, tars, and ammonia gases. Finally, considerable effort was devoted to the development of a background correction approach for the Hg analyses. This was necessary because the detection method selected for the CEM was known to have a variety of spectral interferences from gases that will be present in the sample streams.

A system was designed and constructed in order to blend, heat, and deliver gases that would simulate coal gasifier streams. Cylinders of compressed gases were used for CH₄, CO, CO₂, COS, H₂, HCl, HCN, H₂S, N₂, and NH₃. For our work, we assumed that gasifier streams contained concentrations of individual gas components as shown in Table 1. The basic design of the testing apparatus consists of a Teflon gas mixer for blending metered gases, a gas heating system, a steam generator, toxic gas traps (to be used after the detector), and a gas burner for burning flammable gases and destroying toxic gases not collected by the traps. The tubing from the HCl gas cylinder is made of Teflon, while all other gas lines are made of stainless steel. A schematic diagram of the apparatus is shown in Figure 1. That system was used to test a variety

of analytical instruments, sample transport considerations, and gas stream conditioning approaches.

Table 1. Anticipated Concentrations of Various Gas Components in Gasifier Streams.

GASEOUS SPECIES	CONCENTRATION
Ammonia	0 - 0.5 %
Carbon Dioxide	5 - 20 %
Carbon Monoxide	10 - 60 %
Carbonyl Sulfide	0 - 0.1 %
Hydrogen	15 - 30 %
Hydrogen Chloride	1 - 300 ppm
Hydrogen Sulfide	0 - 0.5 %
Mercury	0.1 - 100 $\mu\text{g}/\text{m}^3$
Methane	2 - 15 %
Nitrogen	0 - 50 %
Water Vapor	5 - 50 %

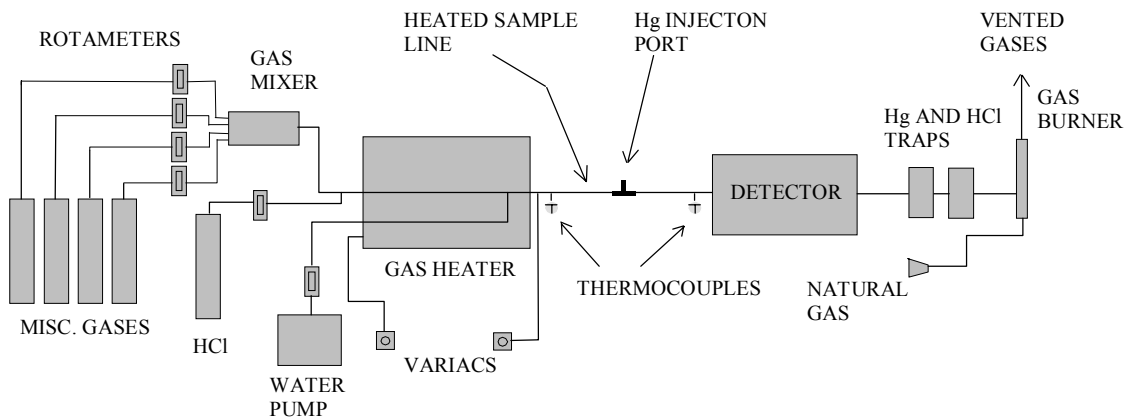


Figure 1. Testing Apparatus Used for Air Toxics Studies.

After assessing the overall operation of the initial system, modifications in the steam generation, gas heating, and gas burner components were made. Some of those changes included replacing a gas chromatography oven with a hot sand bath to heat the gases. In the latter approach, the blended gases are heated by passing them into a stainless steel coil immersed in the sand bath. To achieve a gas temperature of about 200°C, the sand bath is maintained at 300-400°C. In addition, an external steam generation vessel was replaced with a pump from a liquid chromatograph. That pump provides a precise, adjustable water flow in the proper range to give the desired moisture content in the sample gas mixtures. The water is pumped into a separate stainless steel coil in the hot sand bath. The water is vaporized in the steam coil and is introduced into the sample gas stream just before the sample gases exit the sand bath. This

approach for adding moisture worked well and eliminated problems in regulating and metering the steam flow in the initial approach.

GAS CONDITIONING

AMMONIA REMOVAL

In the presence of ammonia (NH_3), chloride losses can occur during sample transport due to the formation and deposition of solid ammonium chloride (NH_4Cl). This compound can be kept in the vapor phase during sample transport by heating the sample lines. However, since most of the HCl monitors being considered operate at temperatures of less than 100°C and require the chloride to be present as HCl rather than NH_4Cl , the presence of NH_3 gases in the sample stream presents a problem. Consequently, it is desirable to remove the NH_3 from the gasifier stream in order to avoid the formation of NH_4Cl prior to determining HCl. Aside from the problems related to HCl analyses, it is best to avoid the formation of NH_4Cl since it could quickly plug sample lines if not sufficiently heated, or it could potentially cause problems by coating optical components of the analytical systems. Work on the removal of NH_3 from gas streams is discussed below.

COPPER REDUCTION TUBE

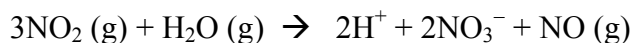
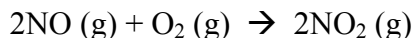
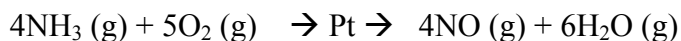
Tests were performed to determine whether a commercially available copper reduction tube could be used to effectively remove NH_3 . The reduction tube consisted of a heated quartz tube containing about 100 mL of granular (minus 20 mesh) copper. Experiments were performed using 1% and 5% NH_3 , total gas flow rates of 25-1000 mL/min, and temperatures of 25-1000 $^\circ\text{C}$. Results of those tests indicated that 95% or more of a 1% NH_3 stream (in nitrogen) could be removed from a gas stream flowing at 1000 mL/min over a hot copper reduction tube. Temperatures of at least 900°C were needed for effective NH_3 removal, which may reflect nothing more than simple thermal cracking. Tests with a 300 ppm HCl stream indicated that less than 50% of the HCl could be successfully passed through the reduction tube at temperatures above 500°C . Therefore, this approach for removing NH_3 was not studied further.

PLATINUM CATALYST ON ALUMINA SUBSTRATE

Tests were performed with a beaded (1/8-inch) catalyst containing 1% platinum (Pt) on an alumina substrate (catalyst G-97B from United Catalysts, Louisville, KY) to determine how effectively it removes NH_3 gases. For these tests, 3% (v/v) NH_3 in a given carrier gas stream was passed through 100 cc of catalyst using a total gas flow rate of about 1 L/min. The temperature of the catalyst was varied from ambient to 400°C , and a given temperature was maintained to within 5°C for 30 minutes before obtaining semiquantitative measurements of the NH_3 concentration exiting the catalyst tube. Those measurements were performed using color-indicating paper sensitive to NH_3 . In base line tests with blends of nitrogen and NH_3 , little or no NH_3 was removed as the temperature was increased to 400°C . When the NH_3 was blended with air rather than nitrogen, virtually no NH_3 was removed at temperatures below about 250°C . However, as the temperature was increased to about 250°C , exothermic reactions began

occurring, which made it more difficult to maintain the desired temperature. Also, the formation of water was evident (condensation was observed after exiting the catalyst tube) and no NH₃ was detected with the color-indicating paper. After heating the catalyst tube outlet to avoid condensed water, a Sensidyne pump and color-indicating tubes (accurate to within 25%) were used to help determine the NH₃ concentration exiting the catalyst tube at 300°C. Results indicated that the NH₃ concentration was less than 1 ppm_v. Thus, it appears that nearly 100% of the NH₃ was removed at only 300°C. Also, it is interesting to note that when the temperature of the catalyst tube was ramped back down to near room temperature, no NH₃ could be detected at the outlet of the catalyst tube, even after several hours at 100°C or less. After purging the catalyst tube over night with air only, the catalyst was once again unable to remove NH₃ at temperatures below 250°C within 30 minutes at a given temperature.

The water formed during the catalytic oxidation of NH₃ was very acidic (pH < 1) and was probably nitric acid. The acid caused considerable corrosion of the stainless steel thermocouple sheath. When the catalyst tube was at 300°C and the outlet of the tube was heated to avoid condensation, gases exiting the tube were bubbled into deionized water for several minutes. Analysis of this water sample by ion chromatography (IC) indicated that it had a lot of nitrate and a considerable amount of an unidentified compound, which is believed to be a nitric acid precursor. Nitric acid is often commercially made by the catalytic oxidation of NH₃ using the Ostwald process, as shown below:



Attempts were made to maintain the oxidation of NH₃ without promoting the subsequent formation of nitric acid by initially activating the catalyst at about 250°C and then subsequently decreasing the temperature. As the temperature was gradually decreased, it was held at each desired temperature for periods ranging from 2 to 12 hours. The NH₃ was completely removed and acidic water was noted regardless of temperature. This was true even after 12 hours at 60°C, which was the minimum temperature attained with no external heat supplied to the catalyst. The catalytic oxidation reactions were disrupted only after terminating the NH₃ flow and purging the catalyst tube with either air or nitrogen. After doing so, the catalyst tube was heated to 200°C and the NH₃ flow was resumed. No NH₃ removal was observed and no moisture was formed, even after 7 hours at that temperature. Apparently, a minimum activation energy is required in order to initiate the catalytic oxidation of NH₃. Also, these results indicate that lowering the reaction temperature after initial activation of the catalyst is not a viable approach for preventing acid formation when using air containing 3% NH₃.

Attempts were made to avoid nitric acid formation by decreasing the oxygen content of the gas stream by blending the air with additional nitrogen. In doing so, it was hoped that there would be sufficient oxygen for oxidizing the NH₃, but not for the subsequent oxidation of the

NO byproduct to nitric acid precursors. Calculations indicated that a gas stream with 3% NH₃ would require 4% oxygen as the stoichiometric amount of oxygen necessary for reacting with the NH₃. A gas stream containing about 5% oxygen would contain 25% excess oxygen for the oxidation of NH₃, but would be well short of the oxygen needed for subsequent reactions leading to the formation of nitric acid. For our initial tests, 3% NH₃ in an air/nitrogen blend containing the stoichiometric amount of oxygen necessary for reacting with the NH₃ was passed through the catalyst at a rate of 1000 mL/minute while heating the catalyst to 300°C. After several hours at that temperature, some water was being formed, suggesting that some NH₃ decomposition was occurring. However, no major decrease in the NH₃ concentration was noted using color-indicating paper sensitive to NH₃. At 5% excess oxygen, the condensate was slightly basic, and most (but not all) of the NH₃ was being removed after operating over night. After increasing the air flow to give 10% excess oxygen, nearly all of the NH₃ was being removed, but the condensate was very acidic. These results suggest that it would be difficult to adjust the oxygen-to-NH₃ ratio in order to completely remove NH₃ at 300°C without forming acid.

In subsequent tests, 3% NH₃ in an air/nitrogen stream containing 10% excess oxygen was passed through the catalyst tube at 270°C. After one hour at that temperature, the pH of the condensate was neutral and nearly all of the NH₃ was being removed. Readings obtained using a Sensidyne gas sampling pump with color-indicating tubes indicated that there was about 25 ppm NH₃ exiting the catalyst tube at this point. The temperature of the catalyst tube was then gradually decreased. Within several hours, no NH₃ was detected using the color-indicating tubes, and the pH of the condensate was still neutral. This held true down to 150°C. However, at 100°C, the pH of the condensate became basic and NH₃ removal was minimal. These results suggest that it may be possible to remove all of the NH₃ without forming acid through the proper selection of *both* temperature and oxygen concentration.

This work showed that the catalyst being studied could effectively remove NH₃ and could potentially do so without excessive oxidation of the gas stream. Because of these encouraging results, tests were performed to determine whether Hg and HCl could be passed through this catalyst material. Unfortunately, problems were encountered for both Hg and HCl. Results of experiments involving Hg and HCl with this catalyst material are discussed later in the respective sections of the report entitled "Mercury Studies" and "Hydrogen Chloride Studies."

PLATINUM WIRE CATALYST

Ammonia Removal Efficiencies

Preliminary tests with a stream containing 2 µg/m³ elemental Hg in air indicated that the Hg could be successfully passed over a hot Pt wire. Therefore, we investigated whether a catalyst bed made of pure Pt wire could effectively remove NH₃. A Pt wire plug was prepared by compressing about 10 feet of 0.010-inch diameter Pt wire into the interior of a 1/4-inch OD quartz tube. The tube was heated by applying current to a piece of nickel-chromium wire wrapped around the tube. A total gas flow rate of about 850 mL/min was used with NH₃ concentrations of 5% in a nitrogen/air blend. The ratio of air to nitrogen was adjusted to provide

about 15% excess oxygen for the oxidation of NH_3 . At a bulk bed temperature of only 200°C , the Pt wire reduced NH_3 levels to about 1 ppm based on semiquantitative analyses of the gases using colorimetric detection tubes. The water formed from the oxidation reactions had a neutral pH. After 16 hours at that temperature, the pH of the condensate was still neutral. At a temperature of 400°C , no NH_3 (< 0.5 ppm) could be detected in the gases exiting the catalyst tube. Thus, at that temperature, essentially all of the NH_3 appeared to be destroyed in the air/nitrogen/ NH_3 blends when that detection method was used.

With continued testing, it was apparent that the color-indicating tubes were not always entirely reliable for measuring residual (trace levels) of NH_3 in gases downstream from the catalyst. This may be due to the high humidity in the gas stream when NH_3 is oxidized. Also, the measurements may be inaccurate at low levels in the gas matrices involved, particularly when using a simulated gasifier stream. Therefore, we switched to the use of IC to determine low levels of NH_3 gases. This was a more reliable measure of low NH_3 concentrations. In that approach, gases were typically bubbled through a 1/8-inch OD Teflon tube into 100 mL of deionized water in a 125-mL Erlenmeyer flask, which was subsequently analyzed by IC. Backup water traps were occasionally used to check for breakthrough from the first trap, which was determined not to be a problem at the gas flow rates normally used for testing.

Based on IC analyses of absorbing solutions, it was found that NH_3 removals by the catalyst were not consistent. This indicated that methods to improve NH_3 removal efficiencies, such as lowering gas flow rates, using higher catalyst temperatures, or using greater catalyst surface areas, needed to be explored further. With continued testing, we were able to consistently obtain excellent NH_3 removal efficiencies by doubling the size of the catalyst bed and by adding a preheat zone just upstream from the catalyst. For the preheat zone, a 6-inch section of the 1/4-inch OD quartz tube housing the catalyst was heated to roughly 900°C using a nickel-chromium wire. The enlarged catalyst bed contained 20-25 feet of 0.010-inch diameter Pt wire. For tests performed in the absence of CH_4 , CO , and H_2 , the catalyst was maintained at a temperature of roughly 900°C . With the changes noted above, 99.99% or more of the NH_3 was removed from gas streams consisting of NH_3 , H_2S , N_2 , and air. In particular, for NH_3 concentrations of 1.5% in the initial (before adding air for oxidation) gas stream, NH_3 levels were consistently reduced to less than 1 ppm.

Additional tests were performed using a Pt catalyst with NH_3 and H_2S streams blended with air/nitrogen mixtures. For those tests, a total gas flow rate of 1000 mL/min was used with a catalyst temperature of about 900°C . The NH_3 and H_2S concentrations were held constant at 1%, while the ratio of nitrogen to air was varied to investigate excess air requirements. Initially, 800 mL/min of air and 200 mL/min of nitrogen were used. The nitrogen flow was then increased in increments of 100 mL/min while the air flow was decreased in increments of 100 mL/min. Gases exiting the catalyst tube were bubbled into deionized water and then analyzed for ammonium ion by IC. Results of those analyses indicated that NH_3 removals were complete until the air flow was only 200 mL/min (added to 800 mL/min of nitrogen). At that point, small amounts of NH_3 began getting through the catalyst and a white, solid aerosol began to deposit on the tube downstream from the catalyst. The implications of this work are that the excess air requirements are rather high (greater than 200%) in order to attain complete removal of NH_3 . For an actual gasifier stream, which contains a variety of other oxidizable gases such as CO ,

CH₄, and H₂, this would require an air stream flowing at several L/min for every 1 L/min of sample gas. When some of the tests were repeated at a total (sample gas plus added air) gas flow rate of 2.5 L/min, significant amounts of NH₃ began to get through. Results of these tests suggest that a fairly low sample gas flow rate may be required in order to keep the total gas flow rate at an acceptable level.

Additional tests with a Pt catalyst were performed to study excess air requirements. In these tests, 500 mL/min of a simulated gasifier stream consisting of 50% CO, 15% CO₂, 25% H₂, 8% CH₄, 2% H₂S, and 1% NH₃ was blended with 3000 mL/min of air and passed over a hot (900°C) Pt wire catalyst. Also, a 900°C “preheat” zone was used to increase the gas temperature prior to entering the catalyst. These tests differ from the previous tests in that 1) a simulated gasifier stream was used instead of using a blend of only N₂, NH₃, and H₂S, and 2) a more realistic NH₃ concentration in the final blended (after addition of air) gas stream was used. Gases exiting the catalyst tube were bubbled into water to quantitatively collect the NH₃. IC analyses on the water indicated that the NH₃ removal was complete. When the air flow was decreased to 1000 mL/min, the removal of NH₃ was still complete. Trace amounts of NH₃ began to appear when the air flow was decreased to 500 mL/min. Results of these tests with a simulated gasifier stream indicate that excess air requirements for complete oxidation of the simulated gasifier stream are only on the order of 50% (assuming that the NH₃ and H₂S are not preferentially oxidized). It appears that higher sample gas flow rates can be used without exceeding the desired total (after diluting with air) gas flow rate of several liters/minute. As an additional note, it was observed that brownish deposits formed on the interior walls of the quartz tube housing the catalyst, both in the actual catalyst zone and the empty “preheat” zone prior to the catalyst. Analysis of the residue by scanning electron microscopy with energy-dispersive x-ray analysis (SEM-EDX) indicated that it consisted mostly of nickel and iron, which may or may not be present as oxides.

Next, tests were performed using a nitrogen stream flowing at 400 mL/min and containing 3% NH₃ and 2% H₂S. This gas stream was blended with air flowing at 600 mL/min. Thus, NH₃ concentrations in the final blended gas stream were about 1.5%. For these tests, a catalyst (20 feet of Pt wire) temperature of 900°C was maintained, and a gas preheat zone maintained at that temperature was also used. Gases exiting the catalyst tube were bubbled into water and analyzed by IC to determine the amount of residual NH₃ in the gas stream. Results of the IC analyses indicated that residual NH₃ levels in the gas stream after the catalyst were only about 50 ppb. Thus, this NH₃ removal approach can be highly effective.

In all of the tests where NH₃ removal was effective, liquid condensate was observed downstream from the catalyst. Some of the liquid condensate was analyzed by IC to see if it contained any ammonium ion, which would indicate that some NH₃ was actually getting through the catalyst. Although small amounts of ammonium ion were found in the condensate, this equated to a residual NH₃ level in the blended gases of only several ppm (starting concentration was 1%). The NH₃ was probably not detected in the gases exiting the catalyst tube because of the very low levels involved and because of the substantial dilution that occurred while bubbling the sample into the collection solution.

A new version of the catalyst module was also tested in a simulated gasifier stream for its ability to remove NH₃. The new catalyst module consisted of Pt wire at 900°C which was placed in between two alumina beds at 900°C. The simulated gasifier stream consisted of 50% CO, 15% CO₂, 25% H₂, 8% CH₄, 2% NH₃, and 2% H₂S. For these tests, 0.5 L/min of simulated gasifier stream was blended with 1.0 L/min of air. Gases exiting the catalyst tube were bubbled into deionized water to collect any NH₃ passing through the catalyst. The water samples were then analyzed for ammonium ion using IC. Results of the analyses indicated that more than 99.9% of the NH₃ was removed using this alternative catalyst unit.

Effects of HCl

A series of tests were performed in which HCl was added (prior to air injection) to a simulated gasifier stream to give a concentration on the order of 1 ppm_v. Flow rates of simulated gasifier stream and air were 0.5 and 1.0 L/min, respectively. A catalyst temperature of 900°C was used for these tests, and no gas preheat zone was used. Gases exiting the catalyst tube were bubbled into deionized water to collect any NH₃ exiting the tube. Results of IC analyses on the water indicated that NH₃ removals decreased significantly in the presence of HCl. Those tests were repeated multiple times with the same results. It was speculated that HCl was rapidly combining with the NH₃ to form ammonium chloride, which may not be destroyed as effectively by the catalyst as NH₃. Heating the gases to 200°C prior to the catalyst and prior to the air injection point did not help the problem and, in fact, caused an additional problem of carbonaceous deposits forming on the inside of the quartz tube. Relocating the HCl injection point downstream from the air injection port also did not help restore the NH₃ removal efficiencies to the desired levels. However, NH₃ removal efficiencies were fully restored in the presence of HCl by increasing the air flow rate to 1.5 L/min.

Because of the possible effects of HCl on NH₃ removal, the tests were repeated using a higher HCl content. For those tests, about 0.5 L/min of the simulated gasifier stream was used, except the HCl content was increased to about 150 ppm_v. In addition, a 600°C preheat zone was used prior to the catalyst, since we anticipate heating sample gases to that temperature up to the catalyst entry point. The NH₃ was first blended at room temperature with the simulated gasifier stream, followed by injection of HCl further downstream. About 1 L/min of air was added to the gasifier stream. The 600°C preheat zone immediately followed the air injection point. With this design, virtually all of the NH₃ was removed. The NH₃ concentrations were reduced from about 1% to less than 0.5 ppm. The tests were repeated using 1 L/min of simulated gasifier stream plus 2 L/min of air, and the same high NH₃ removal efficiencies were observed.

Aerosols and Condensates

Tests were performed with a simulated gasifier stream consisting of 46% CO, 16% CO₂, 12% CH₄, 21% H₂, 1.5% H₂S, and 3.0% NH₃ by volume. Each of those gases was metered into the gas stream individually. The total gas flow rate prior to mixing with air was about 500 mL/min. Prior to the Pt catalyst, this gas stream was blended with air flowing at about 1.5 L/min, which gave an excess oxygen concentration of about 15% for complete oxidation of the simulated gasifier stream. The NH₃ concentration at the exit of the catalyst tube didn't change

until the Pt was heated to a temperature of about 350°C. When that temperature was reached, the temperature increased rapidly due to exothermic oxidation reactions, and the Pt wire began to glow red hot. At that point, the external heat was turned off. In this initial test with the simulated gasifier stream, the sample transport line downstream from the catalyst tube quickly (within an hour) plugged up with unknown, water soluble deposits that were white to pale yellow in color. In addition, little or no water condensation in unheated portions of the sample line downstream from the catalyst was observed. Considerable amounts of water should be produced if the anticipated oxidation reactions go to completion. Analysis of the deposits by SEM-EDX indicated that the oxygen-to-sulfur ratio was less than 2:1, suggesting that oxidation of the simulated gasifier stream was not complete. It was speculated that these deposits were some type of ammonium/sulfur compound (most of which are water soluble) from the reaction of NH₃ with H₂S.

The experiments with the simulated gasifier stream were repeated, except the air flow was increased by 25%. However, this did not solve the deposition problem. During the tests, it was noted that only about 25% of the Pt wire was glowing red hot. This hot zone was on the end of the catalyst furthest downstream, which led to concerns that the gas residence time over sufficiently heated portions of the Pt was not adequate for completing the desired reactions. Therefore, external heat was supplied by applying current to the nickel-chromium wire wrapped around the quartz tube containing the catalyst. When this was performed, over 75% of the Pt was glowing red hot. At this point, considerable amounts of water were produced, virtually all of the NH₃ was removed, and no solids deposited in the sample transport lines downstream from the catalyst. However, small amounts of white aerosol could still be seen exiting the tube. When the liquid condensate (mostly water) was allowed to evaporate, considerable quantities of solids remained. X-ray diffraction (XRD) analyses indicated that the solid material was composed primarily of ammonium sulfate with substantial amounts of ammonium thiosulfate. Therefore, trace amounts of NH₃ apparently passed through the catalyst without being oxidized, which may be responsible for the aerosols observed. It is possible that some NH₃ passed through the catalyst before the catalyst attained the proper temperature, which could have resulted in considerable contamination in the downstream sample lines.

The hypothesis was made that the aerosol was a result of incomplete oxidation of NH₃ and H₂S, and that none of the other gases in the simulated gas mixture were involved. To test this hypothesis, a series of tests were performed with only NH₃, H₂S, and N₂ in the gas stream. Air was still mixed with the gas stream before being passed over the heated Pt wire. The composition of the gas stream after the addition of the air was about 1% NH₃, 0.5% H₂S, and 12% O₂, with N₂ comprising the balance. The length of the catalyst heater was increased from 2" to 6" to provide temperature uniformity of the hot Pt catalyst and of the gases flowing across the catalyst. With the Pt catalyst at room temperature, no deposits were formed and high concentrations of NH₃ were still present in gases exiting the catalyst tube. When the Pt was heated to only a few hundred degrees Celsius, a thick pale yellow aerosol was formed that quickly deposited on the walls of the exit tubing. These deposits could be avoided by heating the tubing to roughly 100°C. When the Pt temperature was increased until it glowed a dull red, most of the aerosol formation disappeared. However, a slight amount remained, even after an hour at those conditions. The aerosol was found to be highly acidic by placing a piece of wet pH paper in contact with the aerosol exiting the catalyst tube. Also, upon closer examination of the end of

the quartz tube, a small amount of a viscous liquid could be seen. A drop of the liquid was allowed to sit in an open petri dish over night in air. The liquid did not evaporate, and touching it with litmus paper indicated that it was very acidic. Analysis of the liquid by IC indicated that it contained large amounts of sulfate ion. These results indicate that the liquid was probably sulfuric acid, which probably formed by the catalytic oxidation of H_2S to form sulfur trioxide, which then dissolved in the condensate to form sulfuric acid. The aerosol appears to be acid mist from the oxidation of the H_2S .

In related tests, a mixture of H_2S and N_2 was blended with air and passed over the Pt catalyst in the absence of NH_3 . When the catalyst was at room temperature, no deposits were formed downstream from the catalyst. However, deposits did begin to form downstream from the catalyst even with minimal heating (several hundred degrees Celsius or less). When the catalyst was heated to the normal operating temperature of about 900°C , no deposits were observed. Thus, the heavy deposits that had formed initially (catalyst temperature of only several hundred degrees Celsius) on the quartz tube disappeared as the catalyst was heated to higher temperatures. These results indicate that sulfur aerosols can form and deposit very easily, even in the absence of NH_3 (i.e., these particular deposits are not ammonium sulfates).

Additional tests were performed with a stream of NH_3 , H_2S , and N_2 , which was then blended with air prior to the catalyst such that there was 200% excess oxygen for the oxidation of both the NH_3 and H_2S . Total gas flow rates of 1 L/min were used. The Pt catalyst was heated and maintained at $700\text{-}900^\circ\text{C}$ before adding the NH_3 and H_2S to ensure that the downstream tubing did not become contaminated by undesirable gases passing through the catalyst before it had attained the desired temperature. Also, the downstream lines were rinsed thoroughly with deionized water prior to the tests to remove any residual compounds from previous tests. With a constant NH_3 concentration of about 1.5%, the H_2S concentration was gradually increased to about 1%. A white aerosol formed in the gas stream and the concentration of the aerosol in the gas stream increased as the H_2S concentration increased, which adds additional support for the belief that the aerosol being formed is primarily from sulfur compounds and not from NH_3 . However, no solid deposits formed on the quartz tube downstream from the catalyst, even after an hour of operation. Thus, the deposition of solid aerosols near the catalyst can be avoided by ensuring efficient oxidation of the gas stream. In addition to the white aerosol that was observed, small amounts of liquid condensate appeared downstream from the catalyst. Some of the condensate was collected in a beaker and analyzed by IC. Results of those analyses showed that it contained over 95% sulfate. This further supports the belief that the white aerosol is a result of the catalytic oxidation of H_2S to form sulfuric acid mist. It is believed that complete destruction of the NH_3 will result in liquids (containing no dissolved solids) condensing in downstream portions of the catalyst tube, while no dry solids will deposit anywhere in the tube.

Similar tests were run in which NH_3 , H_2S , and N_2 were passed over a hot Pt catalyst. However, in these tests, the amount of air used was approximately stoichiometric for the complete oxidation of the gas stream. These tests were performed to determine if NH_3 would be preferentially oxidized relative to H_2S . In the absence of H_2S , no NH_3 could be detected with color-indicating paper. The sensitivity of the paper to NH_3 was sufficient to conclude that at least the large majority of NH_3 was being oxidized. With the addition of H_2S , a considerable amount of solid deposits formed at the end of the quartz tube containing the catalyst. In

addition, a small amount of liquid condensate was observed in the Teflon line farther downstream. A portion of the solid was analyzed by XRD, while another portion was dissolved in water (sample was completely water soluble) and analyzed for ammonium and sulfate ions by IC. In addition, the liquid condensate was rinsed out with deionized water and analyzed by IC. The XRD analyses indicated that the solid condensates were largely ammonium sulfate, which was also confirmed by the IC analyses. The condensate was also high in ammonium and sulfate ions. In the absence of HCl, residual NH₃ in the gas stream after the catalyst readily combines with the oxidation products of H₂S. Although much of the NH₃ was oxidized, there is not a high degree (if any) of preferential oxidation of NH₃ relative to H₂S.

In another series of tests, various mixtures of air, N₂, NH₃, and H₂S were used. For the tests involving NH₃ or H₂S, concentrations of each of those compounds were about 2%, and roughly 200% excess air was present for the oxidation reactions. In addition to collecting the liquid condensate at the end of the quartz tube after each test, gases exiting the catalyst tube were bubbled into deionized water for a period of 30 minutes to collect water soluble species. In all the tests where the gas stream contained H₂S, a fine white aerosol was observed above the water as the gases were being bubbled into it. Analyses of the collection solutions and liquid condensates by IC indicated that there was no ammonium ion in the solutions, regardless of whether H₂S was present or not. Nitrate ion was present in the collection solutions when NH₃ was used in the absence of H₂S, but not when H₂S was present along with the NH₃. The reasons for this are not known, but it was not deemed necessary to pursue this issue further. As with previous tests, at least 99.9% of the NH₃ was removed.

It will be difficult to avoid the formation of a sulfuric acid aerosol during the catalytic oxidation of gasifier streams. This in turn may necessitate the use of a heated sample cell for the determination of Hg. Results suggest that a temperature of at least 100°C will be required to prevent the condensation of the oxidation products. Also, precautions in the operation of the gas conditioner are advisable to ensure that the catalyst remains at the desired temperature during sampling. If this is not done, there is a significant risk of completely plugging the sample lines, resulting in pressure buildup that could damage portions of the CEM. The problem associated with the fine white aerosols is of less concern for HCl analyses using ion mobility spectroscopy, since large gas stream dilutions are required for that technique in order to maintain a fairly constant gas matrix composition.

The liquids formed during gas stream oxidation will probably need to be kept in the vapor phase during sample transport. Based on tests with N₂/NH₃/H₂S mixtures blended with air, the liquid condensate downstream from the catalyst was found to have a high boiling point of 250-275°C. This was of concern because the Teflon lines connected to the catalyst tube could not be maintained at such temperatures, and the accumulation of large amounts of liquid condensate was undesirable for a CEM. In view of this concern, tests were performed with a simulated gasifier stream consisting of 50% CO, 15% CO₂, 25% H₂, 8% CH₄, 2% H₂S, and 1% NH₃. In those streams, it was noted that the temperature necessary to keep the liquid in the vapor phase was only about 150 to 170°C, which is much more desirable and will allow the use of Teflon fittings downstream from the catalyst. In the initial tests (using only N₂/NH₃/H₂S mixtures blended with air), the high boiling points for the liquids were probably due to the condensate being a strong acid. With the simulated gasifier stream, greater amounts of water were formed

downstream from the catalyst due to the oxidation of other gases such as H₂ and CH₄. Thus, the liquid condensate would be less acidic and would therefore have a lower boiling point.

Although exit temperatures of 150 to 170°C would allow the use of Teflon downstream from the catalyst, there were still concerns about passing those gases directly into a Nafion-based drying system. The maximum allowable temperature of the gas stream entering the dryer is approximately 150°C. Also, drying efficiency decreases as the gas temperature increases, so a temperature of 150°C is undesirable from a drying standpoint. Therefore, tests with the simulated gasifier stream were repeated, with the exception that the oxidation air blended with the simulated gasifier stream was humidified by bubbling it through deionized water. Because actual gasifier streams will have substantial amounts of moisture prior to gas stream oxidation, this more closely simulated field conditions. With the added humidity, the temperature required to keep the liquid in the vapor phase decreased to only 120-130°C, which would allow us to pass the gases directly into the Perma Pure dryer without exceeding temperature limitations. This is believed to be due to a further decrease in acid concentration, which in turn would reduce the boiling point of the liquid. When sampling actual gasifier streams, the elevated levels of moisture in the raw gases will probably result in further decreases in the temperature required to keep the liquids downstream from the catalyst from condensing.

Flame Formation

During tests on the removal of NH₃ from simulated gasifier streams, a periodic problem was noted related to flames forming in the quartz catalyst tube and migrating slightly upstream before extinguishing. This is sometimes called a "cool flame." There is enough energy for a flame to form, but the temperature is below the flashpoint of the gases and the flame quickly extinguishes since there is not enough energy for combustion. This occurred both in the presence of a Pt catalyst and in empty tubes heated to 900°C. Numerous tests were performed to circumvent this problem. While using an empty tube heated to 900°C, tests were performed with a simulated gasifier stream (preblended in a single compressed gas cylinder) in which 0.5 L/min of gasifier stream was blended with 1.0 L/min of air. A flame occurred in those tests. As the air flow was increased to 1.5 L/min, the flame moved upstream and overheated a Teflon fitting that was connected to the upstream end of the quartz tube. With further increases in the air flow rate (2 L/min or more), the gas flow had sufficient pressure to push the head of the flame back towards the catalyst, although the pulsing flame still extended upstream from the catalyst somewhat.

Tests were also performed with a simulated gasifier stream in the presence of a Pt catalyst heated to 900°C. Approaches that were examined to eliminate the flame included 1) increasing the ratio of the dilution air to gasifier stream in order to lower combustible gas concentrations, and 2) decreasing the ratio of dilution air to gasifier stream in order to hopefully suppress flame formation through decreased oxygen content. Those approaches did not help eliminate the formation of the flame. However, it was discovered that the flame occurred only if a preheat zone was used just prior to the 900°C catalyst region. Tests indicated that lowering the temperature of the preheat zone (normally at about 900°C) eliminated the flame. Specifically, the flame did not form until a temperature of roughly 750°C was attained in the preheat zone.

Based on the results noted above, tests were performed with a simulated gasifier stream in which the temperature of the preheat zone was maintained at 600°C, which is the sample line temperature upstream from the catalyst we anticipate using in actual sampling operations. The preheated gases passed over a hot (900°C) Pt catalyst bed. In addition, an alumina bed heated to 900°C was added immediately downstream from the catalyst to serve as a polisher. A simulated gasifier stream containing approximately 50% CO, 15% CO₂, 25% H₂, 8% CH₄, 2% H₂S, and 1% NH₃ was then passed through the catalyst tube. In that gas stream, all of the individual gas components were individually metered and blended together. Initial tests involved using 0.5 L/min of simulated gasifier stream blended with 1.0 L/min of air. The concentrations of CH₄ and H₂ were varied to provide a wide range of combustible gas concentrations. No flames formed in those tests. However, as was the case before, the flame appeared if the temperature of the preheat zone was heated to 750°C or more. The tests with the 600°C preheat temperature prior to the catalyst were repeated using 1 L/min of simulated gasifier stream blended with 2 L/min of air. No flame was observed, and NH₃ levels were reduced to less than 0.5 ppm. These results indicate that excess air requirements for effective NH₃ removal can be substantially reduced and the flame can be avoided by using a 600°C preheat zone, followed by a Pt catalyst at 900°C. After about 24 hours of operation using simulated gasifier streams, no physical degradation of the catalyst was noted, and no decrease in NH₃ removal efficiencies was observed.

Miscellaneous

Tests were performed using a single compressed gas cylinder containing a simulated gasifier stream. The simulated gasifier stream consisted of 50% CO, 15% CO₂, 25% H₂, 8% CH₄, and 2% H₂S. This gas stream was blended with NH₃ to provide a final NH₃ concentration of 1%. During testing, the catalyst began to plug up, which caused excessive backpressure on the system and prevented continued operation. The restricted flow was due to greenish deposits in the upstream portion of the catalyst. Analysis of the greenish material by SEM-EDX indicated that it was nickel oxide. It is possible that the nickel was initially present as another compound, such as nickel carbonyl, and was later converted to the oxide form. All of the nickel deposits could easily be dissolved in hot 10% HNO₃. Analysis of the interior of the stainless steel sample transport line by SEM-EDX indicated that the interior surfaces were badly pitted and corroded. Thus, the stainless steel tubing is the likely source of the nickel, even though the vendor of the compressed gas cylinder containing the simulated gasifier stream believed that the stainless steel should hold up well with this gas blend. The interior walls of a brand new piece of stainless steel tubing was also examined by SEM-EDX. No pitting or grain boundary attack was noted. However, the interior surfaces were very rough, which would make it more subject to chemical attack in view of the increased surface area. The problem was eliminated by going to Teflon lines upstream from the catalyst. This suffices for laboratory testing, but can not be used in the field when the sample transport lines will be heated to temperatures that Teflon could not withstand. For field use, another type of sample transport line is needed.

PALLADIUM WIRE CATALYST

Ammonia Removal Efficiencies

The use of a palladium (Pd) catalyst was tested as a possible alternative to Pt in view of its lower cost relative to Pt and because of its known lower catalytic activity, which in turn could result in effective NH₃ removal without the formation of acid byproducts and aerosols. The Pd catalyst consisted of about 10 feet of 0.010-inch diameter Pd wire, which was placed in a ¼-inch OD quartz tube. In the initial tests, a total gas flow of about 1000 mL/min was passed over a hot (700-900°C) catalyst using various mixtures of N₂, air, NH₃, and H₂S. For the tests involving NH₃ and H₂S, about 200% excess air was present for the oxidation reactions to go to completion. During testing, the gases which had passed over the catalyst were bubbled into deionized water collection solutions for a period of 30 minutes. In addition, the liquid condensate which formed at the end of the quartz tube containing the catalyst was collected. Results of IC analyses on those samples showed that no ammonium ion was present in the collection solutions or the liquid condensate, indicating that the NH₃ removal was 99.9% or greater, regardless of whether H₂S was present or not. Thus, for these test conditions, the effectiveness of the catalyst was the same for both Pt and Pd. As with the tests using Pt, nitrate was present in the collection solutions after testing when NH₃ was used in the absence of H₂S, but no nitrate was detected when H₂S was present.

Because the decomposition of NH₃ is a critical sample conditioning step in our overall analytical scheme, tests were performed to study the range of acceptable conditions for the complete removal of NH₃ using a Pd catalyst. Initial tests involved using an air stream flowing at 1000 mL/min blended with 20 mL/min of NH₃ to give a final NH₃ concentration of 2% (v/v) and an excess air concentration of roughly 500%. Further tests were also done with proportionally increased NH₃ and air flows, which increased the total gas flow rate over the catalyst while maintaining a constant NH₃ concentration and a constant ratio of excess air to NH₃. The gas streams, with total gas flow rates ranging from about 1000 to 4000 mL/min, were then passed over a heated Pd catalyst. The amount of NH₃ in the gases downstream from the catalyst was determined by bubbling the gases into absorbing solutions (water) which were contained in a series of two 125-mL Erlenmeyer flasks. Results of IC analyses on the solutions indicated that little or no NH₃ passed through the catalyst when using a total gas flow rate of 1000 mL/min, which is consistent with results obtained previously. However, at a total gas flow rate of 2000 mL/min, small amounts (less than 0.05% of the initial NH₃ concentration) of the NH₃ began getting through. In addition, the initial water trap collected only about 90% of the NH₃ exiting the catalyst tube at the higher gas flow rate (normally the first solution collects 100% of the NH₃ exiting the catalyst tube). At a total gas flow rate of 3000 mL/min, the NH₃ removal efficiency decreased substantially, and the first water trap was ineffective at collecting the NH₃. The results from these tests indicate that our NH₃ collection procedure may need to be modified when performing tests with gas streams involving total gas flow rates of 2000 mL/min or more.

Similar tests were performed with the exception that Sensidyne color-indicating tubes were used to directly measure NH₃ in the gas stream rather than using absorbing solutions to capture the NH₃ for subsequent IC analyses. The color-indicating tubes have an accuracy of about 25% according to the manufacturer, although this was not experimentally verified using our gas matrix. Unlike the tests with the absorbing solutions, results of these tests indicated that no (less

than 1 ppm) NH_3 was getting through the catalyst, even at total gas flow rates of up to 4000 mL/min with 2% NH_3 . One possible reason for this discrepancy is that small amounts of NH_3 are getting through the catalyst and then subsequently reacting with HNO_3 vapor (produced from the oxidation of NH_3), which could then form some sort of ammonium nitrate compound that would not be detectable with the color-indicating tubes. As noted earlier in the discussion of work with a Pt catalyst, the IC results appear to be more trustworthy than the color-indicating detection tubes for trace levels of NH_3 . Despite this, the colorimetric tubes were still sometimes used for information on general trends in NH_3 concentration as an experimental variable was adjusted.

The percent excess air necessary for complete removal of NH_3 was also examined. A gas stream consisting of 20 mL/min of NH_3 and 1000 mL/min of air was initially used. This constitutes about 500% excess air for the complete oxidation of NH_3 to NO_2 . Measurements for NH_3 using the semiquantitative color-indicating tubes downstream from the catalyst indicated that the majority of the NH_3 was removed under those conditions. While maintaining a constant NH_3 flow, the air flow was gradually decreased to determine how low of an air: NH_3 ratio could be used while still effectively removing the NH_3 . It was determined that an air flow of only 400 mL/min was sufficient to remove the NH_3 , but lowering the air flow below this rate resulted in low (few tenths of one percent) concentrations of NH_3 being detected downstream from the catalyst. Therefore, these results indicate that about 200% excess air should be used for the complete removal of NH_3 under these conditions. However, it should be pointed out that total gas flow rates decreased as the percent excess air decreased, which in turn increased residence times in the catalyst zone. Therefore, this excess air percentage should only be considered as an approximation since the excess air requirements are likely to change as the total gas flow rate changes. Also, as noted previously, the detection tubes used to determine NH_3 concentrations are only semiquantitative. Nonetheless, these results provide ballpark figures for excess air requirements under the experimental conditions studied.

Next, tests were performed with a constant air flow of 1000 mL/min and NH_3 flows ranging from 20 to 200 mL/min to further study excess air requirements. The approximate NH_3 concentrations in the gases downstream from the Pd catalyst were determined using color-indicating tubes. As the NH_3 concentration was gradually increased, no NH_3 was detected downstream from the catalyst until the NH_3 flow at the catalyst tube inlet was about 175 mL/min, which resulted in a reading of about 1 ppm NH_3 in the gases downstream from the catalyst. Results of these tests suggest that only about 75% excess air may be required for complete removal of NH_3 . In other tests, a constant NH_3 flow of 20 mL/min was blended with air flowing at 1000 to 2500 mL/min and then passed over the hot Pd catalyst. The gases exiting the catalyst tube were bubbled into absorbing solutions, which were subsequently analyzed for ammonium ion using IC. Results of the IC analyses indicated that there was complete removal of NH_3 for the flow rates tested. These tests are more indicative of actual field sampling operations in that we intend to use a gasifier stream flowing at about 1000 mL/min and then blend it with air as needed. Therefore, although tests were performed previously which involved 2% NH_3 flowing over the catalyst, the NH_3 concentration in the blended gas stream will never be as high as 2% since the NH_3 concentrations in raw gasifier streams will probably start at 1% or less and will then be blended with air before passing over the catalyst.

Next, tests were performed to investigate the Pd catalyst temperatures required for the complete removal of NH₃. For these tests, 400 mL/min of a nitrogen stream containing 3% NH₃ and 2% H₂S was blended with air flowing at 600 mL/min. Thus, NH₃ concentrations in the final blended gas stream were about 1.5%. Gases exiting the catalyst tube were bubbled into water and analyzed by IC to determine the amount of residual NH₃ in the gas stream. Results of those analyses are shown in Figure 2. Excellent NH₃ removal efficiencies were observed at catalyst temperatures in the range of 700-900°C, but were particularly high at temperatures of about 900°C. At temperatures near 900°C, NH₃ levels were reduced from 1.5% to less than 0.5 ppm. When the gas flows were increased by factors of 1.5, 2.0, and 2.5 while maintaining a catalyst temperature of 900°C, residual NH₃ in the blended gas stream gradually increased from 0.3 to 30 ppm. Thus, using total gas flow rates greater than about 1 L/min did not effectively destroy the NH₃ in the gas stream under the conditions used.

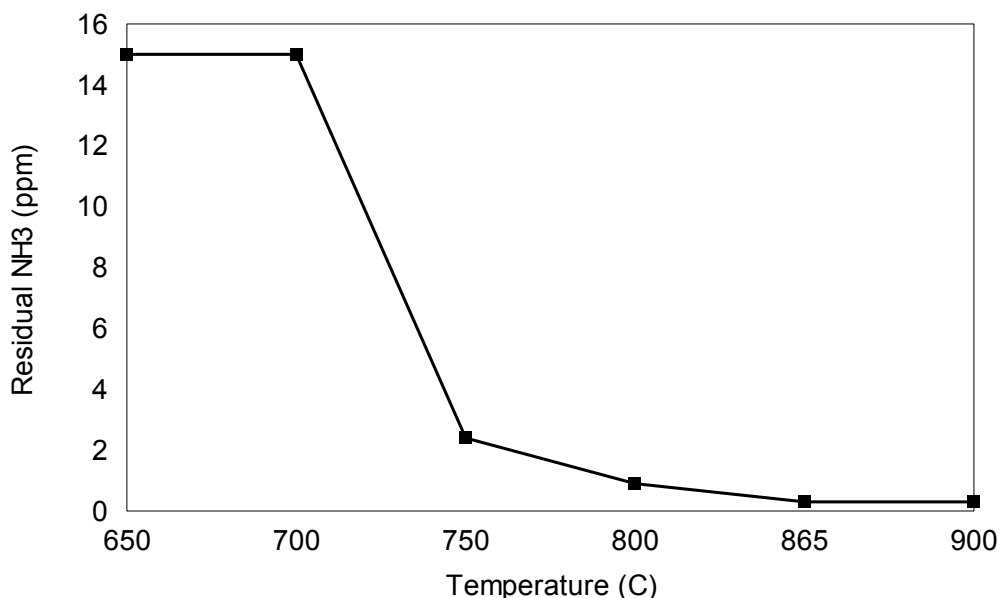


Figure 2. Effect of Pd Catalyst Temperature on NH₃ Removal.

Aerosols and Condensates

Tests were performed to investigate the proper temperature needed downstream from the catalyst to prevent the condensation of gases into solid deposits. This work was complicated by difficulties in removing all of the NH₃ from the gas streams, which substantially affected results on aerosol condensation. Through continued testing, it was determined that small amounts (<1% of the initial concentration) of the NH₃ were still passing over the catalyst unaffected. Efforts were then focused on removing these trace levels of NH₃. The amount of Pd catalyst was increased from 10 feet to 20 feet of wire, the gas preheat zone upstream from the catalyst was lengthened, and the packing characteristics of the catalyst in the quartz tube were improved. With these changes, NH₃ was completely removed from the gas streams. However, because of problems noted in the "Miscellaneous" section below, the use of a Pd catalyst was discontinued.

Miscellaneous

For tests performed at a total gas flow rate of 3000 mL/min or higher, the 1/4-inch OD quartz tube downstream from the catalyst overheated. Consequently, the Teflon line connected to the downstream end of the quartz tube (about 12 inches from the catalyst) also overheated and burned through the Teflon. For effective sample transport, we prefer to couple Teflon lines to the exit of the catalyst tube. Therefore, tests were performed to study approaches for cooling the gases sufficiently to enable the use of Teflon lines downstream from the catalyst tube without extending the length of the quartz tube or using costly or cumbersome cooling devices. While using air, a total gas flow rate of 3 L/min was passed through the 1/4-inch OD quartz tube. The Pd catalyst in the tube was heated at 900°C. Directing a fan on the downstream portions of the catalyst tube had little effect on the temperature of the gases exiting the tube. Next, a 2-inch long chromel coil was placed inside the quartz tube downstream from the catalyst. The coil consisted of about 12 inches of a wire 0.02 inches in diameter. The coil improved cooling by causing turbulence and increased the degree of contact between the tube walls and the hot gases. Using this internal coil decreased the exit gas temperature from about 260°C to 180°C, which was now in a suitable range for PTFE Teflon. In actual practice, a chromel wire would not be placed inside the catalyst tube. However, it is anticipated that substituting chromel for Pd or Pt would still provide effective cooling.

Using quartz cooling coils at the downstream end of the catalyst tube was also investigated as a method for cooling the gases to the point where Teflon fittings could be used. When a quartz cooling coil was used, gas temperatures at the exit of the tube were reduced to 30°C when using air flow rates of 3 and 5 L/min. The quartz coil consisted of 30 inches of quartz tube formed into a coil 10 inches long and one inch in diameter. When the length of the coil was reduced by 50%, the gas temperature was about 90°C at a flow rate of 3 L/min. In other work, it was later found that increasing the diameter of the quartz tube (housing the catalyst) to 3/8" provided a number of benefits, including reduction of backpressure upstream from the catalyst. Therefore, the 1/4" diameter quartz tube was permanently replaced with a 3/8" diameter quartz tube. With the larger diameter tube, the linear velocity of the gases decreased considerably, and the gases were sufficiently cooled by the time they exited the tube. Therefore, the addition of a cooling coil was no longer needed.

While performing tests on NH₃ removal with a Pd catalyst, an overall bulk bed temperature of about 900°C was generally maintained. However, due to localized heating of the catalyst surface, complete meltdown of the catalyst was encountered on several occasions. At a minimum, fusion of pieces of the catalyst to one another was routinely observed. This in turn resulted in decreased NH₃ removal efficiencies due to decreased available surface area. Because of these problems, we discontinued the use of a Pd catalyst for oxidizing the sample gas streams. Because the melting point of Pt is several hundred degrees Celsius higher than that of Pd, using Pt expands the "temperature window" at which the catalyst can operate to effectively remove NH₃ without melting or fusing the catalyst. In the work with Pt catalysts, which was discussed earlier, no melting or fusion problems were noted with extended use.

FINAL DESIGN OF CATALYST TUBE

A sample transport temperature (prior to the catalyst) of 600°C will probably be used. The sample gases will enter a 3/8-inch OD quartz catalyst tube. The hot sample gases will first be passed over a bed (about 1 1/2 inches long) of granular (-6 to +12 mesh) alumina at 900°C or higher, which will oxidize most of the gas stream. This will be followed immediately by a 1-inch zone of Pt catalyst (pieces of Pt wire) to serve as a polisher to remove residual traces of NH₃ or other unwanted compounds (e.g., hydrocarbons) from the gas stream. Finally, the gases will pass through a pyrolysis zone at about 900°C in order to convert Hg to the elemental form prior to the detector.

OXIDATION WITHOUT CATALYST

Tests were performed using a simulated gasifier stream (50% CO, 15% CO₂, 25% H₂, 8% CH₄, 2% H₂S, and 1% NH₃) flowing at 0.5 L/min through *empty* quartz tubes with outer diameters of 1/4" and 3/8". The simulated gasifier stream was blended with 1.5 L/min of air prior to the quartz tube. The portion of the quartz tube that would normally house the catalyst was heated to 900°C. In addition, a preheat zone at 900°C was used immediately prior to the catalyst. In those tests, virtually all of the NH₃ was removed, even with no catalyst. Thus, the catalyst is not of critical importance for the removal of NH₃. However, because aromatic hydrocarbons (a strong interference in the determination of Hg by AA) are much more difficult to thermally decompose, an oxidation catalyst will still be used. In addition, the catalyst will be helpful to remove tars, since heating at 900°C is not expected to destroy those compounds. Finally, using a catalyst will help ensure complete removal of NH₃ under a wide variety of conditions in the field.

NAFION TUBING

The use of Nafion-based dryers to remove NH₃ gases from sample streams was investigated. The sample gas is transported in the Nafion tubing while passing a countercurrent purge gas stream over that tubing. According to literature provided by the manufacturer (Perma Pure), this drying system may result in some losses of NH₃ into the purge gas. The magnitude of such losses were unknown. However, if the losses were considerable, it could potentially be used to remove NH₃ from gasifier streams. Also, it could potentially be used as a polishing step after the use of an oxidation catalyst. To evaluate the use of Nafion dryers for this purpose, we used a dry sample stream containing 5% NH₃ in air flowing at 500 mL/min. Countercurrent purge gas flow rates of 1000 and 2500 mL/min were used, which provided purge:sample gas flow ratios of 2:1 and 5:1. The sample gases and purge gases were bubbled into deionized water absorbing solutions, which were subsequently analyzed for ammonium ion concentrations by IC. Results of the IC analyses indicated that at least 95% of the NH₃ was retained in the sample gas stream, regardless of whether a 2:1 or 5:1 purge:sample flow ratio was used. Therefore, this approach did not appear to have potential for removal of NH₃ from sample gases. However, it was later learned that the presence of moisture is required in order for NH₃ losses to occur (NH₃ is reportedly captured by water vapor and is removed along with the moisture as ammonium

hydroxide). Unfortunately, in the presence of sulfur-bearing gases under oxidizing conditions, ammonium sulfates are anticipated to form, which are expected to quickly plug the openings in the Nafion membranes.

MOISTURE REMOVAL

The potentially high moisture content (up to 50% by volume) of coal gasification streams requires that most of the moisture be removed from the gas stream prior to entering the analytical detection systems. For this purpose, a gas drying system from Perma Pure was selected for use in the overall CEM design. This unit, shown in Figure 3 below, is a Perma Pure GASS™ (Gas Analysis Sampling System) dryer designed to handle a 1-2 L/min gas flow with up to 50% moisture. That system contains two Perma Pure PD-1000-24AFS dryers with Nafion tubes as well as an internal Model FF-250-FG Filter Coalescer. By properly adjusting the temperature of the coalescer, it may also be possible to remove some of the acid gases without condensing water. This dryer is one of the key components to the gas conditioning system used for both the Hg and HCl determinations.



Figure 3. Gas Drying System from Perma Pure.

TAR REMOVAL

Studies were performed at a 800 kW (thermal input) biomass gasifier to determine whether a Pt catalyst could effectively remove tars from the gas stream. Tar removal is needed prior to

analyzing Hg or HCl in coal gasifier streams. About 1 L/min of gasifier stream was blended with 2 L/min of air and passed over a hot Pt catalyst in a quartz tube. The quartz tube was long enough so that the downstream end of the tube was at 50°C or less, thereby making it easy to see whether tars were depositing. The catalyst zone was initially heated to 900°C to activate the reactions. The catalyst tube contained three zones. The first zone consisted of α -alumina to oxidize the combustible gases such as CH₄, CO, and H₂. This would help prevent overheating of the Pt catalyst zone by oxidizing the portion of the gas stream where a catalyst was not required. The second zone contained Pt wire to serve as a catalyst for oxidizing tars and other organic compounds that were not oxidized in the alumina zone. The third zone contained a commercially available Pt catalyst on an alumina substrate. That catalyst material has an extremely high surface area relative to the wire and served as a backup catalyst in case the first catalyst zone did not sufficiently oxidize the gas stream. For comparative purposes, tests were also performed with hot (900°C) α -alumina alone (no catalyst) to see if the tars could be oxidized in this manner.

When using an empty catalyst tube, tars quickly deposited in the quartz tube and the deposits became very heavy within just a few minutes. Using alumina at 900°C did not prevent tar buildup. However, when using the Pt catalyst, the tars were completely removed. The catalyst was initially heated to 900°C to start the reactions. After the reactions (highly exothermic) began, the external heat source was decreased but not turned off. Sampling was performed for 30 minutes with no tars getting through the catalyst. At that time, sampling was discontinued. After the sampling system was taken back to the laboratory and examined, it was noted that a quartz wool plug that was used in the catalyst tube had become partially fused. In addition, there was some pitting and other indicators in the quartz tube itself that suggested temperatures in the Pt zone were near the melting point of quartz (about 1600°C). Therefore, precautions should be used to keep the temperature from reaching such extremes. Turning down the external heat source further would be one option for decreasing the overall temperature of the catalyst bed.

SAMPLING ISSUES

SAMPLE TRANSPORT LINES

Consideration was given to the type of sample transport tubing to use between the gasifier and the catalyst. Stainless steel was considered as one option, but the composition is inherently reactive with the gas matrix involved. Therefore, additional options were considered, including the possible use of Hastelloy B, Hastelloy X, alloy C-276, and Ni-200 .

A metallurgical engineer suggested that alloy C-276 would be the best choice for the given conditions of temperature and gas matrix composition. It was noted that Ni-200 will be quickly pitted by HCl in the gasifier stream. Hastelloy-B will be limited to lower temperatures because of the corrosive nature of the gasifier streams. Hastelloy-X is generally used in oxidizing conditions and is high in iron content, which will be degraded by the corrosive gases. The C-276

is high in Mo (15-17%) content and will help decrease the effect of the corrosive gases. Also, that alloy is expected to hold up under the sample transport temperatures of 600°C that are anticipated, although this is approaching its upper temperature limit. Haynes 242™ alloy, which had not been previously considered, was suggested as a better option. The higher Mo (24%) content of that alloy is expected to result in better performance (in terms of corrosion) than the C-276 alloy. Unfortunately, after contacting numerous vendors who stock the 242 alloy, we were unable to locate a vendor who manufactures any tubing out of that material. Some vendors who manufactured C-276 tubing in the desired size (3/8-inch OD) were located. However, with that vendor, a 20-foot section selling for \$650 must be purchased. In addition, the necessary fittings in upstream sections of the sample transport system would cost an additional \$600 if made of the C-276 alloy. Consequently, the total cost of the tubing plus the fittings would come to over \$1200, which was too costly in view of budget constraints.

Because of cost considerations with alloy C-276, the use of electropolished 316 stainless steel was reconsidered. There could be some tradeoffs with respect to reactivity of the metals to gasifier streams. Although stainless steel is expected to be inherently more reactive to the sample gases than C-276 alloy, the reactivity of the stainless steel can be substantially diminished by electropolishing. The C-276 alloy, on the other hand, is inherently less reactive but can not be electropolished nearly as efficiently at the 300 series stainless steels. Therefore, it is possible that the reactivity of electropolished stainless steel could be comparable to the C-276 alloy that is not electropolished. Also, as opposed to a cost of over \$1200 for C-276 tubing and fittings, getting electropolished stainless steel tubing and fittings will cost only about \$350. For the electropolished stainless steel, the overall reactivity of the metal is diminished in part because of the reduced (90% or more) surface area on the interior of the tube. Electropolishing is superior to mechanical polishing, with friction coefficients 3 to 4 times lower than those typically obtained by mechanical polishing. Also, during the electropolishing operations, a chromium-enriched surface is typically produced due to preferential removal of Ni and Fe. This further improves corrosion resistance. In view of cost considerations, the electropolished steel may be an attractive sample transport option. In the future, it may be desirable to test the C-276 alloy and compare it to electropolished type 316 stainless steel during prolonged use.

Next, because of potential problems associated with contacting metals with corrosive gases, we considered using silica-coated stainless steel (sold as Silcosteel® by Restek Corporation). Silcosteel has a fused layer of silica of uniform thickness. Depending on consumer preferences, the thickness can range from 100 to 5000 angstroms. However, we were concerned about the differences in thermal expansion coefficients between the silica and the steel, which could potentially result in the silica flaking off as the tubing is repeatedly heated and cooled. Therefore, we took a small piece of Silcosteel having roughly 1000 angstroms of silica and subjected it to 10 heating (to 600°C) and cooling cycles in a muffle furnace. The tubing was maintained at 600°C for only a few minutes for each cycle. The interior of the tubing, as well as a fresh piece of tubing, were then examined by SEM-EDX for physical appearance and chemical composition. Results of the analyses showed that the silica was still evenly distributed (on a macro scale) after heating, and there was no evidence of any flaking or other degradation. However, a color change was noted after heating. The fresh tube was bluish in color, while the heated tube was purple. Personnel at Restek noted that a color change from blue to purple can indicate that the thickness of the silica layer decreased. Although they have made similar

observations when heating their tubing in a muffle furnace, the mechanism for the possible silica “loss” is unknown. In view of this, we performed additional tests to determine whether the thickness of the silica layer would continue to decrease with repeated heating (to 600°C) and cooling cycles. Fresh Silcosteel was subjected to 10, 20, and 30 heating cycles. In addition, a fresh sample was heated in air at 600°C overnight. Visually, there was a color change from sample to sample, which could possibly indicate a change in the thickness of the silica layer. However, analyses of the interiors of the tubes by SEM-EDX showed uniform silica coatings for every sample, and there were no signs of any flaking or pitting. Based on this information, personnel at Restek now believe that we are not losing silica, and that the color changes are probably due to a changing index of refraction as the sample is heated. Therefore, Silcosteel appears to be a viable sample transport material for our purposes. An area of concern at the anticipated sampling temperatures is that the temperatures are starting to approach the point at which solid state diffusion of carbon in the steel may occur, in which case the silica could start to flake off. However, if the Silcosteel degrades with prolonged use, it will not be costly to periodically replace necessary sections of the sample tubing. Alternatively, it may be advisable to go to silica-coated super alloys that will be able to withstand the sampling environments better. Although this would initially be more costly, it might be the least expensive approach in the long run.

MONITORING FLOW DURING FIELD SAMPLING

Consideration was given to monitoring sample gas flow rates during field sampling operations. The heated gases can not be run into a flow meter prior to gas stream oxidation because of potential problems with analyte losses and because of problems from tars. One possibility for measuring flows is to use an orifice plate. The pressure drop across the plate would be monitored and the magnitude of the pressure drop would be correlated with volumetric gas flows. Similarly, in the Ames Laboratory alkali monitoring system, the sample flow is monitored by a differential pressure flow cell. In that system, the flow element consists of a 1/4-inch OD stainless steel rod that is 1 1/4” long with a 1/8” hole in it. The differential pressure generated by the flow of the sample through the steel tube is then monitored and correlated to volumetric flows. In any event, because of effects of gas densities among the gases present, knowledge of the composition of the gasifier stream is required in order to obtain accurate flow calculations. The situation is even more complex when gas stream oxidation is used and gas flow readings are taken after the oxidation occurs. This is because some of the primary matrix gases are converted to gaseous species with completely different gas densities, and some of the gases are converted entirely to water which will subsequently be removed by the gas conditioning system.

The Hg and HCl CEMs have not yet been field tested. Problems may be encountered in the field which will require modification of some of the gas conditioning components. Therefore, until the overall technology (combined analytical and sampling systems) is proven in the field, work focused on whether the system will track changes in analyte concentrations at a given flow rate, and an emphasis was not placed on uncertainties in the sample flow rate at this time. The total dry gas flow rate (after gas stream conditioning) and the flow rate of the dilution/oxidation air will both be monitored. The approximate flow rate of the gasifier stream

will then be calculated by difference. Using this approach, the calculated flow rate of the gasifier stream should be accurate to within 50%, which is adequate for our purposes at this stage in the development of the CEMs.

USE OF AN INERTIAL FILTER

Although an inertial filter was not field tested in this work, such a filter was considered for sampling gasifier streams. A Model 7611 IGS (inertial gas sampling) cross-flow filter with an eductor from Mott Corporation was purchased from other funding sources and would be available for short-term use to test its suitability for sampling gasifier streams. With this filter, a high velocity gas enters the eductor to develop a high-velocity axial flow through the filter tube. The high axial velocity prevents particulate buildup in the filter. A clean sample flow develops radially through the porous tube wall at a very low face velocity. The porous length of the filter is 12 inches, allowing for a maximum clean sample flow rate of 2 L/min. The cut point for this particular filter is about 0.5 microns. The unit is constructed of type 316 stainless steel porous media, type 316 stainless steel housing and connector, and type 300 stainless steel eductor. For prolonged gasifier sampling, other materials of construction (much more costly) would be preferred once the utility of this filtering approach has been demonstrated.

MERCURY STUDIES

SELECTION OF METHODS TO EVALUATE

The goal of our work was to adapt conventional technologies to the monitoring application of interest rather than trying to develop new analytical technologies which would, in all likelihood, take many years of development. At the time this work was started, there was very little available to choose from in terms of relatively inexpensive Hg CEMs. Based on available information at the time, the analytical methods considered for use in our Hg CEM included cold vapor atomic absorption (CVAA, or AA), cold vapor atomic fluorescence (CVAF, or AF), and gold amalgamation devices using resistivity measurements. After weighing the pros and cons of those methods for our applications, we selected AA and AF for further consideration. AA is one of the most common laboratory methods for determining Hg, while AF has been gaining in popularity in recent years. We decided not to use the gold amalgamation device (“Jerome” analyzer sold by Arizona Instruments) for a variety of reasons. Company representatives informed us that the instrument must be returned to the manufacturer every 6-12 months for electronic calibration (cost of about \$400) and sensor replacement (cost of about \$600) when used intermittently. For the continuous operation desired, the unit may have to be sent in for recalibration and sensor replacement every 2 to 4 weeks. Because of the calibration logistics, calibration frequency, and probable frequent replacement of the sensor, that unit was not considered further for on-line analysis of coal gasifier streams. At the time this decision was made, the problems associated with using gold films in the presence of NO_x (which would be formed during gas stream oxidation) and acid gases were not yet known.

The following sections discuss our work on the development of a Hg CEM. For the purposes of our work, concentration units of ppb_w and µg/m³ are used synonymously, even though they are slightly different. Since testing typically involved observing trends or observing relative concentrations between tests, small uncertainties in the exact Hg concentrations were not important for data evaluation.

ATOMIC ABSORPTION VS. ATOMIC FLUORESCENCE

OVERVIEW OF TECHNOLOGIES

Atomic absorption spectroscopy (AA) involves free neutral ground-state atoms absorbing light energy that is characteristic of that particular element. As light is absorbed by the analyte in the sample cell, a decrease in the transmitted light intensity will result. The transmitted intensity, I_t , is related to the incident intensity, I_o , by the Beer-Lambert Law (Eq. 1), where "a" is the absorptivity of the analyte, "b" is the path length of absorption, and "c" is the concentration of the analyte. The absorbance, "A", of the analyte is given by Eq. 2.

$$I_t = I_o 10^{-abc} \quad (\text{Eq. 1})$$

$$A = -\log I_t/I_o = abc \quad (\text{Eq. 2})$$

The absorbance is expressed in terms of "absorbance units" (AUs) and is linear with analyte concentration. At low absorbance values, milliabsorbance units (mAU) are usually used. A Hg lamp is usually employed to generate the characteristic radiation for Hg. The most common wavelength to use for analysis is 254 nm, since absorption is strongest at that wavelength. Many Hg detectors use both a sample beam and reference beam. The radiation intensity passing through the analyte-free reference cell represents the incident intensity, while the radiation intensity passing through the sample cell represents the transmitted intensity. For the measurement of Hg, the Hg must be present in the elemental vapor phase and not combined with other elements in a molecular form. Problems of special concern for AA include spectral interferences from molecules such as hydrocarbons, H₂S, and SO₂.

AF employs a type of photoluminescence similar to that in AA in that both involve the absorption of light energy that is characteristic of a particular element by a free neutral ground-state atom. However, the desired signal for AF is the emitted or luminesced light energy from the excited atom and not the transmitted light. If the luminesced radiation is the same frequency as the absorbed light, then resonance fluorescence occurs. The AF detector used in this study measures the resonance fluorescence of elemental Hg at 254 nm. The fluorescence light intensity, I_f , is directly proportional to the absorbed light using Eq. 3, where "K" is a constant of proportionality which depends on the element and its environment. If a substitution is made for the transmitted intensity, I_t , then Eq. 4 results.

$$I_f = K(I_o - I_t) \quad (\text{Eq. 3})$$

$$I_f = KI_o(1 - 10^{-abc}) \quad (\text{Eq. 4})$$

Deviations of the fluorescence signal from Eq. 4 can be due to primary or secondary absorption effects. The primary absorption effect is absorption of the incident radiation before it reaches the portion of the sample cell observed by the detector. The secondary absorption effect is absorption of the fluorescence signal before reaching the detector and is usually due to self-absorption by the analyte. Combining Eq. 4 with the absorption effects gives Eq. 5, where "p" and "s" are the path lengths for the primary and secondary absorption effects, respectively. For small absorbencies ($abc < 0.01$ with $p + s < b$), Eq. 5 can be approximated by using Eq. 6, and the fluorescence intensity is directly proportional to the concentration of the analyte.

$$I_f = KI_0 10^{-apc} (1 - 10^{-abc}) 10^{-asc} \quad (\text{Eq. 5})$$

$$I_f = 2.303KI_0 abc \quad (\text{Eq. 6})$$

In addition to absorption effects, the intensity of the fluorescence signal can be decreased significantly due to "quenching" of the signal from certain other gaseous species in the sample. Quenching occurs when the excited analyte atoms transfer their excitation energy via collisions with other molecules. To avoid this problem, Hg is normally collected on gold and then thermally desorbed into an argon (Ar) carrier gas. Because even trace amounts of impurity gases can decrease sensitivity, ultra high purity Ar is preferred. Compared to AA, where numerous compounds interfere at the absorbing wavelength, AF is less subject to false positives.

LABORATORY EVALUATIONS

Two extremely sensitive mercury detectors were tested in the laboratory to demonstrate general analytical capabilities and to investigate their potential use for on-line analysis of Hg at coal gasification facilities. Specifically, a Thermo Separation Products Model 3200 Cold Vapor Atomic Absorption Mercury Detector and a Tekran Model 2500 Cold Vapor Atomic Fluorescence Mercury Detector were investigated. The Thermo Separation Products detector, which is equipped with a 10-cm cell, later became the workhorse for the bulk of our Hg work. The AA and AF units investigated in our work are shown in Figures 4 and 5, respectively.

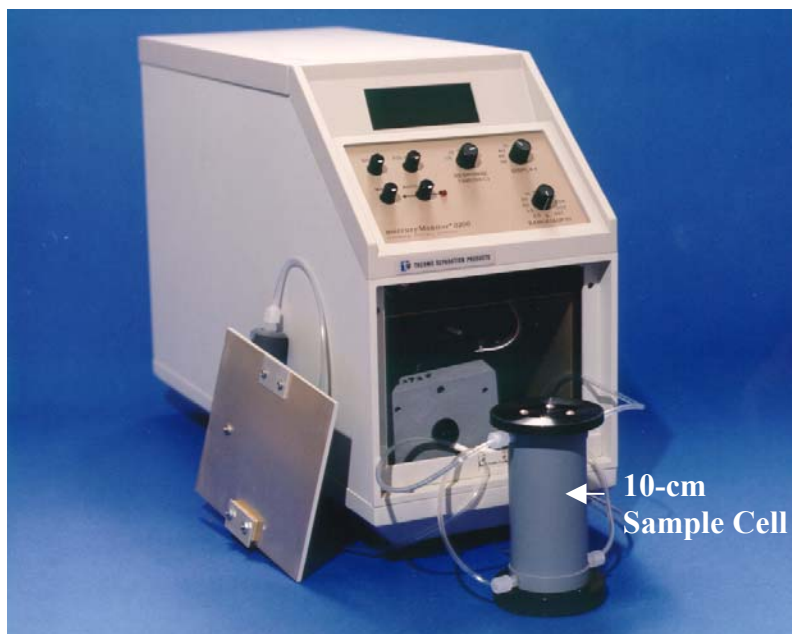


Figure 4. Thermo Separation Products Model 3200 AA Mercury Detector.



Figure 5. Tekran Model 2500 AF Mercury Detector.

Known amounts of vapor phase elemental Hg ranging from 3 to 50,000 picograms (pg) were collected with gas-tight syringes by withdrawing Hg-saturated air above a pool of Hg in an Erlenmeyer flask fitted with a septum. At known temperature and pressure, the Hg concentration in air was calculated from known Hg vapor pressure parameters. The smallest injection volume that could be reliably withdrawn was about 0.2 μL of Hg-saturated air, which corresponds to about 3 pg of Hg at room temperature. For comparative purposes, a series of

injections were performed with the AF detector in which Hg vapor was collected from the flask containing an Ar atmosphere rather than air, thereby eliminating any potential quenching effects from the air being injected along with the Hg.

Gases entering the detectors were spiked by injecting the Hg into the carrier gas upstream from the detector. For a given injection volume, three to six injections were made and the average peak intensities and relative standard deviations (RSDs) were calculated. In addition to manual injections of Hg vapor into the carrier gas, a VICI Metronics Model 340 Dynacalibrator with elemental Hg permeation tubes was used to provide a continuous flow of gases containing 0.1 to 960 ppb_w Hg in air. For the AA and AF tests using continuous Hg streams, three sequential signals at each Hg concentration were recorded, and averages and RSDs were then calculated from those data. For both the injections and continuous Hg streams, instrument responses were obtained by measuring peak heights on a strip chart recorder.

For the AA work, the carrier gas was zero air, except for one series of tests in which research grade Ar was used to allow for better comparisons with the AF data. Unless otherwise noted, research grade Ar was used as the carrier gas for the AF tests in order to avoid possible fluorescence quenching effects from molecular gases. However, a series of tests was performed with the AF detector in which a variety of other carrier gases were used in place of Ar. Those gases, which included CH₄, CO, CO₂, O₂, H₂, and N₂, were used to study the fluorescence quenching effects to determine whether it might be possible to pass conditioned sample gases directly into the detection cell for analysis. It should be noted that the AF instrument is not intended to be operated with carrier gases other than Ar, and that passing other gases through the detector is an aberration from specified procedures in the instrument manual. Flow rates for the carrier gases were typically 100-200 mL/min for AA, and was 115 mL/min for AF unless otherwise noted.

For the AA tests, base line drift was typically about 0.05 mAU/hr and was always less than 0.1 mAU/hr. A mAU reading of 0.1 is roughly equivalent to a Hg concentration of about 0.5 ppb_w in air or an injection of several pg of Hg. Minimal base line noise was observed even for flows up to 1000 mL/min.

Results from the Hg injections into the AA unit indicated that the detector could easily detect less than 3 pg Hg. A theoretical detection limit of 0.3 pg Hg was calculated from the recorder data. The instrument response showed good linearity in the range of 3 to 50,000 pg. RSDs were typically \pm 1-5% for injections of 25 pg or more and were typically \pm 10-15% for injections of lesser amounts.

For the tests with continuous Hg streams into the Hg detector, the dynamic range was spanned at least four orders of magnitude in Hg concentration. A typical signal for a Hg concentration of 0.5 ppb_w is shown in Figure 6. As can be seen, an excellent signal is obtained at that concentration. The amount of base line drift over a period of 15 minutes was negligible relative to the magnitude of the signal. When a 0.1 ppb_w (0.01 ppb_v) Hg stream (near the minimum detectable concentration) was passed through the detector, a distinct signal was observed. The RSDs were \pm 5 % or better for Hg concentrations of 0.1 to 1000 ppb_w, and did not exceed \pm 2% for concentrations above 10 ppb_w.

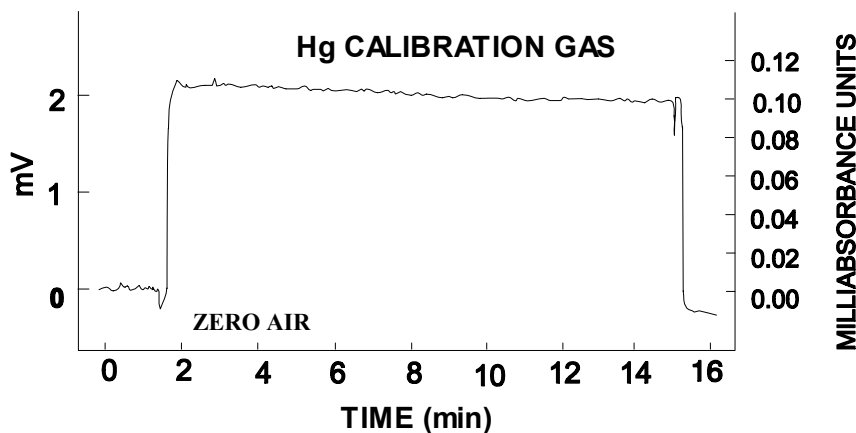


Figure 6. Typical AA Signal for 0.5 ppb_w Hg Stream in Air.

In the tests using Hg (collected in air) injections into the AF unit, the base line drift was typically on the order of 0.5 mV/hr, which is roughly equivalent to a signal produced from injecting about 1 pg Hg. Flow rate changes in the range of 10-1000 mL/min did not affect the base line signal level or base line noise. The instrument response showed good linearity over at least two orders of magnitude in the amount of Hg injected. Over a wider range, some degree of non-linearity resulted from quenching effects related to the increased amount of oxygen associated with the increasing amount of Hg (collected in air) injected into the detector. Collecting the Hg vapor in an Ar atmosphere rather than in air did not significantly affect peak heights for injections of less than 300 pg Hg. However, for injections of 300 to 5000 pg Hg, peak heights for a given amount of Hg increased by up to 40%, which greatly improved the linearity of the calibration curve over a wide range. A theoretical detection limit of 0.1 pg was calculated from these tests. RSDs were $\leq 5\%$ for injections of 25-5,000 pg and 5-25% for injections of 2-25 pg. Using peak areas rather than peak heights would probably have improved precision, even at these low levels of Hg. When continuous Hg streams were passed into the AF detector, a Hg concentration of 0.1 ng/L in Ar could easily be detected.

When Hg was injected into different carrier gases flowing into the AF detector, no quenching effects were observed for CH₄, substantial quenching was observed for N₂, and severe quenching was observed for O₂, H₂, CO, and CO₂. For the latter gases, a signal reduction (compared to signal levels observed with Ar as the carrier gas) of 95% or more was observed for Hg injections of 2500 pg or less. For Hg injections of 500 pg or less, the decrease in signal strength was roughly 75% for N₂ and was 99% or more for O₂, CO₂, CO, and H₂. The most severe quenching was observed for O₂. The degree of quenching generally appeared to decrease as the amount of Hg injected increased in the range of 2 to 5,000 pg. This is shown in Figure 7 below. For emphasis, the results obtained for 2500-pg injections of Hg are shown in graph form in Figure 8.

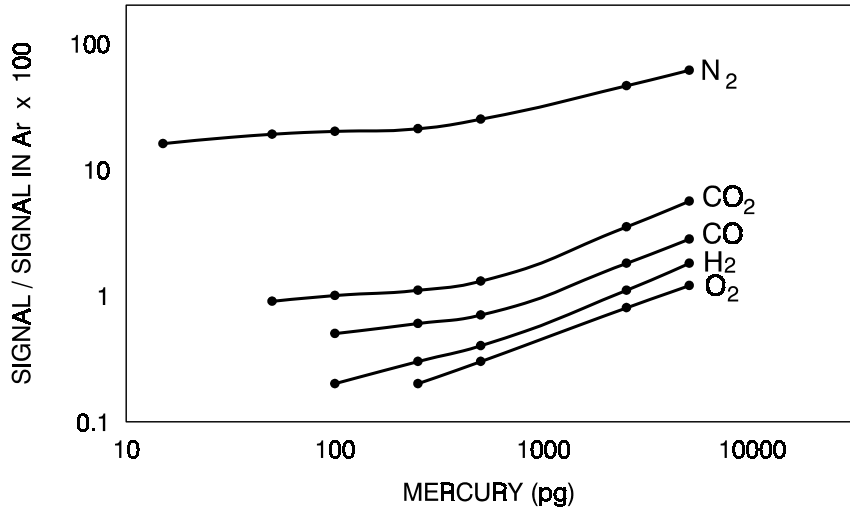


Figure 7. Quenching Effects for Various Gases vs. Amount of Hg Injected.

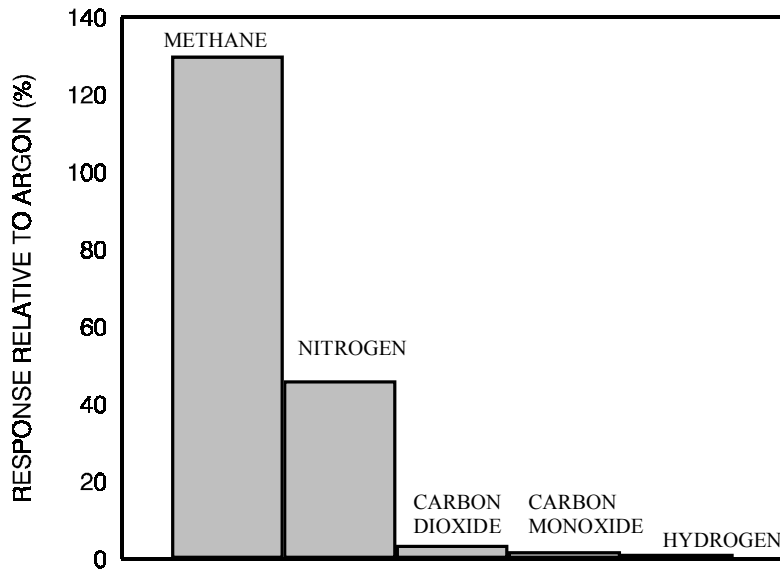


Figure 8. Fluorescence Quenching Effects for 2500-pg Hg Injections into Various Gases.

SELECTION OF ANALYTICAL APPROACH

Both Hg detectors investigated are compact, have minimal base line noise, and offer rapid analysis, low cost, and simplicity. In addition, they both have sufficient sensitivity to determine vapor phase Hg in coal gasification effluents. The AF unit exhibited less base line drift than the

AA unit, although the amount of drift in the AA base line was still acceptable in view of the concentrations of Hg anticipated to be present in coal gasification streams.

An advantage of using AA is the potential for passing conditioned effluent gases directly into the absorption cell, although extensive gas conditioning will be needed. Disadvantages of using AA include interferences from hydrocarbons and other molecular gases, including SO₂ and H₂S. For passing gases directly into the AA cell, background corrections for those gases will be required if they can not be selectively removed. The possibility existed that extensively conditioned effluent gases could be directly analyzed by passing those gases into the AF detection cell. Unfortunately, the extent of the quenching from most of the major gases in a combustor or gasifier stream precludes the possibility of direct gas analysis at the anticipated Hg concentrations. However, AF can still potentially be used for effluent monitoring if the Hg is first collected by gold amalgamation or other suitable collection material and then released into a high purity Ar stream, which is the normal operating procedure with that instrument. That approach avoids interfering gases and also concentrates the Hg prior to evolution and detection. Early in the project, there were concerns that there may be problems associated with using gold cartridges in some process gas streams. It appears that suitable gas conditioning approaches are now available to circumvent those problems (4). However, at the time our work began and a selection of a suitable technology was needed, the necessary sample conditioning technology had not yet been made. Therefore, AA was selected for use in our Hg CEM after weighing the considerations noted above. At this point, the Thermo Separation Products Hg detector was intended to be part of the Hg CEM being developed, which is why it was thoroughly evaluated in the laboratory.

MERCURY TRANSPORT THROUGH STEEL LINES

Recoveries of elemental Hg through stainless steel (Type 304) sample lines were studied as a function of temperature and carrier gas composition. For these tests, 100-pg injections of elemental Hg vapor were made into the gas streams. Peak heights obtained for injections into zero air when using Teflon lines were used as the reference representing 100% recovery. Full Hg recoveries were obtained using zero air in stainless steel sample lines at room temperature, but recoveries decreased to only 20% as the sample line was heated to 200°C (see Figure 9 below). When simulated gasifier streams (mixtures of CO, CO₂, CH₄, COS, H₂, and H₂S) were used without added moisture, no Hg was detected at any temperature between 25 and 200°C. After using the simulated flue gases, poor Hg recoveries were obtained using zero air in stainless steel lines at room temperature. Several days of purging the sample line with zero air were required before full Hg recoveries could once again be obtained at room temperature.

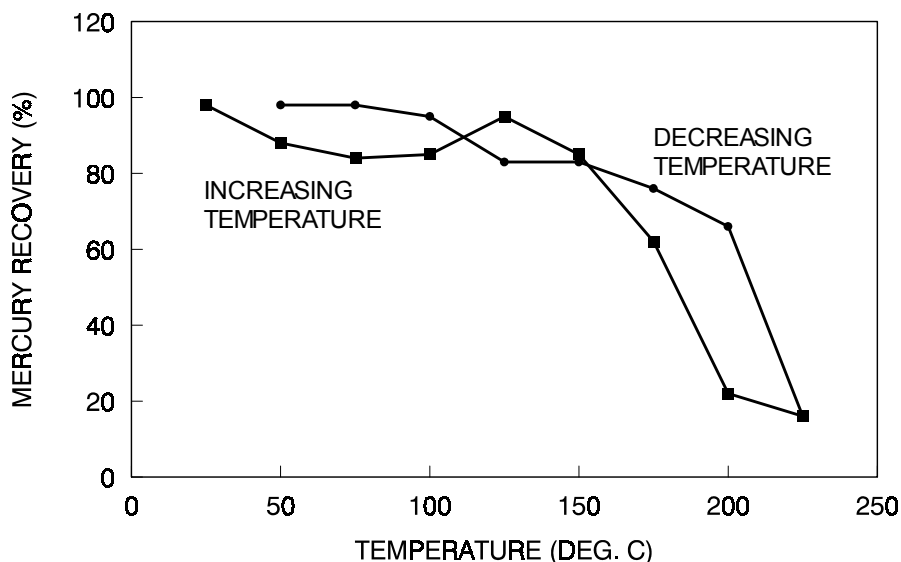


Figure 9. Recovery of Elemental Hg from Steel Lines as a Function of Temperature.

Next, 100-pg injections of elemental Hg vapor were made into Teflon sample lines containing simulated gasifier streams flowing at 1000 mL/min. Full Hg recoveries were obtained when the carrier gas contained mixtures of only H₂, CO, CO₂, and CH₄, while recoveries decreased to about 75% when the carrier gas also contained either 1% H₂S or 0.5% COS. Because the majority of the Hg was recovered using the simulated gasifier streams, even in the presence of sulfur-containing gases, chemical interactions between Hg and the other gases present are not believed to be the primary cause of the poor Hg recoveries observed previously using the same gas mixtures in steel sample lines. The steel may be catalyzing gas stream reactions with the Hg or wall losses may be occurring directly with the steel after the simulated gasifier effluents have altered the steel surface chemistry.

Recoveries of Hg were also examined by injecting 100 pg of elemental Hg vapor into zero air and nitrogen carrier gases in Teflon and stainless steel lines. Full Hg recoveries were obtained using both steel and Teflon lines (previously exposed to simulated gasifier streams) when using zero air with ambient humidity. However, when the air was dried with magnesium perchlorate prior to the Hg injections, Hg recoveries were very low when using steel lines relative to the recoveries observed when using the Teflon lines. In similar tests with nitrogen, Hg recoveries were much higher when using Teflon lines than steel lines when dry nitrogen was used, and Hg recoveries through the steel lines improved greatly when the nitrogen was humidified prior to the Hg injections. Although these results indicate that the moisture content of the carrier gas affects Hg recovery from steel sample lines, it is important to note that this factor was only important after simulated gasifier effluents were passed through the steel lines. Prior to using the simulated gasifier streams, full Hg recoveries could be obtained through steel lines even when using dry carrier gases.

MERCURY TRANSPORT THROUGH CATALYST BEDS

In work discussed later in this report, a commercially available catalyst (G-97B from United Catalysts) effectively removed toluene at elevated temperatures. That catalyst also effectively removed NH_3 from gas streams. In view of this, tests were performed to determine whether low concentrations of Hg could be passed through that catalyst. An air stream containing 2 ppb_w Hg was passed through about 100 cm³ of the catalyst at 450°C using a gas flow rate of 1000 mL/min, and the gases exiting the catalyst tube were then analyzed continuously by AA. No Hg signal was observed, even after 48 hours of operation. In addition, excessive base line drift was observed throughout the experiment, although the magnitude of the drift was not sufficient to mask any Hg signal. When the catalyst tube was bypassed, a strong Hg signal was observed and the base line drift was greatly reduced. The Hg concentration was then increased to 10 ppb and once again passed through the catalyst. No Hg was detected exiting the catalyst tube even after 8 hours of operation.

It was possible that the Hg was exiting the tube in an oxidized form, which would render it undetectable by AA. To help confirm the absence of Hg emitted from the catalyst tube, those gases were passed over a gold trap, since gold will collect both elemental and oxidized forms of Hg. The gold trap was then heated to 900°C while under an argon purge. This theoretically should release any Hg (as elemental Hg) that was collected, and the evolved Hg was passed into an atomic fluorescence Hg detector. As a check, 2 ng of elemental Hg was injected into the gas stream and collected by the gold trap. When the Hg was thermally evolved (in Ar), the Hg that was released gave a strong signal on the AF unit. However, when 3 ng of Hg was injected into the catalyst tube while the gases exiting the tube were being passed over a gold trap, little or no response was observed with the AF unit during subsequent heating of the gold. Therefore, the use of this particular catalyst does not seem well suited for conditioning gasifier streams prior to Hg analysis.

Next, we investigated whether the Hg retention by the catalyst was due to the alumina substrate or the Pt on the substrate surface. A 9-mm ID quartz tube was packed with about 2 cm of catalyst or catalyst substrate. The catalyst substrate was received from United Catalysts and was identical to the substrate material in the Pt catalyst used in the tests discussed above. Initial tests involved injecting 200 pg of elemental Hg into the catalyst substrate using a carrier stream of air flowing at 500 mL/min. Gases exiting the quartz tube were then analyzed for Hg using AA. Full Hg recoveries were obtained both at room temperature and at 450°C (the temperature necessary for destroying toluene) when using the substrate material. However, no Hg was detected at any temperature in the range of 25 to 600°C when the Pt catalyst was used. When follow-up tests were performed in a hydrogen atmosphere (i.e., a reducing environment), the same results were obtained. Although conclusions are not conclusive, it currently does not appear that Hg oxidation is the explanation for the lack of Hg signals. Additional experimental work would be required to verify this.

Because of the possibility that the Hg retention by the catalyst was due to some physical or chemical properties inherent in the manufacturing of the catalyst, additional tests were performed to determine whether pure Pt retains Hg at 450°C. Instead of using the commercially available catalyst, a Pt trap was prepared by pressing 60" of pure Pt wire into a 1-inch section of a 1/4-inch OD quartz tube. Injections (about 5 ng) of elemental Hg were made into carrier gases

upstream from the trap. The carrier gas flow rate was about 300 mL/min, and the trap was maintained at 450°C by a small tube furnace. Tests were performed by 1) injecting the Hg into high purity argon with subsequent Hg detection by AF, and 2) injecting the Hg into air streams with subsequent Hg detection by AA. Thus, tests were performed both in oxidizing and non-oxidizing atmospheres. Results of the tests indicated that little or no Hg was retained by the heated Pt wire in either atmosphere. In order to ensure that the lack of Hg retention by the Pt wire was not a result of Hg simply bypassing the trap due to insufficient contact time, a test was performed whereby the same Pt trap was used at room temperature downstream from the tube furnace. In that test, the Hg was quantitatively collected, as evidenced by the peak areas observed during subsequent thermal evolution of the Hg at 900°C, followed by AA detection of the evolved Hg. Therefore, the hot Pt wire does not retain trace amounts of elemental Hg, and the lack of Hg retention at 450°C is due to the temperature and not to inadequate residence times.

At first glance, there might appear to be a discrepancy between the results obtained when using the commercially available Pt catalyst versus the Pt wire. The catalyst substrate did not retain Hg, while the Pt catalyst on that substrate did retain Hg, implying that the Pt component of the catalyst was responsible for the Hg retention. On the other hand, the pure Pt wire retained little or no Hg. One possibility is that there may be a minute amount of Hg retained per unit surface area of Pt for each injection. The loss could be undetectable when the Pt wire is used because of the low surface area (about 12 cm²) of the wire plug. If, on the other hand, the commercially available catalyst had a large surface area of Pt relative to the Pt wire, the retention of even small amounts of Hg per unit surface area of Pt could result in major Hg losses. Based on information provided by United Catalysts, the porosity of a catalyst pellet (about 1/8 inch diameter) is about 30%, which is considerable. By using information on bulk density and surface area per gram of catalyst, it was calculated that 2 cm³ of catalyst has a Pt surface area roughly 25,000 times that of the Pt wire plug that was used. This value takes into account the fact that the Pt coverage on the catalyst substrate is only about 10%. Therefore, it is possible that a small percentage of the Hg is retained by each cm² of Pt, even at high temperatures. The Hg loss could be undetectable with the Pt wire due to the relatively low surface area, while total retention of the Hg may be observed when using the commercially available catalyst because of its extremely high surface area.

In the tests discussed earlier, little or no Hg was retained by the Pt wire when 5 ng of Hg was injected into an air stream flowing over the wire (contained in a quartz tube) at a rate of 300 mL/min. Since some tests on the removal of toluene (discussed later in this report) involved using a gas flow rate of 1 L/min, additional tests were performed to study the effect of the Pt wire on Hg in a gas stream flowing at that rate. A 2 ppb_w Hg stream was passed over the Pt wire at a flow rate of 1 L/min while heating the Pt at 450°C. As before, gases exiting the catalyst tube were analyzed continuously for Hg using AA. The signal observed with the Hg detector was about 80% of that observed when heating the quartz tube in the absence of the Pt wire. Diminished AA signals were also observed when the Pt was heated at 500° and 550°C. However, when the Pt temperature was held at 600°C, the signal from the Hg detector was the same as that observed when passing the gases through an empty tube at that temperature.

Tests were also performed to determine if low levels of elemental Hg vapor could be passed over the catalyst in the presence of a simulated gasifier stream. The catalyst consisted of

Pt wire and was followed immediately by a bed of alumina, both of which were heated to about 900°C. A 5 ppb_w Hg stream in a simulated gasifier matrix was passed through the catalyst tube and the gases exiting the tube were bubbled into an aqueous KCl trap (for oxidized Hg) followed by an acidified KMnO₄ solution (for elemental Hg). Difficulties were encountered because backpressure began to increase in the catalyst tube during testing. This resulted in difficulties in regulating gas flows and also resulted in small flame pulses (which quickly dissipated) shooting upstream at regular intervals. It was also noted that, after several days of operation, portions of the catalyst tube (including the alumina bed immediately downstream from the catalyst) turned a dark red in color. The alumina was analyzed by SEM-EDX. Results of those analyses clearly showed that the alumina was heavily coated with iron oxides. The source of iron is not known, but it appears to have contributed to the backpressure problem by coating the alumina and inhibiting gas flow. The gases upstream from the flowmeters pass through stainless steel lines, but the gases are dry and at room temperature. The gases are not heated until after they enter the quartz catalyst tube. It is hard to imagine that iron is picked up from the stainless steel lines when dry gases are flowing at room temperature. The gas manufacturers did not believe any contaminants of this nature are present in their gases, and corrosion resistant regulators specifically recommended for the gases being used were installed. The source of the iron was not investigated further, but it is clear that the catalyst tube will need to be watched carefully during prolonged use.

The iron-contaminated alumina and the quartz tube were leached with hot HCl to remove the iron oxides, and the tests with Hg in a simulated gasifier stream were repeated. However, unlike the previous test in which the gases were individually blended, these tests used a single compressed gas cylinder containing 50% CO, 15% CO₂, 25% H₂, 8% CH₄, and 2% H₂S. Results of these tests showed that only partial (50%) Hg recoveries were being obtained downstream from the catalyst. In view of this, several modifications were made to the catalyst module.

A new design was tested which consisted of Pt wire at 900°C in between two alumina beds at 900°C. Initial tests with this catalyst system were performed to determine whether we could pass Hg through the catalyst unit while using only air. In those tests, a 20 ppb_w Hg stream in air was passed through the catalyst at a flow rate of 0.5 L/min. The gases exiting the catalyst tube were continuously analyzed in the gas phase by AA. The same Hg signals were obtained when the gases were passing through the catalyst tube as when they were bypassing the catalyst tube. Thus, for gas streams consisting of Hg in only air, 100% Hg recoveries were obtained while passing the gases through the redesigned catalyst unit.

Next, tests were performed with Hg in a simulated flue gas stream consisting of 50% CO, 15% CO₂, 25% H₂, 8% CH₄, 2% H₂S, and 20 ppb_w Hg. About 0.5 L/min of simulated gasifier stream was blended with 1.0 L/min of air and passed through the catalyst module. Gases exiting the catalyst tube were bubbled into 40-50 mL each of KCl solution followed by acidified KMnO₄ solution. This mimics the Ontario Hydro sampling approach. Although a collection solution for removing SO₂ prior to the KMnO₄ was not used, a strong purple color persisted in the KMnO₄ solution throughout the tests. For comparative purposes, the calibration gases containing the Hg were bubbled directly into the absorbing solutions (i.e., they were not blended with the gasifier matrix stream and were not passed through the catalyst tube). All of the solutions were analyzed by conventional CVAA spectroscopy. Results of the analyses indicated that full Hg recoveries

were obtained through the catalyst tube and that all of the Hg was present as elemental Hg, even when using the simulated gasifier stream.

After that success, the tests were repeated with the exception that the Hg concentration was lowered to 5 ppb_w and HCl was added to the simulated gasifier stream to provide an HCl concentration of about 125 ppm. Results of the solution analyses for those tests indicated once again that full Hg recoveries were being obtained through the catalyst tube. However, with the addition of the HCl, about 25% of the Hg was now oxidized. Numerous additional tests were performed with modified catalyst designs in an attempt to pass all of the Hg over the catalyst and subsequently convert all of the Hg to elemental form. The complexity and difficulty of this gas conditioning step became evident, and this portion of the gas conditioning system remains an area of concern. Additional modifications in the catalyst system may be required to avoid any oxidized Hg in the gas stream entering the Hg detector while using simulated gasifier streams.

MERCURY TRANSPORT IN NAFION DRYERS

Because of the high moisture content of coal gasifiers, most of the water needs to be removed from the sample gas without affecting the Hg content. As one potential approach for doing this, a chemically selective membrane (Nafion) was investigated as a possible gas conditioning approach for moisture removal prior to the Hg determinations. The drying system is based on transporting the sample gas with Nafion tubing and running a countercurrent purge gas over that tubing. Little information was available on whether low levels of elemental Hg could be successfully transported with Nafion tubing. Specifically, the issue is whether or not some of the Hg will be pulled into the purge gas stream and constitute a loss in the analyte. To investigate this possibility, tests were performed in the laboratory using a small Nafion-based dryer (Perma Pure Model MD-110-48F) intended for bench-top use. If the Hg could not be successfully transported with this simple dryer, then it would certainly not be possible to transport it with a more complex and scaled up system based on the Nafion technology.

For our tests, elemental Hg streams (in air) were transported with the Nafion tubing while the purge gas stream (dry compressed air) flowed countercurrent to the sample gas flow. Specific conditions used were Hg concentrations of 1.6, 3.1, 6.2, and 18 $\mu\text{g}/\text{m}^3$; sample gas flow rates of 500, 1000, and 2000 mL/min; and ratios of 2, 5, 10, and 20 for the relative flow rates of the purge gas to sample gas. The Hg in the sample gas stream was determined continuously using a CVAA Hg detector. For comparison, tests were also performed through the Nafion with no purge gas flow. Similarly, for comparative purposes, tests were performed whereby the Hg streams bypassed the dryer and passed immediately into the Hg detector. In order to determine whether there might be some loss of analyte when using Nafion, absorption signals obtained for all of the tests with Nafion were compared to those obtained while bypassing the Nafion. The signals obtained while bypassing the Nafion were taken to represent full (100%) signals. All other data were compared to those values and the data were reported as a percentage of the full signal values. All tests were performed in triplicate and the results obtained for a given set of experimental conditions were averaged. Results of the tests indicated that low levels of Hg could be successfully transported with the Nafion-based drying system under all of the conditions tested. In other words, losses (if any) of Hg into the purge gas stream or from surface

adsorption were negligible in all cases. Specifically, any losses were 2% or less of the input Hg stream.

Next, follow-up tests were performed using the large dryer incorporated into the CEM. This dryer was a Perma Pure Gas Analysis Sampling System designed to handle a 1-2 L/min gas flow with up to 50% (volumetric) moisture. As was the case with the laboratory Nafion dryer, dry compressed air was used for the purge gas stream. At low flow rates of less than 200 mL/min, signal rise times were 20-30 minutes, which is clearly unacceptable. Signal rise times were decreased to several minutes when using a gas flow rate of 500 mL/min, even though the Hg concentration at this flow rate was substantially lower than that at the lower flow rate. Thus, it is clear that low gas flow rates must be avoided. Flow rates of 0.5, 1.0, and 2.0 L/min were tested, which corresponded to Hg concentrations of 6.2, 3.1, and 1.6 $\mu\text{g}/\text{m}^3$, respectively. The results of those tests were very interesting. Relative to the Hg signals observed when bypassing the dryer, the Hg signals were 81, 89, and 93% for Hg concentrations of 6.2, 3.1, and 1.6 $\mu\text{g}/\text{m}^3$, respectively. Thus, Hg recoveries were the *highest* when the Hg concentrations were the *lowest*, which is also when higher gas flow rates were used. Once again, the critical importance of gas flow rate is seen. Studies on transporting elemental Hg through Nafion-based dryers in the presence of simulated gasifier streams is still required.

The situation was much more complex when similar tests were performed using a humidified nitrogen stream containing about 20 $\mu\text{g}/\text{m}^3$ HgCl_2 . For these tests, only a single sample flow rate was used with a purge gas flow rate twice that of the sample gas flow rate. The gas stream was humidified to minimize sorption of the HgCl_2 onto the walls of the sample transport system. For those tests, a pyrolyzer was used just prior to the Hg detector to convert the HgCl_2 to elemental Hg, which is required for detection by AA. Also, because of the humidified gases, a magnesium perchlorate trap was used as a drying agent after the pyrolyzer (used to convert HgCl_2 to elemental Hg) and before the Hg detector. When the sample gas was passed into the Nafion dryer, the signal on the Hg detector was only about 25% of that observed when the sample gas bypassed the dryer. Initially, this seemed to indicate that Nafion was probably removing 75% of the HgCl_2 . However, different results were obtained when the sample and purge gases were bubbled into KMnO_4 absorbing solutions, which were subsequently analyzed by AA. Results of the solution analyses indicated that 50% or more of the HgCl_2 was remaining in the sample gas when going through the Nafion dryer, and that less than 25% of the Hg was going into the purge gas stream. The remaining 25% of the HgCl_2 was not accounted for. This could be due to retention of the HgCl_2 on (or in) the Nafion walls. The results from the solution analyses are believed to be the most indicative of what is actually happening to the HgCl_2 . The AA readings for the direct gas analysis may have been deceptively low when the sample gases exited the Nafion dryer. Since virtually all of the humidity was being removed by the Nafion, humidified gas was being transported to the Hg detector when the sample gas bypassed the Nafion, but dry gas was being transported to the detector when the sample gas went through the Nafion drying system. Therefore, because of the difficulties in transporting HgCl_2 , there may be a sample transport issue related to gas humidity levels. Additional work in this area is required.

GENERAL TRANSPORT AND CONVERSION OF HgCl_2

Because of concerns regarding transport of HgCl_2 during sampling and the effective conversion of that Hg species to elemental Hg (required for detection by AA), a variety of tests were performed on the transport of HgCl_2 and on the conversion of the HgCl_2 to elemental Hg using a pyrolyzer. For generating HgCl_2 gases, a HgCl_2 permeation tube from VICI Metronics was used. The permeation tube was housed in a VICI Metronics U-tube, which in turn was placed in an oil bath in a convection oven maintained at a temperature of 100°C . Dry nitrogen was used for the carrier gas in these tests. The HgCl_2 stream from the oven, which had a nominal Hg concentration of about 15 ppb_w , was passed through a pyrolyzer heated to 900°C to convert Hg to the elemental form. Gases exiting the pyrolyzer were then analyzed directly for elemental Hg by AA. In addition, gases were bubbled into acidified KMnO_4 solutions to collect Hg at various points in the apparatus to study the effectiveness of HgCl_2 transport. Sample collection points included the oven outlet, pyrolyzer inlet, and detector inlet. Also, gases at the detector inlet were bubbled into a double-trap system where the first trap collected ionic Hg and the second trap collected elemental Hg. This test was done to determine whether there was any recombination of Hg and chloride after the pyrolyzer, which would render that Hg undetectable by AA. All solutions were subsequently analyzed by conventional CVAA.

Results from the solution analyses indicated that all of the Hg coming out of the oven was being successfully transported to the pyrolyzer and subsequently to the Hg detector. In addition, results from the tests with the double-trap system showed that all of the Hg at the detector inlet was elemental Hg. This indicates that the pyrolyzer was successfully converting all of the HgCl_2 to elemental Hg and that the elemental Hg was not re-combining with chloride downstream from the pyrolyzer. As additional support for these observations, the absorbance reading obtained for the direct gas analysis with the Hg detector was precisely what it should be for the amount of Hg reaching the detector, which again indicates that virtually all of the Hg remained in the elemental form downstream from the pyrolyzer.

As noted earlier, oxidized forms of Hg need to be reduced to elemental Hg in order to be detected by AA. One potential method for doing this is to use a pyrolyzer to convert oxidized Hg species to elemental Hg. However, the recombination of elemental mercury with chloride ions after the pyrolyzer is of potential concern. Although the tests discussed above indicated that there was no recombination under the conditions studied, the effects of added HCl (among other variables) were not included. Thermodynamic calculations were performed to determine whether complete pyrolysis of HgCl_2 can be expected for the concentrations of Hg anticipated to be present in gasifier streams. Results of those calculations indicated that, for a given pyrolyzer temperature, pyrolysis efficiency would be expected to decrease with increased HgCl_2 concentration. However, for the Hg concentrations that would typically be found in gasifier streams, complete pyrolysis of the HgCl_2 at 900°C should not be a problem if the HCl content is low (e.g., 1 ppm). For high concentrations of HCl (e.g., 100 ppm or more), the calculations indicated that the pyrolysis efficiency might be significantly decreased. This requires experimental verification.

Tests were performed to determine whether the recombination of Hg and Cl to form HgCl_2 between the pyrolyzer and detector is of concern when using elevated levels of HCl. For these tests, about 100 pg of elemental Hg were injected into a gas stream at room temperature flowing

at 500 mL/min. The gas stream consisted of either room air or a mixture of room air with a blend of HCl and nitrogen. For the gas stream containing HCl, the gases were blended such that the final HCl concentration was about 400 ppm_v. Results of the tests showed that the Hg signal (using peak height) from the AA decreased by about 10% when HCl was present. However, this magnitude of change can be attributable to uncertainties in total gas flow rates when combining the two gas streams. These tests were repeated, except the gas stream was first passed through a pyrolyzer prior to the Hg detector. The pyrolyzer consisted of a 1/4" OD quartz tube (about 20" long) packed with a 1-inch plug of quartz wool that was maintained at 1000°C by a tube furnace. When HCl was present in the gas stream, the magnitude of the Hg signal was reduced by 65%. It is not known whether similar results would be observed in actual gasifier streams. However, this is a problem that should probably be watched carefully, even though HCl levels in gasifier streams would seldom be as high as those tested.

As a sample transport consideration, dry HgCl₂ streams were passed through virgin PFA, PTFE, and FEP Teflon lines to determine whether one form of Teflon may be most suitable for transporting cooled gasifier streams to the detector. For these tests, the Hg concentration was about 20 ppb_w (in air) and the total gas flow rate was about 400 mL/min. A HgCl₂ permeation tube from VICI Metronics was used. The permeation device was housed in a U-tube, which was placed in an oven maintained at 100°C. The gases containing HgCl₂ were passed through a pyrolyzer at 900°C before entering an AA Hg detector. After equilibrating the piece of Teflon tubing attached to the exit of the permeation tube holder for at least a day, 4-ft sections of each type of 1/8" OD Teflon tubing were attached to the sample transport line at the exit of the oven just prior to the pyrolyzer. Only one type of Teflon was tested at a time. The maximum reading on the Hg detector was observed and the amount of time needed to reach that value was noted. Test results indicated that there was no significant difference in Hg levels or equilibration times when using the different types of Teflon. Therefore, for the purposes of our work, the type of Teflon used to transport cooled sample gases does not appear to be an important issue.

Similar tests were performed with the exception that a Teflon cartridge (volume of 8 cm³) containing various materials was put in the HgCl₂ stream just prior to the pyrolyzer. The materials put in the cartridge were 1/8" in diameter and included PTFE Teflon, Pyrex glass, soda lime glass, quartz, and boron nitride. These tests were performed to help determine the effects of various materials on HgCl₂ transport at temperatures near room temperature. Gases containing a nominal 20 ppb_w of Hg as HgCl₂ were passed through a pyrolyzer at 900°C before passing into an AA Hg detector. Tests were performed both with dry and humidified nitrogen. For the tests with humidified nitrogen, a magnesium perchlorate trap was inserted after the pyrolyzer and just prior to the Hg detector. The system was first equilibrated by passing the span gases through the sample lines and pyrolyzer until a steady Hg signal was obtained. Then, the Teflon cartridge was added just prior to the pyrolyzer while zero air was flowing through the lines. The gas stream was immediately switched to span gases and the signal profile for the Hg reading as a function of time was observed. The magnitude of the Hg signal observed after obtaining a constant signal was also recorded. Several span gas/zero air cycles were performed to ensure experimental consistency, and results were observed to be very consistent from cycle to cycle. Under the experimental conditions tested, it appears that the different materials all equilibrated quickly. Also, the same Hg signals were obtained regardless of the material in the cartridge and regardless of whether the gases were humidified or not.

CALIBRATION DEVICES

ELEMENTAL MERCURY PERMEATION TUBES

For much of our Hg work, elemental Hg permeation tubes supplied by VICI Metronics were used. No other calibration devices for elemental Hg vapor were commercially available. Through the course of this work, it was discovered that some of the permeation tubes did not meet the vendor's specifications listed on the tubes. This was discovered after sending one of the uncertified permeation tubes to the vendor for certification. Although the uncertified tube was reportedly accurate to within 25%, the certified value for that tube was only within 50% of the uncertified value. Such inconsistencies have a significant impact on much of our research with Hg. After discussing these problems with the vendor, they revised the emission rates and uncertainties for all of our uncertified permeation tubes. This emphasizes why checks on equipment vendors is an integral part of our research from a quality control standpoint.

MERCURIC CHLORIDE PERMEATION TUBES

After receiving a new HgCl₂ permeation tube from VICI Metronics, some unusual readings were obtained while performing tests to ensure that the HgCl₂ was being transported effectively. Therefore, a series of absorbing solutions was used to determine the Hg species being emitted from the permeation tube. It was determined that the Hg coming from the permeation tube was 15% elemental and 85% oxidized. In view of this, four other HgCl₂ permeation tubes were checked and were found to be putting out significant amounts of elemental Hg. Most of the tests were performed with the permeation tubes heated (in a convection oven) at 100°C. Based on results from blank runs performed without the permeation tubes present, the carrier gases being used did not appear to be contaminated with elemental Hg, nor did the sample lines appear to be contaminated. It is of further interest to note that the ratio of elemental Hg to HgCl₂ decreased to near zero with continued testing, but it took at least several days before the elemental Hg contaminants diminished to trace levels. It is possible that elemental Hg somehow forms and builds up during storage of the tubes, and is then emitted when the tube is heated. Alternatively, some researchers from other institutions believe that elemental Hg is commonly a contaminant in the HgCl₂ from the beginning. With regard to HgCl₂ permeation tubes, it is worth noting that there are currently no certified calibration devices for HgCl₂ that are commercially available.

INTERFERENCES IN THE DETERMINATION OF Hg BY AA

PRIMARY MATRIX GASES

The magnitude of potential interferences in the determination of Hg using CVAA was examined by using continuous streams of various gases which passed directly into an AA Hg

detector (Thermo Separation Products, Model 3200). This was done for confirmation of published absorbance values, as a check on equipment calibration, and to provide useful information related to the background correction approach that was being considered. For these tests, diluted streams of CH₄, CO₂, CO, COS, H₂S, SO₂, O₂, and H₂ were examined by blending 10 mL/min of a given gas with 1000 mL/min of the nitrogen carrier gas stream. This provided 1% concentrations for each gas of interest. The SO₂ and O₂ were included since some of the gas conditioning approaches being considered involved oxidation of the gas stream. Experimental absorbance readings were in good agreement with published values for a given gas. As expected, the strongest interferences were for the sulfur-containing gases. The absorbance produced by COS was comparable to that produced by H₂S, although H₂S is of much greater concern because it will be present in gasifier streams at much higher concentrations than COS. By using published absorptivity values and our own experimental data, we determined that about 500 ppm_v H₂S will produce a signal equivalent in magnitude to the signal from a 1 ppb_w Hg stream. Based on the anticipated H₂S levels in coal gasification effluents, the interference from H₂S could produce an absorption value equivalent to that observed for a 10 ppb_w Hg stream. This interference is severe enough that either background corrections must be made or else the H₂S must be eliminated before the sample gas enters the detection cell. During gas stream oxidation, SO₂ would be formed, which interferes 30 times more strongly than H₂S. In addition to those interferences, a substantial absorbance was noted for gases from the CO cylinder. However, this was found to be due to impurities in the CO rather than to the CO itself.

MOISTURE

Water vapor is another gas that was considered as a possibility for causing spectral interferences. Discrepancies in the literature and disagreements among analytical chemists were noted on whether non-condensed moisture is an analytical interference in the determination of Hg by AA. Results of our own tests indicated that non-condensed moisture is indeed an interference. A nitrogen gas stream with about 100% relative humidity at room temperature gave a reading of about 0.06 absorbance units, which is equivalent to a reading obtained from a gas stream containing several hundred ppb Hg. Tests were also performed at reduced relative humidity levels to ensure that erroneous readings were not being obtained due to moisture possibly condensing in the sample cell. Data from those tests corroborated the initial results. If a sample gas stream can be delivered to the Hg detector at 1% relative humidity at room temperature, the magnitude of the absorbance reading due to moisture would be equivalent to the reading from a Hg concentration of about 3 ppb by weight. It is clear that the performance of the background correction unit is of critical importance. The ability of the Perma Pure gas drying system to remove moisture without affecting Hg is therefore a critical issue.

AROMATIC HYDROCARBONS

The catalytic oxidation of toluene was investigated since aromatic hydrocarbons absorb strongly at the wavelength (254 nm) being used for Hg analyses and therefore constitute a significant analytical interference. The commercially available Pt catalyst (G-97B from United Catalysts) was tested as a potential method for destroying vapor-phase aromatic hydrocarbons

prior to Hg analysis. If a specific vapor-phase hydrocarbon such as toluene can be readily removed with the catalyst, it is anticipated that the catalyst will also be effective in destroying many other aromatic hydrocarbons in the vapor phase that may be present in the gas stream. Therefore, for our purposes, the catalytic oxidation of toluene (a benzene ring with a methyl group attached) was investigated.

An air stream was blended with toluene to give a toluene concentration of about 2%. The blended gases were passed through 100 cm³ of the catalyst at a rate of 1000 mL/min while the temperature was slowly increased. Grab samples of the gases exiting the catalyst tube were collected and analyzed for toluene by UV spectroscopy and for CO₂ (a byproduct of toluene decomposition) by gas chromatography. Results of the tests indicated that little or no toluene was removed by the catalyst below 440°C. At temperatures of 440-460°C, water vapor (another byproduct of toluene decomposition) began to be observed. In addition, no hydrocarbons were detected in the gases exiting the catalyst tube and the CO₂ concentration corresponded to the amount anticipated with the quantitative destruction of the toluene. Therefore, this catalyst showed good potential for effectively removing vapor-phase aromatic hydrocarbons.

Although the commercially available catalyst effectively removed toluene, it was later learned that low concentrations of Hg could not be successfully passed through the catalyst. Therefore, an alternate catalyst was needed. In this regard, tests were performed to determine whether toluene could be effectively destroyed using a Pt wire bed. A stream of 2% toluene in air was passed over the Pt wire plug at various temperatures using a total gas flow rate of 1000 ml/min. The desired temperatures were maintained by using a small tube furnace to heat the quartz tube containing the Pt. There was little visual evidence of toluene oxidation (e.g., water formation) as the temperature of the Pt was increased from 450° to 600°C. Also, UV spectrophotometric analysis of the gases exiting the tube containing the Pt indicated that little or no toluene was removed at those temperatures. However, when the temperature of the tube furnace was increased to 650°C, water condensation was observed downstream from the Pt and the analyses of the gases exiting the tube indicated that most of the toluene was being destroyed. In order to quantify the magnitude of the toluene removal, a gas-tight syringe was used to withdraw 200 µL of gas both upstream and downstream from the Pt. The 200-µL gas samples were then injected into an AA Hg detector. The absorbance readings obtained with the AA for the gases entering and exiting the catalyst tube indicated that more than 99% of the toluene was being removed.

Highly exothermic reactions were involved with the toluene removal. After initiating the catalytic oxidation reactions by using the tube furnace to provide external heat, the exothermic reactions were sufficient to maintain a high Pt temperature without using the furnace. At that point, the portion of the quartz tube containing the Pt was removed from the furnace. Based on the color of the Pt, it was estimated that a temperature greater than 900°C was being sustained without any external heat source. These tests indicate that a Pt wire plug can probably be used to effectively remove aromatic hydrocarbons from gas streams. However, because of the highly exothermic reactions, some concern arose as to whether the oxidation of actual gasifier streams could result in excessive temperatures for the sample transport lines. Based on the composition of a typical gasifier stream and possible reactions during oxidation of the gases, thermodynamic calculations indicated that oxidation of the gas stream would result in temperatures sufficient for

the removal of aromatic hydrocarbons. By adjusting gas flows and the degree of sample line insulation, it is anticipated that excessive sample line temperatures can be avoided.

It was possible that the exothermic reactions could be self-sustaining even in the absence of a catalyst. Therefore, tests were performed to determine whether the catalyst was actually needed by repeating the tests with toluene. However, in these tests, the Pt wire plug was placed between two quartz wool plugs. The oxidation reactions were initiated by heating to 600-700°C as before, and the Pt and quartz wool plugs were then completely removed from the external heat source. The Pt plug glowed red hot, while the quartz wool plugs at each end of the Pt did not glow at all. Therefore, this is truly a catalytic reaction rather than just a self-sustaining set of exothermic reactions that do not require a catalyst once initiated.

Next, an air stream containing both 2% toluene and 2 ppb_w elemental Hg was passed through a heated Pt wire cartridge to see if the Hg could successfully pass through the cartridge while effectively destroying the toluene. Initially, only toluene was added to the air stream. The oxidation reactions were initiated by heating the Pt to about 650°C in a tube furnace. Once the reactions were underway, the portion of the tube containing the Pt was removed from the tube furnace, since the exothermic reactions (in the presence of a catalyst) were sufficient to maintain a high enough temperature for the Pt to glow red hot. In order to determine the degree of toluene removal, 200 µL of gas were withdrawn before and after the Pt. Those samples were then injected into a clean (air only) carrier gas stream and analyzed by AA. Results of those tests indicated that 98% of the toluene was being removed. Next, elemental Hg was added continuously (using a permeation tube) to the toluene stream and the gases exiting the Pt cartridge were passed directly into an AA Hg detector. However, results on the amount of elemental Hg passing through the heated Pt cartridge were inconclusive because of erratic data obtained with the AA when attempting to analyze the gases exiting the Pt cartridge directly. The erratic signals were observed even in the absence of Hg. This could be related to problems from the moisture produced from the oxidation of toluene, even though a magnesium perchlorate drying trap was used prior to the Hg detector. In other words, the drying trap may not have been completely effective. Another possibility relates to the small amounts of toluene that were able to pass through the Pt cartridge unaffected. Because toluene is a strong interference with the determination of Hg by AA at 254 nm, even small fluctuations in the amount of toluene passing through the Pt cartridge will result in an erratic AA signal.

The tests with toluene and Hg were repeated. However, the experimental setup was modified by 1) placing a water knockout bottle (in an ice bath) between the catalyst and the magnesium perchlorate trap, and 2) using 10-ng injections of elemental Hg rather than continuous Hg streams. In order to determine the degree of toluene removal, 100 µL of gas were withdrawn before and after the Pt catalyst. Those samples were then injected into a clean (air only) carrier gas stream and analyzed by AA. Results of those tests indicated that more than 99% of the toluene was being removed. Next, elemental Hg was injected (performed in triplicate) into the toluene stream, and the gases exiting the Pt cartridge were passed directly into an AA Hg detector for analysis. When Hg was injected into an air/toluene stream prior to the catalyst, the average peak areas for the Hg signals were within 1% of those obtained when using air only. Therefore, it appears that the catalyst can effectively remove volatile aromatic hydrocarbons without affecting low levels of Hg.

D₂ BACKGROUND CORRECTION APPROACH

BACKGROUND

As discussed earlier, AA was selected as the method of choice for monitoring Hg in coal gasification streams after carefully evaluating two commercially available Hg detectors (one each based on AA and AF). However, interferences from sulfur-containing gases and aromatic hydrocarbons are of concern in AA. Based on the anticipated H₂S levels in coal gasification effluents, the interference from H₂S could produce an absorption value equivalent to that observed for a 10 ppb_w Hg stream. Since gas stream oxidation will be used to remove tars and NH₃, the H₂S will be converted mostly to SO₂, which absorbs even more strongly than H₂S at the wavelength being used for the Hg determination. This necessitates either background corrections or the elimination of H₂S before the sample gas enters the detection cell.

Since our work began, a number of Hg CEMs employing AA have been developed, some of which use a Zeeman-modulated background correction approach (5). Although that background correction approach appears to have good potential for the application of interest, we chose to investigate an alternate approach for performing the background corrections. Specifically, the effectiveness of using a broadband spectral correction approach employing a deuterium (D₂) lamp as the broadband radiation source was tested. No Hg CEMs currently employ this background correction method. Both the Zeeman modulation and broadband correction approaches are commonly used in laboratory AA instruments. Therefore, the decision was made to explore the merits of using the latter background correction method for Hg monitoring in process gas streams.

The Ames Laboratory Hg CEM uses two UV lamps. One is a Hg lamp and the other is a D₂ lamp. The principle of operation for the background corrections is based on the fact that the Hg UV lamp emits mostly in a very narrow spectral line at 254 nm, while the D₂ lamp emits in a relatively broad band over the same spectral region. The Hg channel of the analyzer responds to both Hg and interfering gases at 254 nm, while the D₂ channel of the analyzer responds only to gases which absorb over a much broader spectral region. The absorption region for Hg is so narrow compared to the broad band associated with the D₂ lamp that Hg should not be detected with the D₂ system. Therefore, the Hg content of a gas stream can theoretically be determined by subtracting the signal from the D₂ channel (absorption due to interfering gases only) from that of the Hg channel (absorption from both Hg and interfering gases).

In addition to using a D₂ lamp for background corrections, using such a lamp for both the background correction and source lamp for the Hg determination was considered. However, after performing a variety of tests, it appears that the resolution necessary for the determination of Hg with that approach would be inadequate for the sensitivity required. For background corrections, the possibility of using a commercially available AA instrument with an internal D₂ background correction system was investigated. Based on data provided by two manufacturers

of such instruments (Perkin-Elmer and ATI), blank readings had too much base line variability for determining Hg in gasifier streams at the anticipated Hg concentrations.

Catalytic oxidation of the sample gas stream will be used to remove tars (as well as other hydrocarbons) prior to analysis, and H₂S will be converted to SO₂. The oxidized sample stream will then be passed over a high temperature pyrolyzer and subsequently dried using a Nafion-based drying system prior to entering the Hg detector. Therefore, for our purposes in evaluating the basic principles involved with our Hg CEM, it was assumed that hydrocarbons and moisture will be absent from the gas streams entering the Hg detection system. Consequently, spectral interferences from SO₂ are expected to be the primary issue during sample analysis by AA. All subsequent laboratory tests with the D₂ background subtraction approach were performed based on that assumption.

TESTS WITH OPTICAL BREADBOARD SETUP

After obtaining encouraging preliminary results on the base line stability with a D₂ lamp, the decision was made to build our own Hg analyzer employing a D₂ background subtraction approach. The initial design of the D₂ background correction module was formulated, assembled on an optical breadboard, and tested using a single photo diode. Experimental results indicated that the use of photo diodes in conjunction with the D₂ lamp should not add significant analytical uncertainties in the determination of Hg at the ppb level. The signal strength from the photo diode was excellent. The optical system was later modified to include a reference beam measurement of the D₂ lamp emission using a second photo diode. A holder for the photo diodes was constructed to stabilize their positions. Excellent results were obtained with the stabilized photo diodes. The amount of base line drift over a period of 8 minutes was nearly zero and the absorbance standard deviation of the base line signal (i.e., noise) was only about 24×10^{-6} . An absorbance standard deviation of less than 100×10^{-6} for background measurement would have no significant impact on the accuracy of the Hg determination.

Tests on the stability of the ratio of the photo diode signals measured simultaneously from the sample and reference beams indicated that this ratio was excellent for our purposes. Next, a 1000 ppm SO₂ stream in nitrogen was passed through the cell in order to determine the accuracy of the readings. The absorbance value obtained with the background correction module agreed with literature values, and the noise level observed while using the SO₂ stream was very low.

Tests were performed with the Thermo Separation Products Hg detector and the D₂ module operating in series. A drift of about 1 mAU/hr was observed with the D₂ module, which was higher than desired. The drift was primarily due to the D₂ lamp and/or power supply rather than the light-measuring electronics of the D₂ module. This was not of immediate concern since it is likely that more stable D₂ lamps are commercially available. Nonetheless, the optics were modified to help reduce the drift resulting from lamp and/or power supply instabilities. Also, the D₂ module was enclosed to help minimize the potential presence of interfering gases in the optical path.

A second series of tests was performed with the AA Hg detector and D₂ module operating in series. For these tests, SO₂ was used as an interfering gas since gas stream oxidation will be used. A 2% SO₂ (in nitrogen) gas stream was blended with air to give a final SO₂ concentration of about 0.05%. When elemental Hg was introduced to the carrier gas, the final Hg concentration was about 20 ppb_w. Excellent signals were obtained with the Hg detector for SO₂, Hg, and SO₂/Hg blends. Response times were very rapid and memory effects were minimal. However, a disadvantage of having SO₂ in the sample stream is that SO₂ absorbs about 30 times more strongly than H₂S at the wavelength (254 nm) being used for determining Hg. Therefore, oxidizing the sample stream could increase the detection limit of the monitor for Hg due to the formation of SO₂. On the other hand, the presence of aromatic hydrocarbons (strong absorbers at 254 nm) in an unoxidized gasifier stream would also have the same effect. Whether or not the magnitude of the interferences is better or worse with gas stream oxidation depends on the relative levels of aromatic hydrocarbons and sulfur-containing gases, which will probably vary from gasifier to gasifier.

The D₂ module gave the same background reading for SO₂ as it did for the SO₂/Hg blend. This is of critical importance and indicates that the D₂ module was operating correctly. However, the observation was made that the absorbance reading from the D₂ module was about 30% larger than the value expected for the SO₂ concentration being used. A variety of tests indicated that this phenomenon was not being caused by the electronics or optics of the system. It is possible that the deviation from the expected value is being caused by SO₂ spectral complexities in the wavelength region being used for analysis by the D₂ module. The ratio of the absorbance reading from the Hg detector to that from the D₂ module was fairly constant (about 0.78) for SO₂ concentrations ranging from 0.02% to 0.5%. Therefore, the need for a spectral correction factor was not considered to be of concern, since a correction factor can be applied to give accurate background readings. This correction factor should be accurate as long as SO₂ is the interfering gas with the greatest absorbance. This situation is expected to be the case when oxidizing the gas stream.

Additional work was done with the D₂ background correction module coupled in series to the Thermo Separation Products Hg detector. For these tests, 0-300 mL/min of 2% SO₂ were blended with room air flowing at 900-2000 mL/min in order to confirm that the ratio of the absorbance reading from the Hg detector to that of the D₂ module remained constant, as should theoretically be the case. However, it was observed that the ratio increased by 10-15% as the total flow of the dilution air and SO₂ increased from 900 to 2000 mL/min. Detailed analysis of the data indicated that the mAU readings from the Hg detector and D₂ module tracked well with each other as the SO₂ concentration was varied, as long as the total gas flow rate was unchanged. However, the mAU values did not track as well with each other when the total gas flow rate was changed by altering the dilution flow and keeping a constant SO₂ flow. Also, the D₂ readings tracked better with the changing SO₂ concentrations than the readings from the Hg detector did, suggesting that changing total gas flow rates may somehow cause inaccuracies in the mAU readings from the Hg detector. This caused some concern about whether a single correction factor independent of gas flow rate could be used.

Experiments were performed with the D₂ background correction module coupled to the AA Hg detector to demonstrate the accuracy of determining low levels of Hg in gas streams

containing high levels of SO₂. This represents a worst case scenario. For these tests, gas streams containing 2 ppb_w (0.2 ppb_v) elemental Hg and 0.3% SO₂ were used. The total gas flow rate was about 1000 mL/min. The absorption signal from SO₂ in the Hg detector was about 100 times higher than that from the Hg. In addition, tests were performed using 4 ppb_w elemental Hg and 0.4% SO₂ at a total gas flow rate of 500 mL/min.

A calibration curve (Hg concentration versus mAU reading) was prepared using the Thermo Separation Products Hg detector for Hg concentrations ranging from 0.1-5 ppb_w in the absence of SO₂. For the tests involving low levels of Hg with high concentrations of SO₂, the background reading (in mAU) from the D₂ module was used to correct the readings from the Hg detector to give a background-corrected mAU value. These background-corrected mAU values were then compared to the calibration curve to give a background-corrected Hg concentration. For the tests using 2 ppb and 4 ppb elemental Hg with high concentrations of SO₂, background-corrected Hg concentrations of 3.5 and 5 ppb were obtained, respectively. In view of the low Hg concentrations involved and the fact that the interfering gas gave absorption values up to 100 times higher than the Hg did, these results were considered to be encouraging in this worst-case scenario.

After making several refinements in the experimental design, additional tests with Hg in the presence of varying concentrations of SO₂ were performed. For these tests, Hg concentrations ranged from 2 to 12 ppb_w and SO₂ concentrations ranged from 0.02 to 0.5 % (v/v). Using these gas stream concentrations of Hg and SO₂, the absorbance due to SO₂ was ten to thirty times higher than the absorbance due to Hg. The total absorbance of the Hg and SO₂ stream was measured with the Hg detector. Figure 10 shows the absorbance data from the Hg detector (i.e., the data are not background corrected) for various Hg concentrations in the presence of SO₂ and in the absence of SO₂. This shows the large magnitude of the absorbance from the interfering gas (SO₂) and demonstrates the importance of the background correction. Figure 11 is a plot of the net absorbance as a function of the Hg concentration for varying concentrations of SO₂. The net absorbance is the total absorption measured by the Hg detector minus the absorbance measured by the D₂ system (i.e., the background from the interfering gas). The background corrected values were typically within 5% of the values obtained for a given Hg concentration in the absence of SO₂. These data demonstrate that using a D₂ lamp is a viable approach for correcting for SO₂ interferences in gasification streams and that low levels of Hg can be measured in gas streams containing high levels of SO₂ using this method.

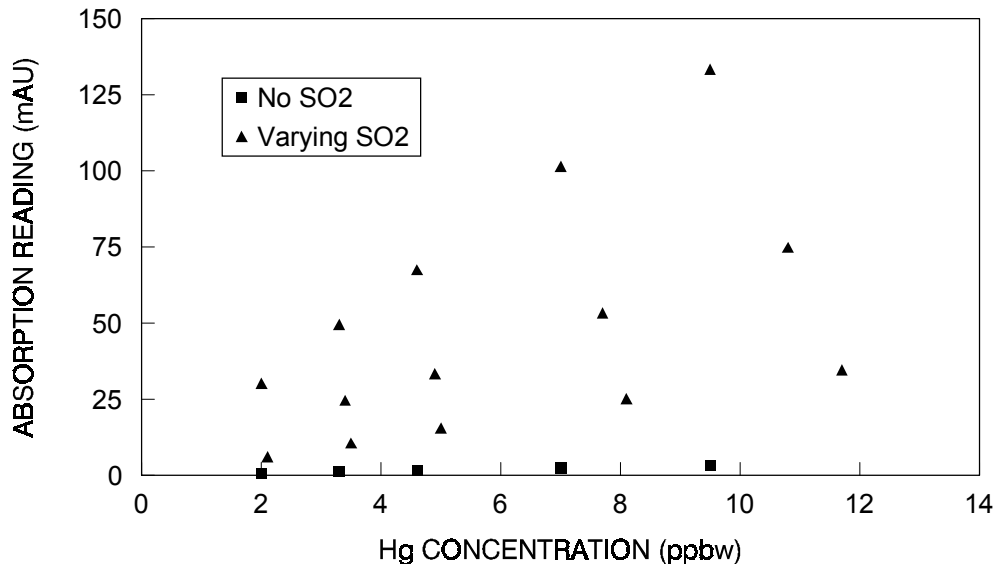


Figure 10. Uncorrected Absorbance Data for Varying Levels of Hg and SO₂.

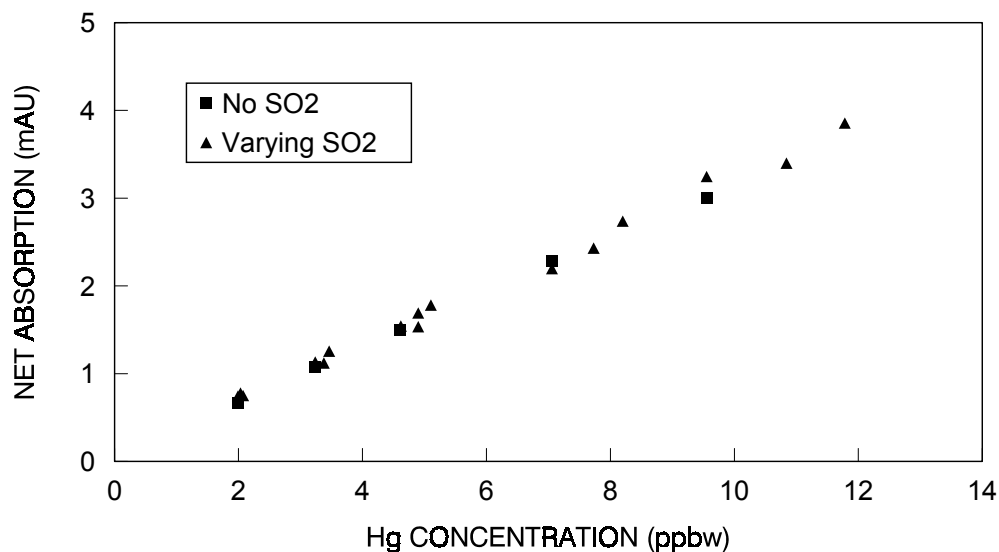


Figure 11. Background Corrected Absorbances for Varying Levels of Hg and SO₂.

A new D₂ lamp and power supply was purchased, and the overall stability of the lamp/power supply combination was much better than the old one. For the new D₂ system, the short term (10 minutes) signal variation with the dual photo diode optical setup was about 30 μAU after subtracting the signal drift. The long term drift was about 2 mAU/hr, which is comparable to that of the old D₂ system. A reading of 2 mAU is roughly equivalent to the signal from a 8 ppb_w Hg stream. Since on-line Hg measurements would be performed over a period of only about 5 minutes, the magnitude of the observed drift is acceptable. However, smaller iris sizes and alternate data processing methods were investigated in an attempt to reduce the amount

of drift. After reducing the iris sizes in the optical setup, the drift was reduced to about 1 mAU/hr. With further testing, it was discovered that the drift was primarily from the reference channel of the system rather than from the lamp or the sample channel. Consequently, the optics were simplified (removed mirrors, etc.) in order to help identify the source of the problem. A careful realignment of the optics was also performed. After these refinements, excellent results were obtained for the long-term drift. Over a period of about 20 hours, the drift was only about 0.1 mAU/hr. A reading of 0.1 mAU is roughly equivalent to the signal from a 0.5 ppb_w Hg stream. Therefore, the lamp, power supply, and measuring electronics have excellent stability, and the previous problem with drift appears to be from an optical alignment problem.

DEVELOPMENT OF PROTOTYPE ANALYZER

Although excellent results were obtained when using a Hg detector and a breadboard D₂ module in series, the Hg detector was a commercially available unit that was discontinued by the vendor. In addition, the Hg detector and breadboard D₂ module were operated as separate units. Therefore, the decision was made to proceed directly to the design and construction of an instrument that would incorporate a Hg detector and D₂ correction module into a single, compact, fully integrated system. DMK Engineering (Palos Verdes, CA) was subcontracted to build the prototype analyzer. During the development of that analyzer, numerous design modifications were made. A variety of different design options for the integrated Hg analyzer were considered, with particular attention being paid to stray light in the optical set up, light intensity, instrumental sensitivity, and effects of solarization of optical components during extended use. The overall optical design that minimized or eliminated problems in those areas was selected.

At an intermediate stage of development, we received the optical/mechanical components of the Hg analyzer. Although the unit was not fully assembled at this time, we wanted to test the basic optical design before proceeding to the final construction stages. Those tests yielded very positive results. A detection limit of 1 µg/m³ was observed and the linearity of the instrument response was excellent in the 1-20 µg/m³ range. This represented a worst case situation, since a variety of features for stabilizing the signals (e.g., use of a reference beam) had not yet been applied to the system. After adding the signal stabilization features, it was estimated that the detection limit would be lowered by a factor of 10.

After completing the initial construction of the instrument, problems with excess noise and drift were encountered. It was discovered that the reference channel photodetector had a cracked window, which in turn was causing much of the noise. Both reference and sample photodetectors were replaced with new ones that had larger active areas for improved light collection. Eliminating the cracked window and using the larger active areas greatly reduced the noise levels. Some machining problems related to a shutter in the instrument were also noted. Because of this, the shutter was not in its optimum position and the light beams were being slightly clipped. The shutter was remachined to eliminate clipping of the beams. This further reduced the noise levels. The reason for the excessive drift was also explored. Testing indicated that the drift was probably electronic rather than optical in nature. A redesigned preamplifier was built in an attempt to reduce the amount of drift without significantly increasing noise. This

greatly reduced the drift for the Hg channel. Next, the Hg channel was integrated with the D₂ background correction channel. Numerous additional modifications were made in the electronics and the shutter mechanism. With these changes, initial results indicated that the noise was reduced to only 0.1 mAU and the drift was reduced to 0.1 mAU/hr. The magnitude of noise and drift now met the design goals for the instrument.

As part of the development of the prototype analyzer, response times obtained with a 10-cm quartz sample cell (to be used in the final instrument) were tested using a 2 µg/m³ elemental Hg stream flowing at 1 L/min. In particular, the time necessary to achieve a steady Hg signal after switching from zero air to span gases was examined, as well as the time necessary to return to the base line after switching from span gases to zero air. Analysis of the gas streams was performed using a Thermo Separation Products AA Hg detector. For comparative purposes, tests were also performed using a Teflon cell fitted with quartz windows. Tests were performed at both room temperature and at about 200°C for the quartz cell, while the Teflon cell was tested only at room temperature. There was essentially no difference in response times at room temperature between a 10-cm quartz cell and a 10-cm Teflon cell. In both cases, it took about 60s for the signal to equilibrate after switching to span gases, and it took about 10s for the signal to return to the original base line after switching back to zero air. The relatively long time necessary to achieve a steady signal when switching to span gases appears to be due to a “pressure pulse” in the VICI Metronics calibration system that was used to generate the elemental Hg streams. This causes a temporary excessive rise in the mAU reading before the signal falls and steadies out at a constant value. Heating the quartz cell improved response times only slightly.

EVALUATION OF PROTOTYPE ANALYZER

Original Optics

The prototype Hg CEM employing a D₂ broadband correction feature was tested in our laboratories to assess its overall performance as well as its strengths and limitations. Air streams containing known concentrations of elemental Hg were generated with a VICI Metronics Model 340 Dynacalibrator in conjunction with an uncertified elemental Hg permeation tube from VICI Metronics. These gases were then blended with either N₂ or SO₂ and were subsequently passed directly into the analyzer via unheated Teflon lines. As with the tests with the breadboard optical setup, tests were performed only with dry gases. Also, unless otherwise noted, a heated sample cell was not used.

The possibility of flow rate effects on base line drift or noise was checked by passing air into the analyzer at various gas flow rates. Specifically, air flow rates of 500, 1000, and 2000 mL/min were used consecutively while the analyzer was running continuously. About 5 minutes of testing was performed at each gas flow rate before going to the next flow rate. Within the range of air flow rates tested, there was no effect on either the Hg or D₂ base lines. This was true for both base line noise and drift. Therefore, the sample flow rate in this range is not of concern.

Levels of base line noise and drift were assessed for both the Hg and D₂ channels in the analyzer. In the Hg channel of the instrument, base line noise was typically about 0.02 mAU and the base line drift varied from 0.1 to 0.4 mAU/hr. For the D₂ channel, noise levels were typically 0.2 to 0.3 mAU and base line drift was typically about 0.3 mAU/hr. Thus, the D₂ channel was substantially noisier than the Hg channel. The D₂ channel was expected to be less noisy than the Hg channel, and the noise in the D₂ channel is currently one of the limiting factors affecting detection limits and the accuracy of the analyzer when using high concentrations of interfering gases. It may be possible to obtain a quieter lamp and power supply combination than the one currently used in the instrument. Also, some of the problem could possibly be related to the peripheral electronics, which can also be improved upon if needed. In addition, since noise and drift are affected by lamp and optics alignments, the possibility can not be ruled out than more precise alignment is necessary.

While using only the Hg channel of the analyzer, calibration curves were obtained for air streams (no SO₂) containing Hg concentrations of 0.5-50 µg/m³. These tests were performed to assess detection limits and the linearity of the calibration curves. Excellent calibration curves were obtained with the Hg channel of the detector. For the entire calibration range, the linear regression "R²" value was 0.999. For Hg concentrations in the range of 0-10 µg/m³ the "R²" value was 0.993. The signal observed for a Hg concentration of 0.5 µg/m³ is shown in Figure 12. Based on the raw absorption readings from the Hg channel, a detection limit of about 0.1 µg/m³ was calculated. It must be emphasized that the analyzer uses only a 10-cm sample cell, yet attained a detection limit on the order of 0.1 µg/m³. The detection limit could be reduced by about a factor of 10 by using a 100-cm sample cell. The tradeoff is that the overall analyzer would be substantially larger and less portable. Lesser improvements could probably be made in the detection limit by keeping the 10-cm cell and modifying the electronics and/or signal processing routines. By using the latter approach, the detection limit could probably be lowered to 0.05 µg/m³ Hg or less.

When Hg was added to an air stream such that the final Hg concentration was 50 µg/m³, the D₂ base line was unaffected. Since this Hg concentration is much higher than that anticipated for gaseous effluents from coal-based power generation, it is clear that the D₂ base line will not be affected by Hg in the gas stream. This is critical to the application of the D₂-based background correction approach.

Because of the observation that a D₂ correction factor was needed in the tests with the breadboard optical setup, a variety of tests were performed with the prototype CEM using various concentrations of SO₂ without any Hg present. In one series of tests, 2.0% SO₂ (in a N₂ balance) was blended with air and then passed into the Hg analyzer. Total gas flow rates of 500, 700, 1000, and 1500 mL/min were used, while the flow rate of the 2% SO₂ was varied from 50-300 mL/min. For a given total gas flow rate, the air flow was proportionally decreased as the SO₂ flow increased in order to keep the total gas flow rate the same. This provided SO₂ concentrations of 0.1-0.9% in the final gas stream. The raw mAU readings from the Hg channel and the D₂ channel were both measured and recorded. For each total gas flow rate and SO₂ concentration, the ratio of the mAU value from the Hg channel to that of the D₂ channel was calculated. This ratio is the D₂ correction factor. The D₂ correction factors were also calculated

when passing a stream of 1000 ppm SO₂ (in N₂) directly into the analyzer at flow rates of 100, 250, 500, 750, and 1000 mL/min. For those tests, no dilution of the gas stream was used.

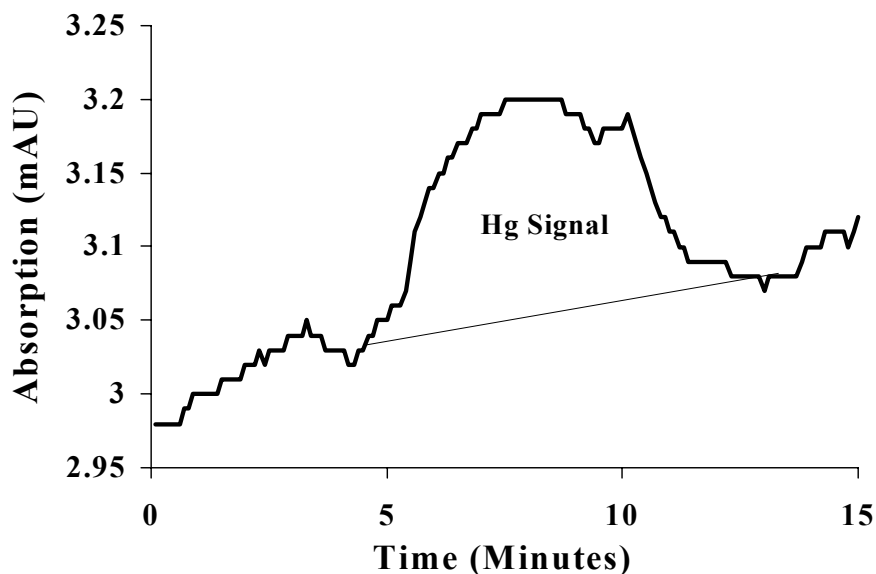


Figure 12. Signal Obtained with the CEM for a 0.5 $\mu\text{g}/\text{m}^3$ Hg Stream.

Results of the tests with SO₂ (no Hg present) indicated that the absorbance from the D₂ channel was significantly higher than that observed in the Hg channel. This is in agreement with the observations made with the breadboard optical design and may reflect the relatively complex SO₂ absorption spectrum in the wavelength region being used for analysis. For a given SO₂ concentration, the Hg/D₂ absorption values (i.e., the D₂ correction factor) was not affected by the total gas flow rate. Similarly, when a 1000 ppm SO₂ stream entered the analyzer at flow rates of 100-1000 mL/min, no flow rate effects on the D₂ correction factor were observed. Although the D₂ correction factor for a given SO₂ concentration was not affected by the total gas flow rate while using 2% SO₂ blended with air, it was affected slightly by the SO₂ concentration. The Hg/D₂ mAU ratio increased from 0.82 to 0.85 as the SO₂ concentration was increased from 0.1 to 0.6%, respectively. Although this is a narrow range, the differences can have a considerable impact on the background-corrected mAU readings when using blends of Hg and SO₂ in the concentration ranges of interest. The Hg/D₂ ratio appeared to be constant for SO₂ concentrations of less than about 0.3%. Despite the current need for a D₂ correction factor, it is possible that this need can be diminished or even eliminated through modifications in the instrument design. This is particularly important since it is undesirable to have a correction factor that is somewhat dependent on the concentration of the primary interfering gas in the sample stream.

Tests were also performed using blends of Hg and SO₂. For these tests, an uncertified Hg permeation tube (VICI Metronics) with a nominal Hg emission rate of 10 ng/min at 30°C was used. Tests were performed to determine the actual Hg emission rate. To do this, span gases from the calibrator were bubbled into KMnO₄ absorbing solutions and then analyzed by CVAA.

Results of those analyses indicated that the actual Hg emission rate was 11.0 ± 0.5 ng/min. Therefore, a value of 11 ng/min was used as the actual emission rate from the tube. This provided Hg concentrations of 9-26 $\mu\text{g}/\text{m}^3$ while using total gas flow rates ranging from 360-1020 mL/min. Although Hg concentrations of 1-10 $\mu\text{g}/\text{m}^3$ may be more typical of gaseous effluents from coal-based power generation, the higher Hg concentrations were used at this point in order to begin with more favorable conditions for the initial assessments of the CEM in the presence of interfering gases. The Hg calibration streams were blended with 2.0% SO_2 (in N_2). The SO_2 concentration in the final blended gas stream was varied from 0.02-0.44% by adjusting the SO_2 flow rate. For these tests, the absorbance at 254 nm due to SO_2 was 15 to 35 times higher than the signal due to Hg. For each SO_2 flow rate, corresponding Hg calibration curves were prepared in the absence of SO_2 by blending the span gases from the calibrator with dry N_2 and measuring raw absorption values with the Hg channel of the analyzer.

Results of the tests with the Hg and SO_2 blends are shown in Figures 13 through 16. In Figure 13, the raw (uncorrected) mAU values obtained for various Hg concentrations with and without SO_2 present are shown. As with the tests with the breadboard optical unit, the severity of the SO_2 interference is clearly shown. In Figures 14 through 16, the background-corrected absorption values are shown and compared with a calibration curve obtained for Hg in the absence of SO_2 . In Figures 14 and 15, in which SO_2 concentrations varied from 0.02 to 0.25%, a fixed value was used for the D_2 correction factor. However, a "sliding" D_2 correction factor was needed at higher SO_2 concentrations in order to effectively correct for the SO_2 interference. To do this, the D_2 correction factors were bracketed along with the SO_2 concentrations in order to provide a "sliding" correction factor dependent on the SO_2 concentration. In other words, as the SO_2 concentration changed, the correction factor for the D_2 channel changed slightly. A sliding D_2 correction factor based on the SO_2 concentration was used for the data shown in Figure 16. The linear regression " R^2 " values for the Hg calibration curves were all about 0.999. The D_2 background correction approach generally did a good job at correcting for the SO_2 interference. This is particularly true for SO_2 concentrations of less than 0.25% in which a fixed D_2 correction factor was applied. Although the mAU readings due to SO_2 were 15 to 35 times higher than those due to Hg, the background-corrected mAU readings were generally (85% of all cases) within 10% of the theoretical Hg mAU values (i.e., the absorption due only to Hg). In fact, the corrected values were within 5% of the theoretical mAU values in about 50% of all cases.

In Figure 17, the results are shown for a 9 $\mu\text{g}/\text{m}^3$ Hg stream containing 0.2% SO_2 . The data are not only corrected for the SO_2 interference using the D_2 data, but are also automatically correlated with a Hg calibration curve prepared in the absence of SO_2 . To obtain this readout, a Hg calibration coefficient is simply input into the analyzer. The D_2 background correction did an excellent job at correcting for the SO_2 and correlating the corrected readings to an actual Hg concentration. It can also be seen that the signals are slightly noisier when integrating the readings from the Hg and D_2 channels, rather than taking readings from the Hg channel alone while analyzing Hg streams in the absence of SO_2 . This is to be expected since the D_2 channel is significantly noisier than the Hg channel.

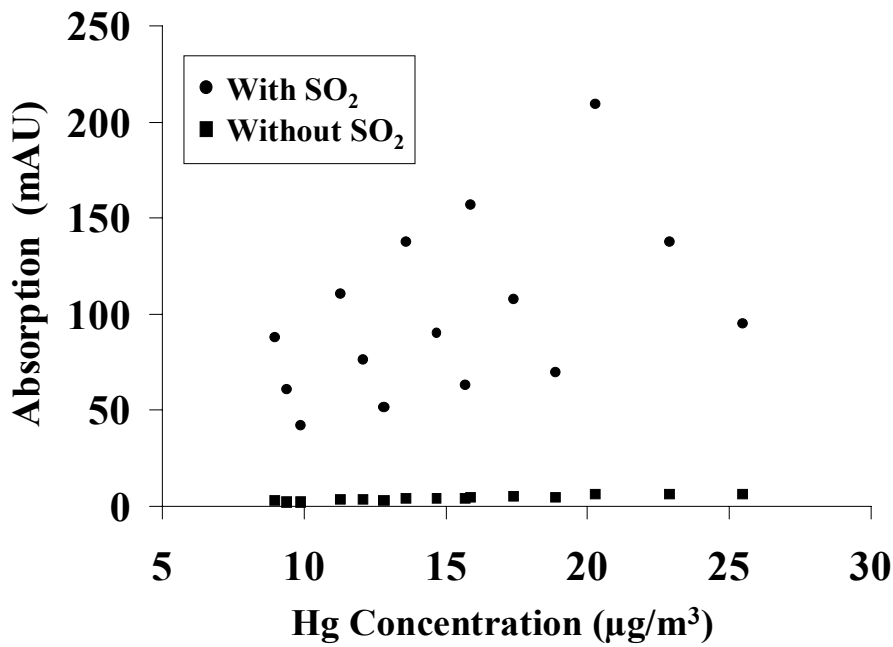


Figure 13. Uncorrected Absorbance Readings Obtained with the CEM for Various Hg Concentrations With and Without SO₂ Present.

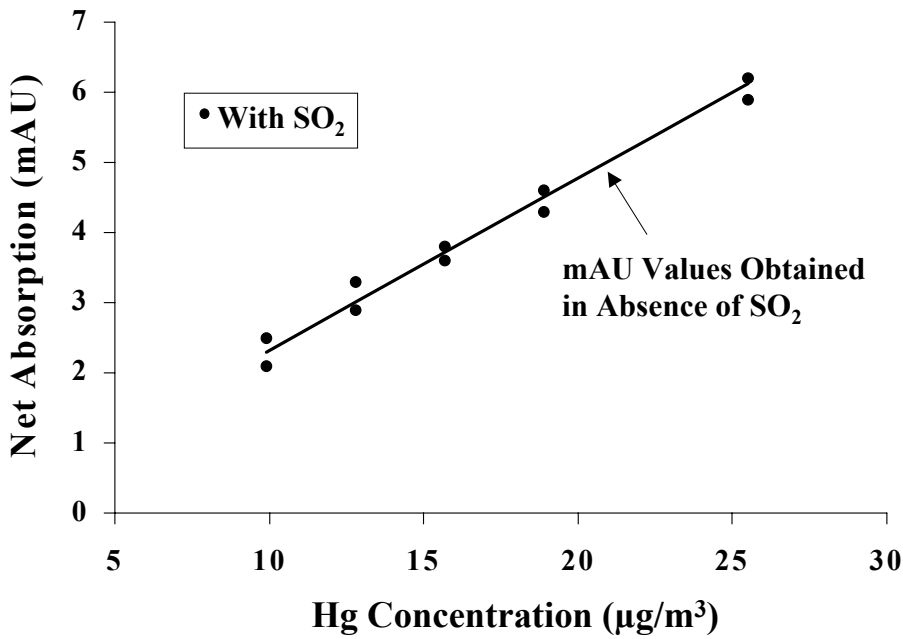


Figure 14. Background-Corrected (Fixed D₂ Correction Factor) Absorbance Readings Obtained with the CEM for Various Hg Concentrations in the Presence of 0.02-0.06% SO₂.

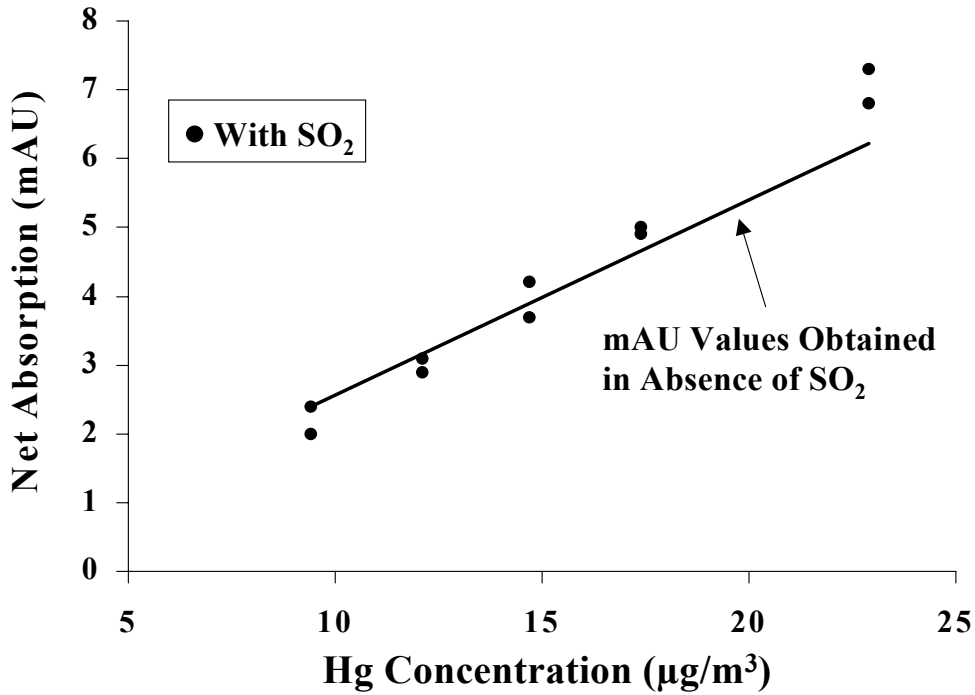


Figure 15. Background-Corrected (Fixed D₂ Correction Factor) Absorbance Readings Obtained with the CEM for Various Hg Concentrations in the Presence of 0.10-0.25% SO₂.

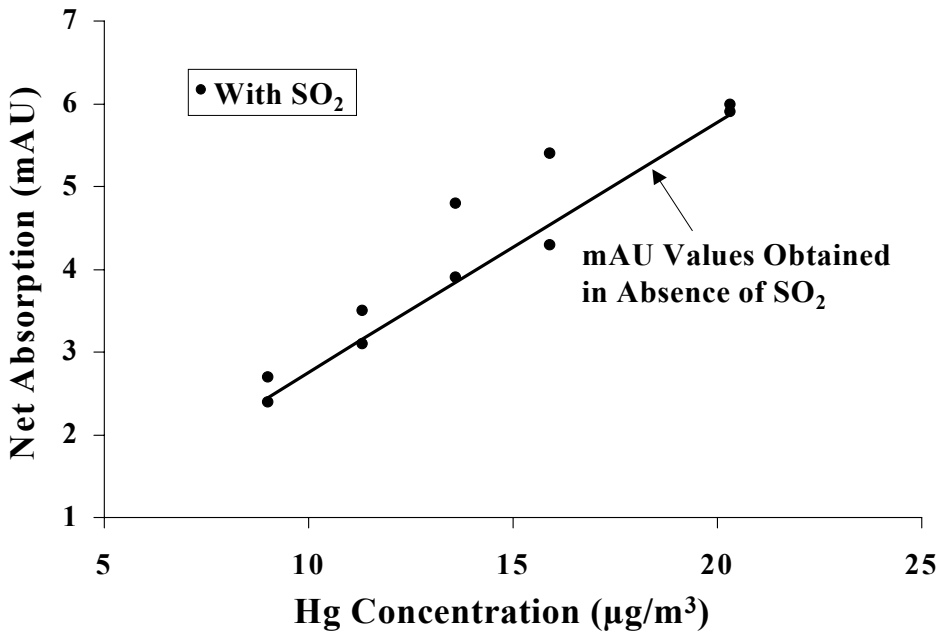


Figure 16. Background-Corrected (Sliding D₂ Correction Factor) Absorbance Readings Obtained with the CEM for Various Hg Concentrations with 0.20-0.44% SO₂.

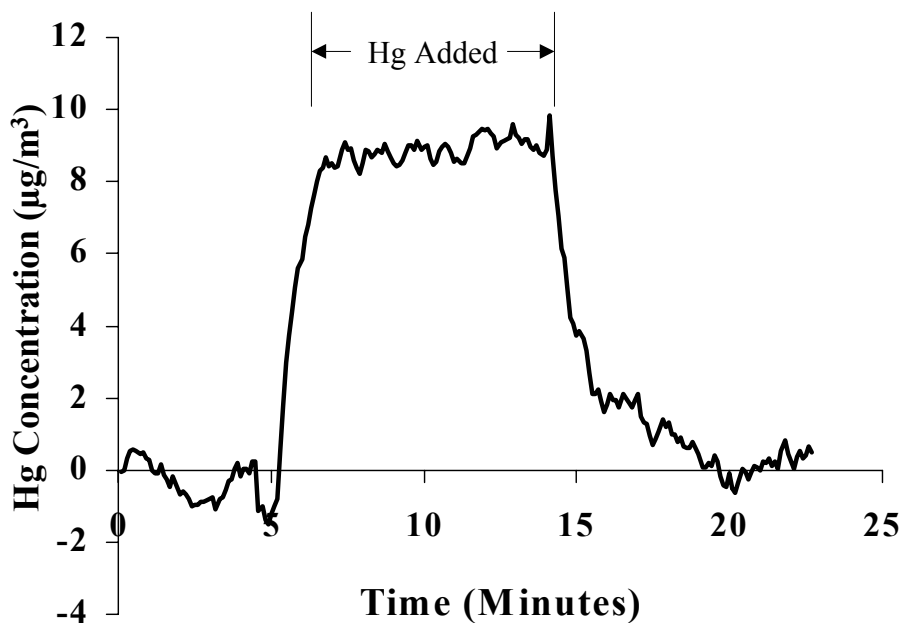


Figure 17. Background-Corrected Hg Concentration Obtained with the CEM for a Gas Stream Containing $9 \mu\text{g}/\text{m}^3$ Hg and 0.2% SO_2 .

A limited number of tests were performed with a heated sample cell. While performing those tests, a prominent cyclic noise problem was noted. The cycles had an amplitude of about 0.2 mAU and a frequency that varied from 10-60 seconds, depending on the cell temperature. This precluded seeing Hg concentrations below about $2 \mu\text{g}/\text{m}^3$ while using a heated cell. The cyclic base line was thought to be due to the temperature controller for the cell heater. In particular, it could be caused by unshielded wires connected to the controller relay. The cyclic noise could also be caused by inadequate line regulation of the power supply such that when the heater switches on, the line voltage drops and causes a drop in the DC power supply, which in turn causes a drop in the power to the Hg lamp. Still another possibility is that the cyclic nature of the base line with a heated cell is related to thermal effects because of the low thermal mass of the detection cell. Tests were performed to determine if the cyclic base line could be avoided with a heated sample cell by using an alternate heating approach. To do this, the sample cell was heavily insulated and the cell heater was turned off. However, the sample line into the cell was heat traced and connected to a Variac for temperature control. Thus, the gas entering the cell was heated in this manner. The heavily insulated sample cell heated up due to the hot gases entering the cell and quickly reached a temperature equilibrium. Testing was performed with the sample line heated to 50, 100, and 200°C. Results of those tests indicated that the cyclic base line was eliminated by this approach. Therefore, the problem was indeed related to the cell heater cycling on and off. Furthermore, the base line noise (about 0.02 mAU) was not affected by increases in temperature. Simple design modifications should allow the sample cell to be heated directly without causing the cyclic base line problem.

Aside from the cyclic nature of the base line observed with a heated sample cell, the instrument sensitivity decreased when the cell was heated. This was not due to the cyclic nature of the base line, but rather from a decreased instrument response for a given Hg concentration. As the cell temperature increased from ambient to 200°C, the magnitude of the Hg signal decreased by about 50%. The Hg signal decreased incrementally with each increase in temperature in that temperature range. One of the possibilities is that there was defocusing of the optics when the cell is heated. If so, the problem could be potentially alleviated by providing better insulation at the ends of the sample cell in order to decrease temperature variations in the cell windows. To see if improved insulation at the ends of the cell would help regain instrument sensitivity, the entire sample cell was heavily insulated and the cell was heated indirectly by heating the sample gases entering the cell (as done earlier to study the cyclic base line problem). However, this did not alleviate the problem of lower instrument response with increased cell temperature. Therefore, apparent defocusing of the optics remains a problem that would have to be dealt with if a heated sample cell is desired.

Although the use of a heated sample cell was investigated, using a heated sample cell may not offer many advantages over a cell at closer to room temperature. The 10-cm sample cell provided very high sensitivity and rapid response. Response times were compared at various temperatures in the range of 25-200°C, and no differences were observed in the rise and fall times (when switching back and forth between zero air and span gases) as the temperature was varied. Therefore, heating the cell did not significantly decrease sorption of Hg onto the cell walls and provide improved instrument response. Unless condensable aerosols are found to be a problem with the cell at room temperature, heating of the sample cell will probably not be necessary.

Modified Optics

Because of the observation that the D₂ correction factor changes slightly with varying SO₂ concentration, thereby complicating the analytical determinations, the optics in the instrument were modified in an attempt to eliminate the need for the D₂ correction factor or at least reduce its importance. After the optical modifications, tests were performed whereby gas streams containing SO₂ concentrations of 0.1 to 0.6% (in air) were passed into the analyzer at a total gas flow rate of 1000 mL/min. The D₂ correction factor (ratio of the mAU reading from the Hg channel to that from the D₂ channel) was determined at each SO₂ concentration. These tests had been performed earlier with the initial optics. As before, the D₂ correction factor increased slightly as the SO₂ concentration increased. Whereas the correction factor with the initial optics was about 0.8, the correction factor with the new optics was about 1.1. Thus, modifying the optics changed this correction factor considerably. However, the actual value of the correction factor is not the primary issue. Rather, the most important issue is the varying D₂ correction factor with changing SO₂ concentration, and that phenomenon was still observed after installation of the new optical components. Therefore, when tests were performed using Hg concentrations of 10-20 µg/m³ in the presence of 0.2-0.44% SO₂, a fixed D₂ correction factor was still inadequate for accurately performing the background corrections at those high SO₂ levels. In fact, results were very similar to those obtained under the same experimental conditions but while using the original optics. Therefore, the problem with the correction factor

changing slightly with changing SO₂ concentration still remains, and accurate background corrections could only be made with a "sliding" D₂ correction factor when SO₂ concentrations were above about 0.25%.

DESCRIPTION OF Hg ANALYZER AND CEM

The Hg analysis component (i.e., detection system) of the Hg CEM is shown in Figure 18, and a simplified schematic diagram of the interior of the analyzer is shown in Figure 19. The Hg analyzer weighs roughly 50 pounds and is housed in a 26" by 9" by 18" case equipped with a carrying handle. The case opens up like a suitcase to provide easy access to all optical and electrical components. A 10-cm quartz cell (volume of about 18 cm³) that can be heated from 30-225°C is used. The cell temperature is selected with a thumbwheel on the instrument cover.

The analyzer contains a temperature-controlled, low-pressure, non-ozone Hg lamp for measuring total absorbance at 254 nm, and a 40-watt D₂ lamp for measuring the background in that region. A single beam splitter is used with a shutter mechanism to alternately switch the beams from the Hg and D₂ lamps through the sample cell to the photo diode detector. A reference beam is used to reduce base line noise and drift by compensating for fluctuations in lamp intensity and other instrumental variables. This is accomplished by sending a portion of each beam to a reference photo diode detector.



Figure 18. Mercury Analyzer Employing a D₂ Background Correction System.

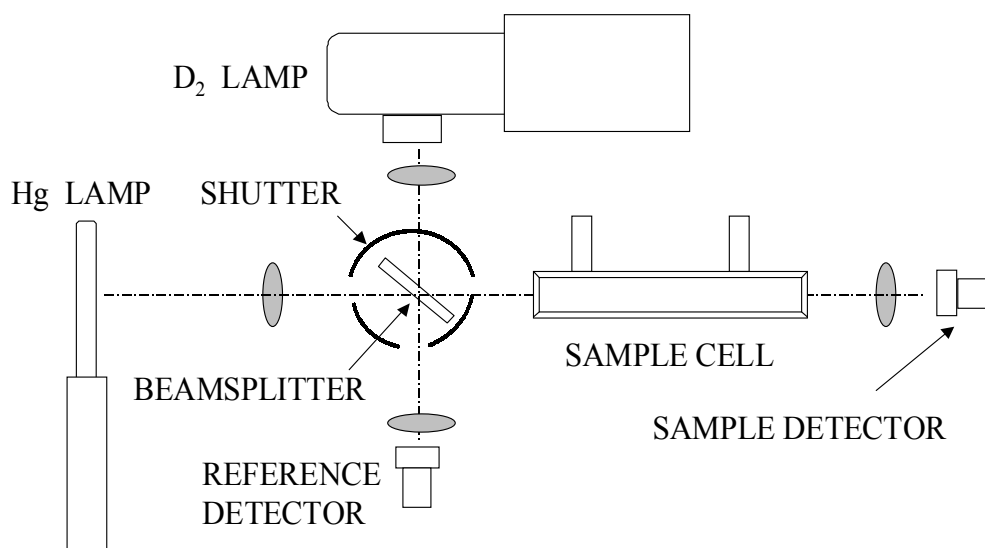


Figure 19. Simplified Schematic Diagram of the Interior of the Hg Analyzer.

A small panel mounted in the cover displays a reading about every three seconds, and up to 48 hours of data can be stored in nonvolatile internal memory. Those data can later be downloaded onto a laptop computer or a PC. By using the panel display, the instrument can be zeroed, data acquisition into the internal memory buffer can be initiated, and one of two data display modes can be selected. The analyzer can also be operated continuously with an external laptop computer or PC through a DB-9 connector. With an external computer hooked up to the analyzer, one of six data display modes can be selected. In addition, there are diagnostic tools, adjustments for data processing parameters, instrument zeroing capabilities, and optical alignment features which can be used if desired. Data smoothing is accomplished with an adjustable digital filter. With the digital filter, there is a tradeoff between signal smoothing and instrument response time. In other words, as the signal is smoothed to a greater degree, the instrument takes longer to respond and reach a steady reading. To simplify the analyzer, the number of detectors was reduced from 4 to 2, and a single beamsplitter with a chopper mechanism was used. This has the advantage of eliminating cross-talk interference between the sources and improves stability since any degradation in the optics and/or detectors will occur equally in both signals.

The discussion above pertains only to the detection portion of the overall CEM and does not include the gas conditioning components required for sampling gasifier streams. Because funds were not available to duplicate the entire gas conditioning system, the Hg analyzer would be connected to the same gas conditioning system used for the HCl CEM. A schematic diagram of the overall gas conditioning and analysis system when sampling for Hg is shown in Figure 20. As noted above, this is basically the same gas conditioning that is used for monitoring HCl (see description of HCl CEM in latter portions of this report). However, when being used for Hg, several modifications are necessary. Specifically, the soda lime scrubber that is used for HCl is

replaced with an activated carbon scrubber, the sample gases bypass the HCl analyzer and enter the Hg analyzer instead, and no instrument air is required for the Hg detector. The Hg scrubber consists of four Model 300 Hydrocarbon Traps (in parallel) from Chromatography Research Supplies. These scrubbers are to ensure that the air stream added to the sample gas prior to the oxidation catalyst is free from Hg contaminants. For more details on the gas conditioning system, refer to the CEM description in the "Hydrogen Chloride Studies" section of this report.

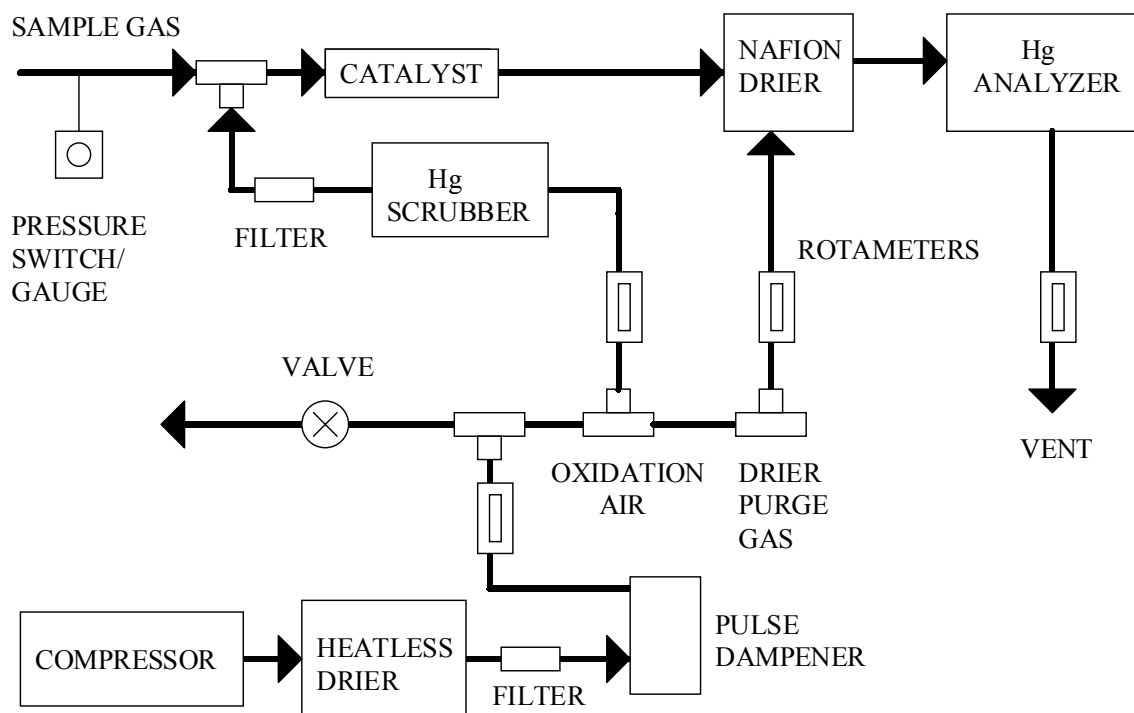


Figure 20. Schematic Diagram of Gas Conditioning System for the Hg CEM.

The use of an oxidation catalyst raises some concerns regarding the Hg analyses, since the detection system responds to only elemental Hg and not oxidized Hg. Therefore, the catalyst module contains a catalyst zone for removing NH_3 and tars, followed by a high-temperature ($900\text{-}950^\circ\text{C}$) pyrolysis zone intended to convert all of the Hg to elemental form prior to entering the Hg analyzer. Even if the pyrolysis zone effectively converts all the Hg to the elemental form, the possible recombination of Hg and chloride as the gases are in transit to the analyzer remains an issue which requires further study.

The operation of the overall CEM is based on the assumption that a properly filtered gas stream is available. Thus, particle filtration is not performed as part of the gas conditioning system in the CEM, but should be performed upstream from the CEM using an inertial filter, standard metal filter, or other suitable filtering device. Also, calibrations are nonautomated and are done "off line" whereby the instrument is calibrated with elemental Hg while bypassing the

gas conditioning system. The off-line calibrations will help ensure that the instrument is properly calibrated. Accurate analyses will then hinge on sample transport issues. However, the calibration issues have not been fully resolved in view of the difficult sampling and gas conditioning problems involved. Although it is often preferred to pass span gases through the entire analytical and gas conditioning system in order to perform calibrations, an issue of concern with that approach is that the calibration gases are in a drastically different gas matrix than the sample gases are in. This is of concern because sample transport difficulties and analyte losses typically vary as the gas matrix is changed. In addition to performing off-line calibrations to ensure proper instrument calibration, elemental Hg spikes into the gasifier streams would be desirable to gain confidence in sample transport issues.

TESTING OF ENTIRE CEM IN THE LABORATORY

After integrating the prototype Hg analyzer with the gas conditioning system, the fully integrated Hg CEM was evaluated in the laboratory using a simulated gasifier stream. The simulated gasifier stream (dry basis) consisted of 22% H₂, 13% CO₂, 7% CH₄, 1.7% H₂S, 44% CO, 0.25% NH₃, 50 ppm HCl, 15 µg/m³ elemental Hg, and a balance of N₂. Also, moisture was added to give a water content of 20%. A single compressed gas cylinder containing blended H₂, CO₂, CH₄, H₂S, and CO was used. The NH₃, H₂O, HCl, and Hg were each added separately to the sample line just prior to the inlet of the gas conditioner. Compressed gas cylinders were used for the NH₃ and HCl, while known amounts of water were fed into the gas stream by using a peristaltic pump. Elemental Hg vapors were added to the sample gas stream by using a VICI Metronics Model 120 Field Calibrator in conjunction with a certified elemental Hg permeation tube. The sample line (316 stainless steel) into the gas conditioner was heated and maintained at 600°C, and the NH₃, H₂O, HCl, and Hg were added to the gasifier stream via union tees in the 600°C sample line. Type 316 stainless steel would not be the preferred choice of materials during prolonged testing, but was used because of its low cost relative to other options and because extended testing of the CEM was not to be performed. Sections (about 8" each) of the NH₃, H₂O, HCl, and Hg lines connected to the union tees in the main sample line were heavily insulated to provide preheating prior to entering the gasifier stream.

For tests with the simulated gasifier stream, about 1 L/min (dry basis) of gasifier stream was blended with 2 L/min of oxidation air, which was preheated to 600°C and added to the simulated gasifier stream just prior to the oxidation catalyst. For comparative purposes, Hg streams (15 µg/m³) in air and nitrogen were passed directly (bypassing the gas conditioner) into the Hg analyzer. Similarly, tests were performed in which the Hg streams in either air or nitrogen were passed through the heated gas conditioning system. Operating the entire gas conditioning/analytical system was complex and required a substantial amount of experience with the systems.

When using streams of only Hg in air flowing at 1 L/min and bypassing the conditioner, full signals were obtained with the Hg analyzer within about a minute when switching from zero air to span gases. When the air stream contained 50 ppm HCl, the reading on the Hg analyzer was within 3% of that observed in the absence of HCl. Since the detector responds to Hg only in

the elemental (reduced) form, these results show that little or no oxidation of Hg occurred in the presence of HCl at room temperature. When switching from span gases back to zero air, the Hg in the analyzer was purged out in less than a minute.

Next, a stream of Hg in N₂ flowing at 1 L/min was passed through the heated gas conditioning system prior to entering the Hg analyzer. No air was added prior to the catalyst for these tests, which were performed with and without 50 ppm HCl in the gas stream. When HCl was absent, the Hg readings were about 50% below expected values. This suggests that wall losses in the gas conditioner were substantial, since little or no Hg oxidation would be anticipated in the N₂ stream. However, it is possible that there were residual traces of oxygen in the system from previous tests. In that event, either the pyrolyzer (at 900°C) downstream from the oxidation catalyst was not effectively converting any oxidized Hg back to the elemental form, or else the pyrolyzer was working as intended and some of the elemental Hg was oxidizing as the gases cooled after exiting the pyrolyzer. When the tests were repeated while bypassing the Nafion dryer, the Hg signals increased by 40-50% (relative), but were still well below the values obtained while bypassing the entire gas conditioner. This shows that the Nafion (or the inlet tubing to the dryer) is one source, but not the only source, of Hg losses when going through the entire gas conditioner. When the tests through the entire gas conditioning system were repeated with 50 ppm HCl in the gas stream, the Hg signals decreased by about 10% relative to those obtained in the absence of HCl. However, this magnitude of decrease is not beyond experimental uncertainties, including uncertainties in the flow meter readings.

During the tests with Hg in N₂ through the conditioner, a quartz wool pad at the upstream end of the catalyst tube began turning brown. Analysis of the brownish material by scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDX) indicated that the material was highly enriched in iron and nickel. This material, which presumably came from the steel sampling line entering the catalyst tube, is undesirable because transfer of those metals downstream could catalyze the oxidation of Hg or could result in sorption of Hg vapors. Also, continued buildup on the quartz wool would eventually lead to gas flow restrictions. Careful consideration will need to be given to the type of material used in the sample lines.

Subsequent tests were performed with streams of air (as opposed to N₂) and Hg flowing through the heated conditioner at 1 L/min. The Hg signals obtained in those tests were comparable to those obtained while using streams of Hg, HCl, and N₂ through the conditioner. When the tests with air and Hg were repeated, but in the presence of 50 ppm HCl, the elemental Hg signals decreased substantially (as was feared) and were only about 15% of those obtained while bypassing the gas conditioning system. Also, when testing with Hg in streams of air and HCl, the Hg signals were considerably more erratic than in previous tests. As discussed above, it appears that either the pyrolyzer is not effectively converting oxidized Hg back to the elemental form, or that the pyrolyzer is working as expected, but elemental Hg downstream from the pyrolyzer is oxidizing in the presence of chloride as the gases cool. Although a larger pyrolyzer would effectively circumvent the first potential problem, it would do little good if the Hg is reoxidizing in the cool-down zone after the pyrolyzer. A number of Hg researchers believe that Hg oxidation occurs in the cool-down zone in a coal combustor, and this could well be what is occurring downstream from the pyrolyzer in the gas conditioning system. This issue was always a concern with the gas conditioning approach being used, but insufficient information was

available on the pyrolytic conversion approach to adequately assess its utility for this application. The tests so far indicate that Hg transport through the gas conditioning system is problematic and requires further study to minimize wall effects and to ensure that all the Hg after the pyrolyzer is (and stays) in the elemental form.

Next, attempts were made to pass elemental Hg in a simulated gasifier stream through the heated gas conditioner. When using 1 L/min of simulated gasifier stream (including H₂O) and adding 2 L/min of oxidation air prior to the catalyst, the background-corrected absorbance readings from the analyzer (even without Hg in the gas stream) were too erratic to get meaningful Hg signals. A variety of possibilities could account for this observation. One possibility is that flow fluctuations in the gasifier/air blends were causing rapid fluctuations in the SO₂ concentration downstream from the catalyst. The Hg analyzer may not be able to accurately perform background corrections in such cases. If so, design modifications in the analyzer would eliminate or alleviate this problem. Another possibility is that the decreased residence time in the catalyst zone (due to the increased volumetric flow rate resulting from the large volumes of steam from the added water) is resulting in incomplete conversion of H₂S to SO₂. In this case, the ratio of H₂S to SO₂ could well be fluctuating. In that event, it would throw the background-corrected absorbance readings off since the analyzer was set up specifically to correct for SO₂ interferences, and some of the numerical factors entered into the analyzer (i.e., the D₂ correction factor) for this purpose could be substantially in error if H₂S is present. Finally, it was noted that the red-hot portion of the catalyst system (where most of the gas stream oxidation was occurring) was pulsing every few seconds. Since this only happened when water was being added (via a peristaltic pump) to the sample stream, the water addition probably has something to do with the pulsing catalyst zone. It is believed that the pulsing was due to water flashing to steam in the sample line. Although the water was preheated prior to entering the main sample line, better preheating of the water and simple refinements in the plumbing for the water injection system would probably solve this problem (assuming that water flashing to steam is indeed the cause of the pulsing in the catalyst zone).

After using the simulated gasifier stream, the gas stream passing through the conditioner was switched back to only N₂ (no oxidation air) and Hg. However, the Hg signals were much lower than previously observed when using only N₂ to transport the Hg through the conditioner. Thus, something apparently "poisoned" part of the sample transport and/or gas conditioning system. No aerosols or deposits were observed in the catalyst tube or in the oven containing the Nafion dryer (although heat tracing precluded immediate observation of the sample line connecting the catalyst tube to the dryer). However, it was suspected that the problem may still be related to traces of sulfur-containing gases in the system. Such gases may be interacting with the Hg in such a manner that the Hg is either combined with sulfur-containing vapors in the gas stream (in which case it would not be detectable by AA), or else is reacting with steel components with the aid of the sulfur-containing gases. After passing simulated gasifier streams through the entire system and then returning to a N₂ flow of 1 L/min, traces of SO₂ could still be smelled at the outlet of the gas conditioner an hour or more later. Over that time period, mAU readings from both the Hg and D₂ channels of the analyzer exhibited a major downward drift, and absorbance readings were much higher (10 mAU or more) than those obtained for N₂ streams that bypassed the conditioner. Since the D₂ channel is not sensitive to Hg, this is most likely due to the desorption of sulfur-containing gases, indicating that those gases have severe

sorption/desorption effects in the gas conditioner. Similar results were obtained while bypassing the Nafion dryer, indicating that major sorption/desorption effects were occurring in other components of the sampling and/or gas conditioning system. Improvements are required to reduce those effects in the gas conditioner.

At the completion of the tests, the heat tracing was taken off the Teflon sample line connecting the catalyst tube to the Nafion dryer. The tube contained numerous spots on the interior walls and was heavily fogged in regions of the tubing. It was determined that a temperature of 200-220°C was needed to vaporize those deposits. The downstream end of the catalyst tube is always maintained at roughly 200°C, while the line connecting the catalyst tube to the Nafion dryer is only maintained at 110°C in order to avoid excessive temperatures in the dryer (which would substantially reduce drying efficiency). Chemical and morphological analyses on the deposits by SEM-EDX indicated that the spots were crystalline and were highly enriched in oxygen and sulfur, and possibly lesser amounts of nitrogen. Thus, the spots are apparently some type of sulfate compounds, such as ammonium sulfates and/or ammonium thiosulfates. The presence of the latter compounds was previously shown to exist if NH₃ was not completely removed from the gasifier stream. Improper operating conditions (excess air percentage, temperatures, etc.) over just a few minutes could have resulted in those deposits that, once formed, may adversely affect sample transport even during proper operation of the gas conditioner. It is very likely that the sulfur-containing deposits in the sample line were responsible for much of the Hg losses observed during sample transport. However, this work is complex, and additional work would be required to elucidate the precise mechanisms responsible for the Hg losses.

HYDROGEN CHLORIDE STUDIES

SELECTION OF METHODS TO EVALUATE

At the start of this project, the literature was reviewed to acquire information on analytical methodologies that may be suitable for determining HCl in hot gases from coal gasification systems. A variety of techniques for monitoring HCl in gaseous streams were identified. One of those methods utilizes a hollow cathode plasma (HCP) detection system. The HCP technique has been used to detect Cl in commercial gas mixtures (6). Although that method looked attractive in some respects, it is not specific to HCl, must operate at reduced pressures, and may have severe molecular interferences. On-line analysis of liquid streams by ion chromatography (IC) was also discussed in the literature (7) and could likely be adapted for gas stream analysis. However, its primary application is for analysis of liquids, and there are concerns regarding instrument complexity and durability. That method has not yet been used for gas stream analysis. Mass spectrometry (MS) has been applied to the analysis of gaseous effluents for HCl (8), but it is complex, expensive, and requires the use of a vacuum system. In view of these considerations, the HCP, IC, and MS methods were not considered further.

Fourier transform infrared spectroscopy (FTIR) should be a good method for determining HCl in flue gases. Although there is an interference from methane at the fundamental vibration of HCl, the interference would be avoided when using gas stream oxidation. FTIR has been used to look at gaseous HCl emitted during laboratory heating of coal (9) and for HCl analyses in emissions from a hazardous waste incinerator and a coal-fired power plant (10, 11). In the latter study, HCl was not detected, even though HCl concentrations were believed to be high enough to detect. The authors noted that they were using nickel coated stainless steel absorption cells and suspected that HCl was being “removed” through reactions with the cell walls.

Gas filter correlation IR (GFCIR) is an attractive non-dispersive IR absorption technique. In that method, an IR beam is modulated by two cells mounted on a rotating wheel. The first cell is filled with the gaseous component to be monitored (thus, gas filter correlation) and the second one is filled with a gas that does not absorb IR energy in the same spectral region as the sample gas. The absorption of the IR beam at specific wavelengths in the sample cell is proportional to the HCl concentration. That method has been used to determine HCl in waste incinerator gases (12) and appeared to be a method worthy of further consideration, even though interferences are of considerable concern for IR absorption methods. For HCl, methane is an interference of particular concern. Based on an EPA report, one GFCIR system did not perform reliably in field tests at a hazardous waste incinerator (13). On the other hand, we spoke with personnel from several different companies who had both laboratory and field experience with a Thermo Environmental Instruments Model 15 GFCIR analyzer. They reported that the instrument generally worked well in the field. However, several of the instrument users noted that the analytical uncertainty was significant in the 1-10 ppm range and recommended “dampening” the signal by taking 60-second averages. Base line drift was also reported to be significant, which sometimes made it difficult to differentiate between 1 and 10 ppm. GFCIR monitors which have heated (180°C) sample cells are commercially available.

Determining HCl by continuous titration has also been discussed in the literature (14). In that study, continuous titration was used to determine HCl in laboratory-generated combustion gases. That approach is probably a viable alternative to monitoring HCl emissions in NETL power producing systems. However, it is probably not the method of choice since it is relatively complex and more prone to breakdowns in the field compared to other options that were being considered.

NETL employed a wet chemical technique using conductivity measurements to determine HCl in simulated gasifier streams (15). That procedure involved using a high boiling point alcohol in a conductivity cell. HCl protonated the alcohol, thereby changing the conductivity of the solution. Although it is an attractive method, considerable problems involving memory effects and slow equilibration were encountered in the analyses. Despite the analytical problems, which may actually be due primarily to sample delivery issues, the method still appears to have promise for monitoring HCl.

In addition to the above methods discussed in the literature, a number of commercially available analyzers were found after extensive interactions with vendors. These include methods based on colorimetry (dry), electrochemistry, electrolytic conductivity, ion mobility spectroscopy, ion selective electrodes, and semiconductor detection systems. Analyzers based

on conductivity, electrochemical, and semiconductor detection are unsuitable for our application due to numerous chemical interferences from gaseous species anticipated to be present in gasifier streams. A dedicated monitor using an ion selective electrode for determining HCl in flue gas appeared promising. Although H₂S interferes with the analysis, this would not be a problem when using gas stream oxidation.

The methods found in the literature and from vendor contacts were screened to determine which methods had the most promise for our application (i.e., monitoring coal gasification streams). Criteria used to initially screen (no testing performed at this point) these methods for possible use in the HCl CEM included sensitivity, accuracy, interferences, cost, complexity, durability, mobility, and stage of development. Based on this initial screening, gas filter correlation IR (GFCIR), dry colorimetry, and ion mobility spectroscopy (IMS) were selected for evaluation in our laboratories. The laboratory evaluations of those three methods are discussed individually below. Based on those evaluations, IMS was ultimately selected as the method of choice for our HCl CEM.

GAS FILTER CORRELATION IR

A Thermo Environmental Instruments Model 15 GFCIR HCl Analyzer was evaluated in our laboratories. That unit is shown in Figure 21 below. The sample cell for this instrument (as designed at the time this work was performed) can operate up to about 50°C. When using compressed gases for the HCl standard, instrument readings were very stable. For a 170 ppm_v HCl stream, the stability of the instrument reading and the signal rise and fall times observed when switching to span gases and then back to zero air are shown in Figure 22. In addition, the base line fluctuations were minimal (about 0.2 ppm HCl or less).



Figure 21. Thermo Environmental Instruments Model 15 GFCIR HCl Analyzer.

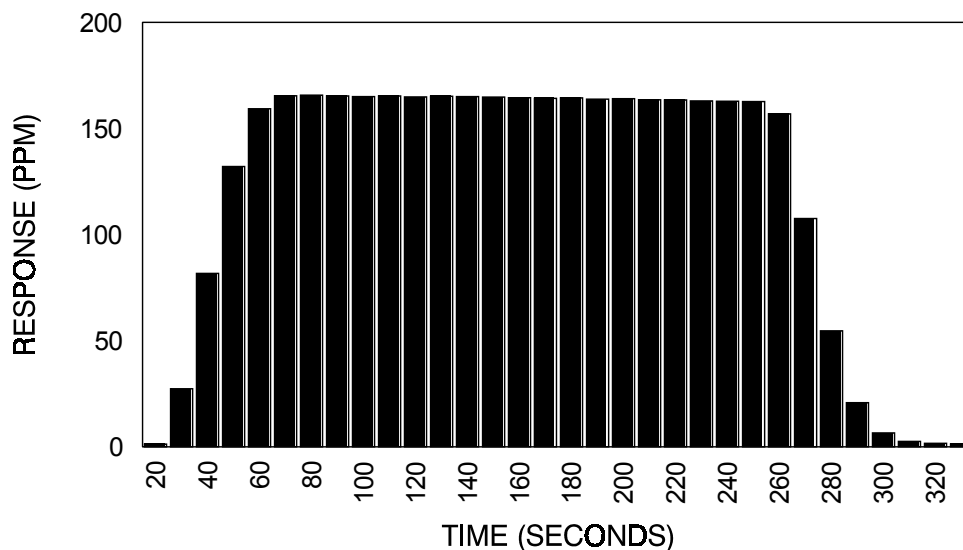


Figure 22. GFCIR Signal Observed for a 170 ppm HCl Stream.

Calibration curves were obtained by blending compressed gases containing 3000 ppm HCl with nitrogen to obtain the desired HCl concentrations. High concentrations of HCl were used to get a better feel for the dynamic range of the detector. The calibration curves were linear from 25-3000 ppm_v HCl. In the range of 0 to 150 ppm HCl (see Figure 23), erratic responses were noted at concentrations below 25 ppm, but were fairly linear above that. The erratic responses observed for low HCl concentrations could be due to uncertainties in blending the calibration gases or to memory effects from HCl sorption/desorption with sample line walls. HCl permeation tubes containing aqueous HCl solutions (from VICI Metronics) were then used to provide gas stream concentrations of 0.2 to 2 ppm_v HCl. As shown in Figure 24, the instrument response showed good linearity from about 0.5 to 2 ppm. Long equilibration times and pronounced memory effects were noted when passing low concentrations of HCl through the sample lines (both Teflon and steel) and flow meters. This could explain why many users of GFCIR for HCl have reported problems in differentiating between different HCl concentrations below 10 ppm. In other words, those problems may be related more to sample transport issues than to instrumental issues.

Tests were also performed to study the severity of the known interference from CH₄. For those experiments, CH₄ was blended with a stream of N₂ containing 100 ppm HCl. The CH₄ concentration in the gas stream was varied from 0 to 12% and the increase in the instrument reading (in ppm) was recorded for each CH₄ concentration tested. Results of those tests are shown in Figure 25. From the ratio of CH₄ concentration to the resulting increase in the instrument reading, it was calculated that 300-400 ppm CH₄ gives a response equivalent to about

1 ppm HCl. This has important implications regarding the use of this instrument for monitoring gasifier streams. Since CH₄ concentrations can be as high as 15% in coal gasification effluents, the potential error in the HCl reading from CH₄ is on the order of 400 ppm if all the CH₄ remains in the gas stream. Consequently, depending on the relative concentrations of CH₄ and HCl in the gasifier effluent, 75% to nearly 100% of the CH₄ will need to be removed prior to HCl determinations using this GFCIR instrument. However, since the intention is to use gas stream oxidation, the CH₄ would not be an issue in that event since all of the CH₄ should be quantitatively removed prior to HCl analysis.

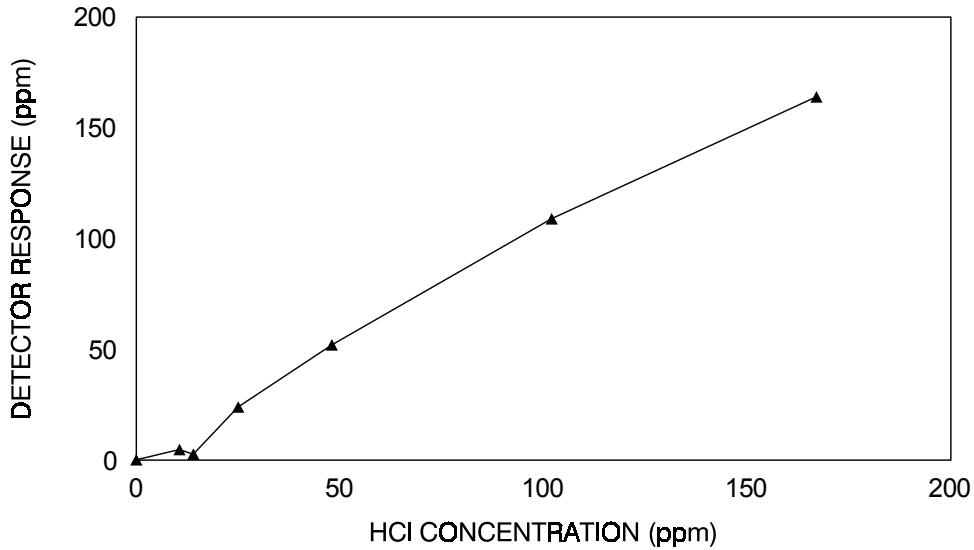


Figure 23. GFCIR Calibration Curve Obtained for HCl Concentrations of 0 to 150 ppm.

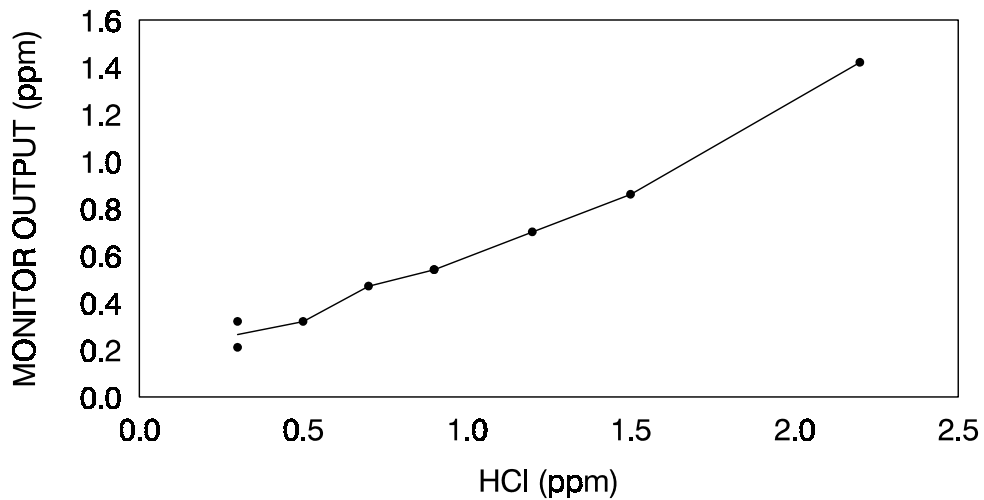


Figure 24. Calibration Curve Obtained Using Permeation Tubes to Provide Low HCl Concentrations.

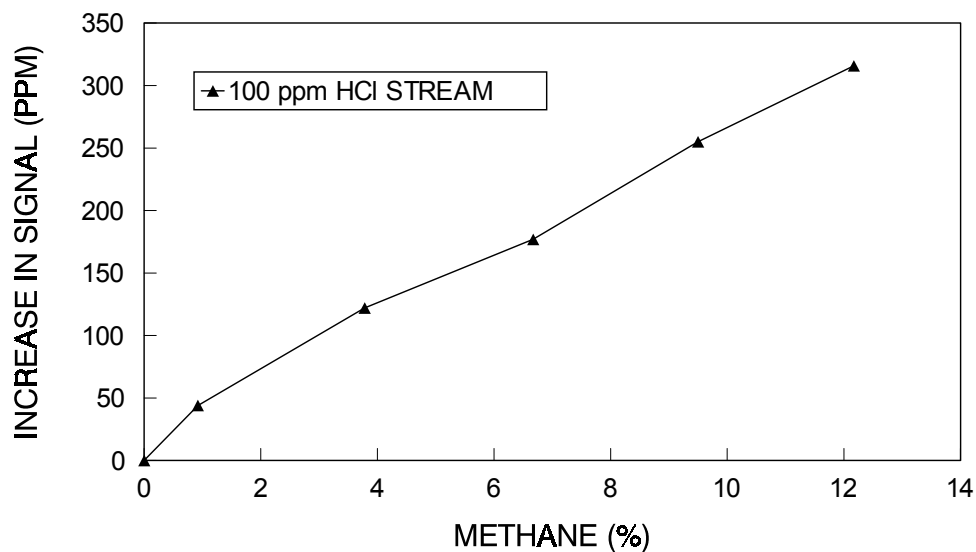


Figure 25. Effects of Methane on GFCIR Signal.

Humidity significantly affected results. When the humidity of the gas stream increased (not quantified), the reading observed for a 100 ppm HCl stream increased by 50%, but returned to its original value after several minutes. These data reflect “flushing” effects due to the added moisture. In view of these results, it is apparent that a consistent humidity level should ideally be delivered to the detector. If the humidity level is fluctuating, equilibration times may not be adequate to provide accurate HCl analyses for the gas stream.

Potential interferences from butane and butene were also examined to ascertain whether hydrocarbons other than CH_4 could result in analytical errors. For these tests, 5-mL volumes of each gas were injected into a stream of N_2 carrier gas with and without 3000 ppm HCl present. When butane and butene were injected into N_2 in the absence of HCl, positive instrument responses equivalent to 10-30 ppm HCl were noted, but negative responses (decreases of 10%) were noted when HCl was present. This suggests that chemical interactions may be occurring between the hydrocarbon gases and the HCl, although these test results would require analytical verification. Thus, definitive conclusions regarding potential interferences from hydrocarbon gases other than CH_4 can not be made from these data.

COLORIMETRIC METHOD

An analyzer using the MDA Scientific (now sold as a Zellweger Analytics analyzer) colorimetric “dot” method was tested previously in the field (MSW incinerator) by other researchers. Accuracy problems were encountered, which were thought to be due to different levels of humidity between sample and calibration gases. Technical experts with MDA Scientific informed us that the relative humidity (RH) of the gas delivered to the analyzer needs to be within the proper range for optimum operation. They believed that their instrument would work for our application and that sample delivery would be the most difficult part. In view of this, we decided to evaluate an MDA Scientific Model 7100 Toxic Gas Monitor (see Figure 26) in our laboratories.



Figure 26. MDA Colorimetric Analyzer for HCl.

The instrument is based on exposing a strip of color-indicating paper to a metered sample stream. Any HCl in the sample gas reacts with the paper to form a colored, circular (i.e., "dot") stain. The intensity of the stain is proportional to the HCl concentration and is quantified by using a photocell to detect the amount of reflected light from the dot. The color-indicating paper is in the form of a continuous strip and is mounted in a cassette cartridge, which is referred to as a chemcassette. This allows the monitor to provide continuous analysis of a gas stream. The standard chemcassette determines HCl in the range of about 0.2 - 50 ppm_v. In addition, a low-level chemcassette is available for determining HCl down to about 50 ppb_v. The low-level chemcassette employs different reaction chemistry than the standard chemcassette. Our tests were performed using both the standard and low-level tapes. A one-minute sampling period is used with the standard chemcassette, while a ten-minute sampling period is generally required for low-level HCl (sampling periods are factory set).

The sample gas temperature at the detector inlet must be at or below 40°C. Also, the manufacturer recommends humidifying the sample stream to about 25-75% relative humidity (RH) at ambient temperature. Significant errors can result if the RH is outside of this range. If dry gases are to be used, a special low-RH calibration should be performed. The instrument manufacturer reports that HCN and HF are possible interferences, but little information was available on the magnitude of those interferences. Both of those gases are expected to be present in coal gasifier streams. Consequently, the HF interference was investigated by using anhydrous HF from a permeation tube with room air as the carrier gas. The HCN interference was studied by using a compressed gas cylinder containing 1% HCN in a nitrogen balance. Compressed gas cylinders containing HCl in a nitrogen balance were used for the tests with the standard chemcassette, while permeation tubes containing aqueous HCl were used for the tests with the low-level chemcassette. Results obtained with the standard and low-level HCl chemcassettes are discussed separately below. The relative standard deviations (RSDs) for all tests were typically $\pm 5\%$ or less for a given set of conditions.

STANDARD CHEMCASSETTE

A calibration curve in the range of 0 to 25 ppm_v was obtained by blending 100 ppm HCl (in a nitrogen balance) with air and passing the blended gases into the analyzer. These results are shown in Figure 27. The measured detection limit for the standard chemcassette was several tenths of a ppm and the calibration curve was generally linear down to several ppm. At lower concentrations, the nonlinearity may be a result of dilution errors in the gas stream. When 25 ppm HCl in N₂ was sent to the detector, results were about 50% higher when the gas stream was humidified. Although it was known that results could be affected by the relative humidity of the gas stream, these results demonstrate that the effects of humidity can be substantial.

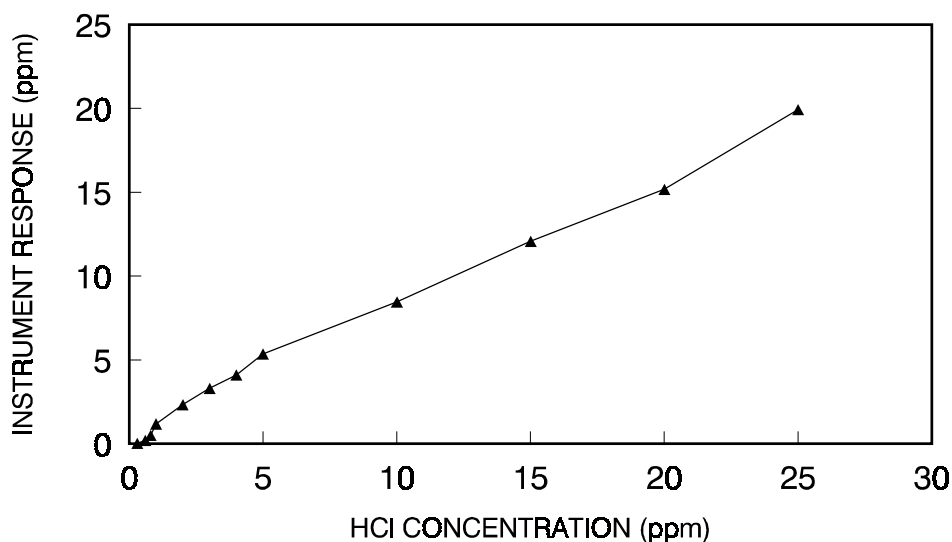


Figure 27. Calibration Curve Obtained with the Colorimetric Analyzer While Using Blended Gases.

When 15 ppm dry HF in air was sent to the HCl analyzer in the absence of HCl, a reading corresponding to about 0.5 ppm HCl was obtained. For tests with HF in the presence of HCl, the presence of 15 ppm HF (the anticipated maximum concentration in coal gasification effluents) in a 1 ppm HCl stream had a negligible effect on the reported HCl concentration. When 100 to 2000 ppm HCN was sent to the analyzer in the absence of HCl, a small positive response on the analyzer was noted. As the HCN concentration was varied, the ratio of the HCN concentration to the instrument response was fairly constant, with 1000 ppm HCN giving a reading corresponding to about 1 ppm HCl. Results of the tests with HCN alone are shown in Figure 28. In gas streams containing 10 ppm HCl, the HCl signal was not significantly affected by the presence of 150 ppm HCN. Based on these tests, it does not appear that HF or HCN will cause significant interferences for HCl determinations with the standard HCl tape.

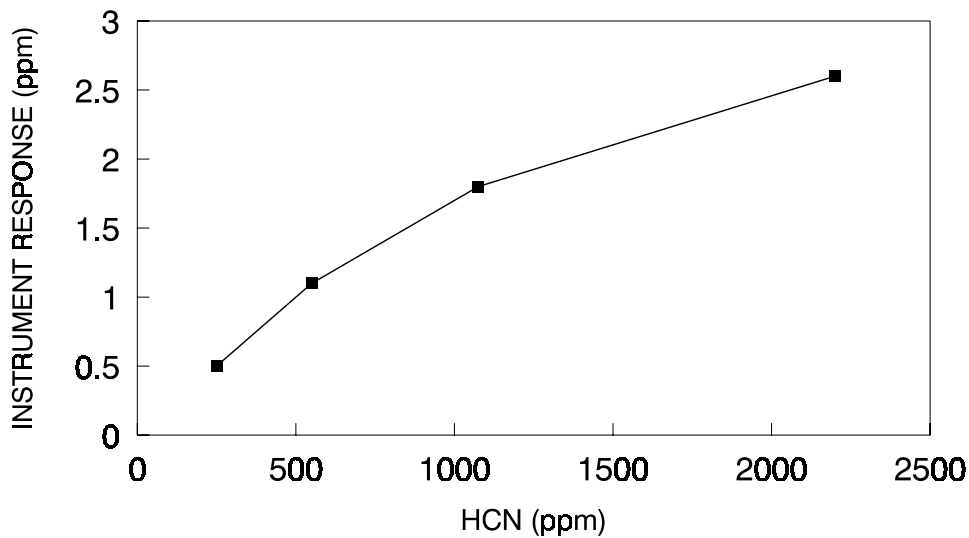


Figure 28. Results of HCN Tests with the Standard Chemcassette.

LOW LEVEL CHEMCASSETTE

For the tests with the low-level chemcassette, the HCl streams were produced using aqueous HCl permeation tubes in a VICI Metronics Model 340 Dynacalibrator. Based on calibration curves obtained when using the permeation tubes, the measured detection limit was about 50 ppb HCl. As the HCl concentration was decreased from 400 to 75 ppb, good linearity in the calibration curve was obtained, as shown in Figure 29. However, as the HCl concentration decreased further, some anomalous readings indicative of desorption wall effects were observed. The permeation tube was removed from the permeation chamber (at 100°C) in the Dynacalibrator, but significant HCl concentrations were still reported by the analyzer for more than two days when air passing through the empty permeation chamber was sent to the analyzer (see Figure 30). When the calibrator was set to send zero air to the HCl analyzer, the analyzer consistently reported "0 ppb". Since the gases from the calibrator passed through

common sample lines in each case, and since the gas flow rate through the sample line was the same for each set of tests, the memory effects appear to be within the calibrator rather than in the analyzer or sample transport lines. After waiting until no HCl was being emitted from the empty calibrator during a constant gas purge, an HCl permeation tube was put back in and a calibration curve was obtained by increasing the HCl concentration (HCl concentration was decreased in the initial tests). Because of pronounced adsorption/desorption effects, the slopes and "x-axis" intercepts for the two calibration curves (one each from increasing and decreasing the HCl concentration) were much different. Those results are shown in Figure 31. This has important implications regarding field monitoring and calibration of analytical instruments, since wall effects can result in lengthy equilibration times (e.g., 24 hours or more).

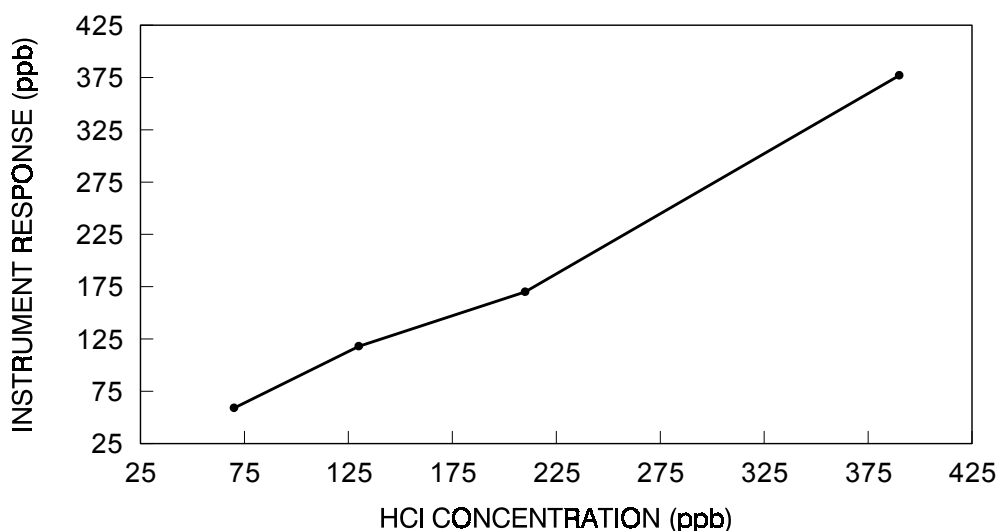


Figure 29. Calibration Curve Obtained with the Low-Level Chemcassette While Using HCl Permeation Tubes.

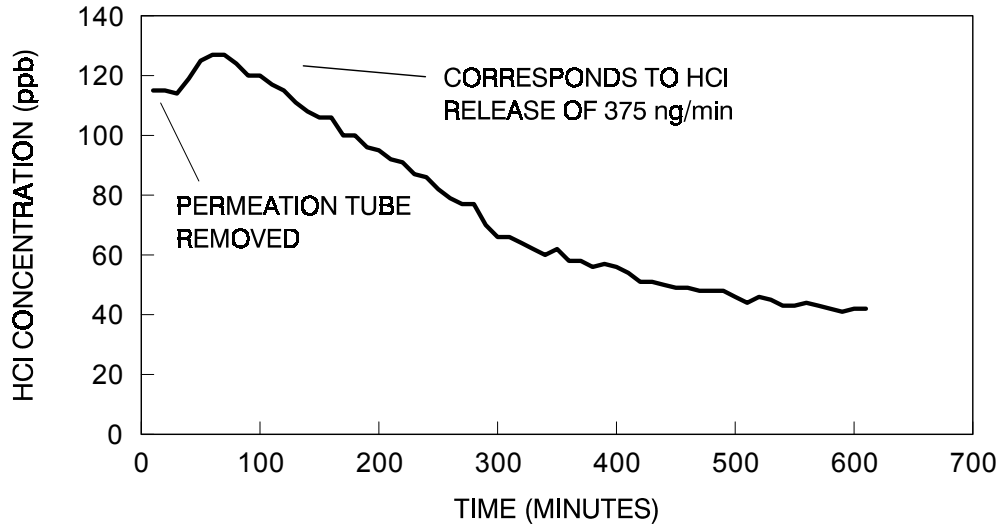


Figure 30. Apparent Memory Effects with the VICI Dynacalibrator.

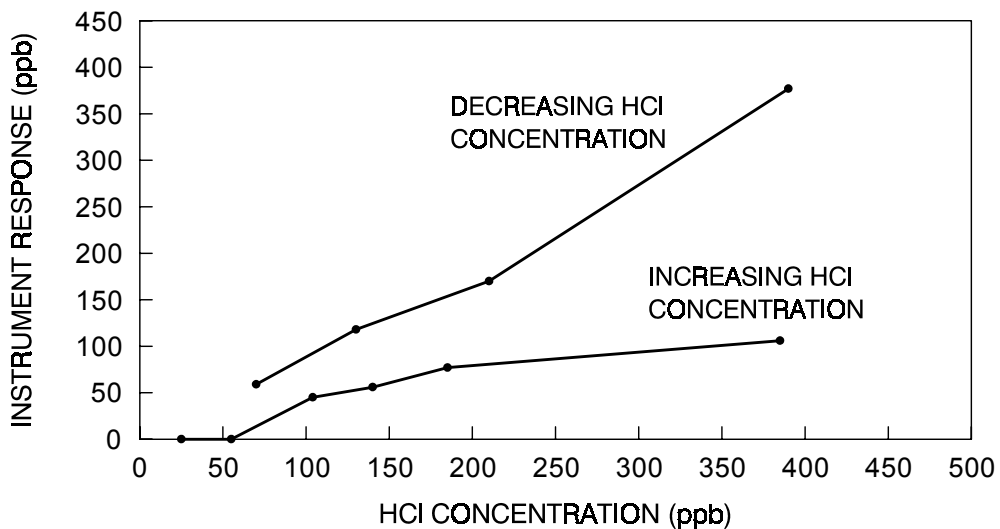


Figure 31. Calibration Curves Obtained with the Low-Level Chemcassette when Increasing and Decreasing the HCl Concentration.

Humidification of the nitrogen stream containing HCl had a more pronounced effect on the HCl reading when using the low-level chemcassette as opposed to the standard chemcassette. However, this is not necessarily due to differences in tape chemistry between the two chemcassettes. The humidity may have provided a "flushing" effect which minimized HCl sorption onto the sample lines. Such a flushing effect could be much more prominent (greater percent change in concentration reading) at the relatively low HCl concentrations used with the low-level chemcassettes.

HF was a more prominent interference when using the low-level chemcassette. When the gas stream entering the analyzer contained only 1000 ppb of HF (i.e., no HCl), an HCl reading of roughly 130 ppb was obtained. Thus, 15 ppm HF (the anticipated maximum concentration in gasifier streams) could cause a signal equivalent to that produced from several ppm HCl. The HF interference should be negligible if the HCl concentration is significantly greater than the HF concentration. However, if the HCl concentrations are 1 ppm or greater, it would be preferable to use the standard chemcassette since HF interferences with that chemcassette appear to be less prominent.

When 2800 ppm HCN was introduced to the analyzer in the absence of HCl, a signal equivalent to only 100 ppb HCl was obtained, indicating that HCN is not a significant interference with the low-level chemcassette in low-humidity gases. When the tests were repeated in the presence of 150 ppb HCl, the HCN again had little effect on the HCl reading.

DISCUSSION

By simply replacing a chemcassette, the colorimetric analyzer can be used to monitor other individual gas species of interest. Another potential advantage to the colorimetric monitor is the smaller amount of internal surface area, which could in turn reduce adsorption/desorption phenomena that can lead to memory effects. Disadvantages of the colorimetric monitor include the sensitivity of the technique to the relative humidity of the sample gases, the need for different chemcassettes employing different chemistry for different ranges of HCl concentrations, and possible complications regarding color formation in the complex gas matrices of a coal gasifier. If CH₄ can be effectively removed from sample gases without affecting HCl concentrations, using the colorimetric monitor with the standard chemcassette does not appear to offer any significant advantages over the GFCIR unit that was investigated. Although the low-level chemcassette can detect lower levels of HCl than GFCIR, our results suggest that data should be viewed with caution when using that chemcassette in complex gas matrices. In view of these considerations, the dry colorimetric analyzer will not be employed for on-line analysis of coal gasifier streams.

ION MOBILITY SPECTROSCOPY

OVERVIEW OF TECHNOLOGY

Because ion mobility spectroscopy (IMS) was ultimately selected as the method of choice for monitoring HCl in coal gasifier streams, it is appropriate at this point to provide a brief overview of the IMS technology. IMS is an atmospheric, time-of-flight monitoring system. Although the IMS technology has existed for several decades, it is still considered by many to be in its infancy. Until the 1980s, work with IMS focused on fundamental studies rather than on specific applications (16). In recent years, the utility of IMS has been demonstrated in numerous practical applications, including monitoring environmental pollutants, measurement of trace

contaminants in products from various manufacturing processes (including monitoring HF at oil refineries), and detection of drugs and explosives (16-18).

Advantages of IMS include minimal zero drift, high sensitivity, little sensitivity to relative humidity, few occurrences of false positives, and real time monitoring capability. Disadvantages include sensitivity to changes in temperature and pressure of the sample gas, matrix dependency, and narrow dynamic range (about 200). The issue of matrix dependency is addressed by using large gas stream dilutions, thereby providing a relatively consistent matrix. Additional areas to be careful of include overloading the IMS with analyte. Overloading can result in the disappearance of reactant ion peaks, the appearance of multiple analyte peaks, and peaks that persist for unusually long times. If severe overloading occurs, it can take several days to purge out the cell.

For HCl, there are not anticipated to be any spectral interferences with the gas matrix for coal gasification streams. However, personnel with Molecular Analytics (the vendor for our IMS system) noted that ion clustering can occur in IMS, and that different chemical species can give byproduct ion clusters in the same spectral region, even if the masses of the original species are much different than that of HCl. Also, N₂O is a known problem due to its large electron affinity. However, it should not be present in gasifier streams. For applications where N₂O may be present, Molecular Analytics has a preconditioner to reduce N₂O to NO.

In the IMS technology, a porous membrane is used to provide some selectivity, filter particles, and reduce humidity effects (19). The membrane also restricts the amount of analyte that reaches the detector, and different porous membranes can be used to alter the analytical range of the analyzer. The compounds of interest pass through the membrane and are picked up by the carrier gas and transported to the reaction region of the IMS cell. In that region of the cell, the gases are ionized using beta particles from a suitable radiation source. Although ion formation has been accomplished by a variety of techniques, radioactive Ni⁶³ foil is the most common ionization source (16). The detector requires a small amount of O₂ (about 1%) in order to properly ionize the analyte species. An electric field is used to attract the ions to a shutter, which opens and closes periodically to allow the ions to enter the "drift" portion of the cell. In the presence of a constant electric field, the ions drift down the tube and are separated because of differences in the size, shape, and mass of the individual ions. Drift time also depends on the electric field strength, length of the drift tube, temperature, and pressure (18). Because the time of transport is related to mass, the drift time in the tube is ion specific and therefore allows specific gaseous species of interest to be identified. The concentration of a specific ion is proportional to the height of the peak from the detector. A continuous flow of air or nitrogen at ambient pressure is usually used as the drift gas to sweep through the tube. IMS also requires a dopant gas to aid in the rejection of interferences, improve analyte ionization, improve sensitivity, and provide greater separation between the product and reactant ions (16,20).

An air driven sampling probe using an eductor is usually used because sampling typically occurs at atmospheric pressure. Thus, the sample is diluted with dry air, which reduces the dew point of water in the sample stream to near or below room temperature. By using large dilutions with air or nitrogen, matrix effects can largely be avoided since the matrix will then be the gas used as a dilution stream. Without this dilution, matrix-specific calibrations would be required.

Because of the extremely high sensitivity of IMS, a 100:1 dilution of a gasifier stream could theoretically still be used even with an initial (undiluted) HCl concentration of 10 ppm or less.

LABORATORY EVALUATIONS

Response to HCl

We received a Model 20-HCl Stack Master IMS Analyzer (see Figure 32) on loan from Molecular Analytics for our evaluation. By changing a membrane in the analyzer, an analytical range of either 1-20 ppm or 1-200 ppb can be selected. For the initial tests, compressed gases were used to examine general instrument response and the linearity of calibration curves. Air was blended with a 100 ppm HCl gas stream (in a nitrogen balance) to give HCl concentrations ranging from 1 to 25 ppm. When the HCl flow was first sent to the detector, it took about 20 minutes for the HCl to equilibrate with the sample transport lines and portions of the IMS system. However, after this initial equilibration period, the unit responded rapidly (within 60 seconds) to changes in HCl concentration. The detector gave a linear response for HCl concentrations ranging from 1 to 25 ppm, as shown in Figure 33. The discrepancy between the HCl reading on the instrument and the nominal HCl concentrations may reflect gas metering uncertainties or calibration issues.



Figure 32. Ion Mobility Spectrometer for Monitoring HCl.

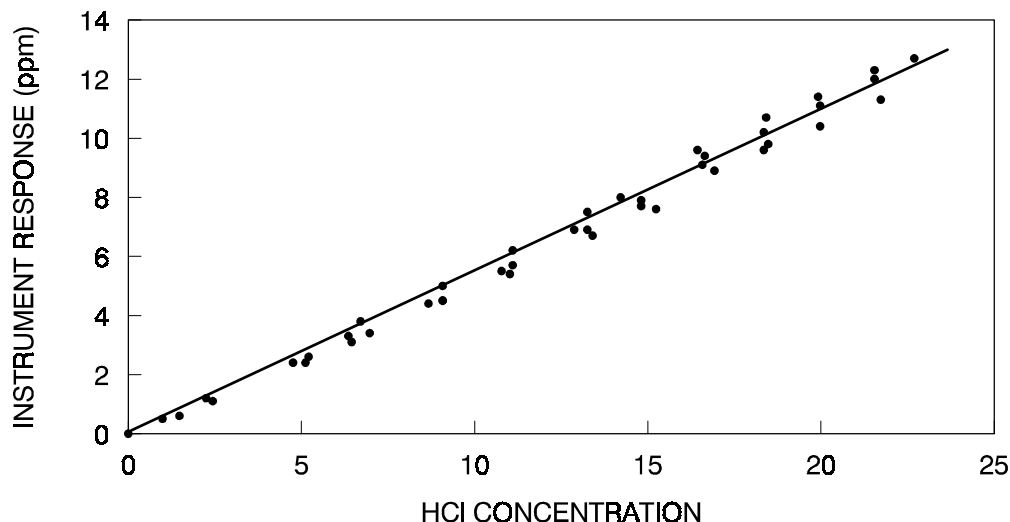


Figure 33. Calibration Curve Obtained for IMS Unit While Using Blended Gases.

After changing the membrane in the analyzer, studies were performed using an HCl permeation tube to assess instrument response in the 1-200 ppb range. The same permeation tube was used for all the tests, and the HCl concentration was adjusted to the desired level by either changing the tube temperature or the flow rate of the dilution air in the calibrator. The flow rate of the calibration gases ranged from 0.6 to 4.8 L/min. Prior to each reading, at least 2 hours were allowed for system equilibration. A detection limit of less than 5 ppb was observed in these tests. A typical calibration curve for HCl levels less than 50 ppb is shown in Figure 34. An excellent calibration curve was obtained. The small amount of data scatter (deviation from linearity) that was observed is believed to be largely from variations in equilibration times.

Considerable memory effects were observed when using ppb levels of HCl, which is one of the reasons why long equilibration times were used. The time necessary to reach equilibrium when switching from zero air to span gases (where HCl adsorption onto walls is occurring) was comparable to the time necessary for equilibration when switching from span gas to zero air (where HCl desorption from walls is occurring). Depending on the level of HCl present in the gas stream, it took 30 to 90 minutes to reach 90% of the final signal. However, the long equilibration times are believed to be largely due to the permeation tube calibrator (see page 71) and/or the connecting lines rather than due to the analyzer itself. Typical signal profiles when switching from zero air to span gas and then back to zero air again are shown in Figure 35.

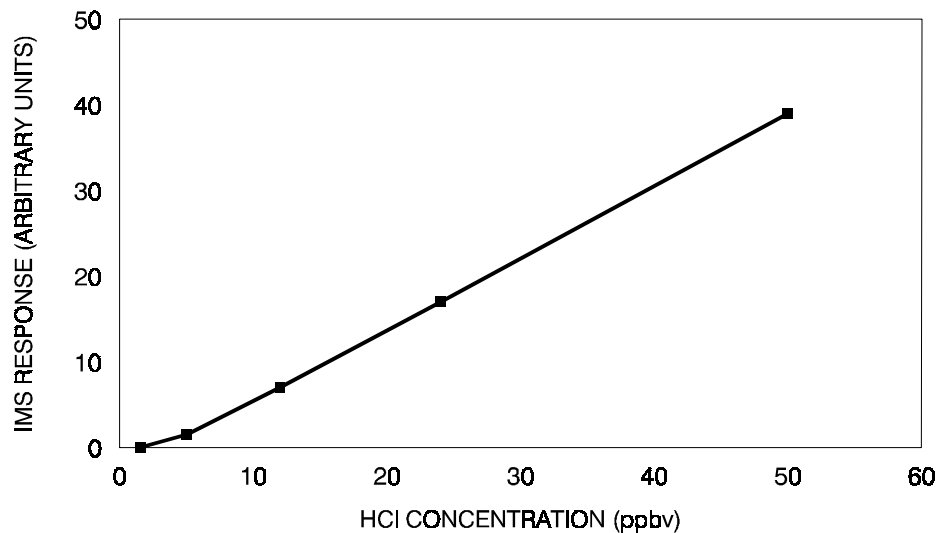


Figure 34. Calibration Curve Obtained Using Permeation Tubes with the IMS Analyzer.

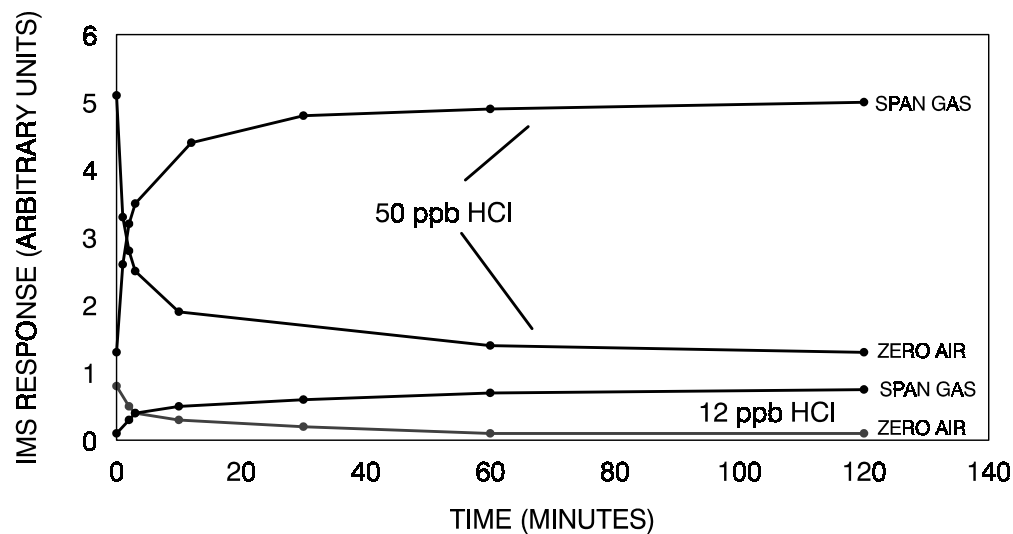


Figure 35. Signal Responses Vs. Time for 12 and 50 ppb HCl Streams.

Response to Other Gases

The effects of moisture and other gases on the response of the IMS unit were investigated with the analyzer operating in the 1-20 ppm range. The relative humidity of the gases appeared to affect the IMS reading, but is likely due to the humidity altering wall effects (sorption of HCl), which in turn affects the analyte concentration in the gas stream. Introducing HCN and H₂S increased the analyzer reading slightly, but those gases will probably not be present at high enough concentrations in real gasifier streams to appreciably affect the HCl signal.

The presence of HF also appeared to affect the HCl reading while the instrument was operating in the 1-20 ppm range, but the procedure for introducing HF into the gas stream required refinement before definitive conclusions could be drawn. The possible interference from HF was of concern because of the possibility that significant amounts of HF may be present in coal gasification streams. Although HF is anticipated to be present at substantially lower concentrations than HCl, the HF levels could still be sufficient to cause significant analytical errors. Consequently, additional tests with HF were performed after refining the HF delivery system in order to help quantify the severity of the HF interference. Results of those tests indicated that a given concentration of HF produced a signal similar in magnitude to that observed for the same concentration of HCl. Next, the membrane inside the analyzer was changed to switch the unit to the 1-200 ppb range. While using the “low concentration” membrane, tests with HF were performed to see if the results supported or contradicted our results obtained at the higher concentration range. For these tests, air streams containing 0-200 ppb HF were sent to the IMS unit at a rate of 1 L/min. A linear instrument response was obtained for HF concentrations in this range. More importantly, a given concentration of HF gave a response equivalent to that observed for the same concentration of HCl. Thus, these results agreed with earlier results obtained at higher concentrations using a different membrane.

Despite the observation that HF and HCl gave comparable responses for a given concentration, both in the ppm and ppb range, Molecular Analytics personnel believed that HF was not a major interference. They believed there is a 10:1 rejection ratio for HF, meaning that it takes 10 ppm HF to give the same response observed for 1 ppm HCl. The possibility was considered that the HF permeation tube used for testing was defective. Consequently, a gravimetric determination on the rate of mass loss from the permeation tube over a 24 hour period was performed. In addition, the HF calibration gases were bubbled into a carbonate solution to collect the HF emissions. The solution was subsequently analyzed for fluoride ion by IC, and the HF emission rate was calculated. The gravimetric analysis and the IC analyses both confirmed that the HF permeation tube was good. After a number of discussions with Molecular Analytics personnel, it was suspected that the dopant tube in the IMS analyzer was bad. Therefore, Molecular Analytics sent us a new dopant tube. After installing the new tube, the tests with HF were repeated. The instrument response to HF was about five times lower than previously observed, while the response to HCl was comparable to that observed previously. Thus, the “rejection ratio” for HF appears to be at least 5:1 rather than the 1:1 ratio observed previously. A research staff member at Molecular Analytics also believes that we previously saw small responses to HCN and H₂S because of the bad dopant tube. Because of the HF rejection ratio, as well as the fact that HF concentrations are expected to be substantially lower than HCl concentrations, the HF interference is not anticipated to be significant for our purposes.

Discussion

After performing laboratory studies with IMS, GFCIR, and the dry colorimetric method, IMS was selected for use in the HCl CEM. The IMS analyzer which was loaned to us was then purchased for this project. IMS is the only technology we evaluated that can easily detect HCl at low ppb concentrations. This allows for a broader application of the HCl CEM. Also, the low detection limit allows for gas stream dilution as a method for lowering the moisture dew point without lowering the analyte concentration to levels at or below the detection limit of the

analyzer. This would be important if the Nafion dryer proves to be unreliable for the application of interest. An added advantage is that there are few known interferences for HCl.

GENERAL HCl TRANSPORT STUDIES

In the initial stages of the HCl studies, tests were performed to determine if known amounts of HCl could reliably be passed through the testing apparatus shown in Figure 1 (see page 3). This was done by flowing HCl gases through the apparatus and then bubbling the gases exiting that system into absorbing solutions. Because a suitable in-house method for rapidly determining chloride in liquids was not initially available, analyses of the liquids were performed using titrimetric procedures during the early stages of this project. The procedure involved bubbling gases into aqueous absorbing solutions containing 3 ml of approximately 0.01 N AgNO₃ solution. In that procedure, the HCl reacts with the AgNO₃ to form AgCl, which then precipitates from the solution. An Altex SelectIon 2000 Ion Analyzer was then used with a silver billet electrode and a glass reference electrode to perform argentometric titrations with the AgNO₃ solution. During the titration, KCl solution was slowly added and mV readings were taken for every 0.1-0.2 mL of the KCl solution used. That procedure was used to determine the amount of AgNO₃ remaining in solution, which was in turn used to calculate (by difference) the amount of AgNO₃ which reacted with the initial chloride (as HCl) in the sample, and consequently the amount of chloride present in that sample. The procedure in essence measures the Ag ion activity. Ethanol was added to the analysis solutions to further decrease the solubility of AgCl that precipitates as KCl solution is added, thus improving the break in the titrimetric curve.

Initial tests were performed by adding liquid chloride standards to collection tubes containing the absorbing solution. The solutions were then analyzed as described above. Results indicated that chloride recoveries ranged from 97-103%, thus confirming the validity of the sample analysis portion of the tests. Next, studies were performed to determine whether a known amount of HCl could be reliably delivered to a detector. As the first step in this evaluation, tests were performed to determine whether good HCl recovering could be obtained directly from a compressed gas cylinder containing 3000 ppm HCl in nitrogen. At low gas flow rates (e.g., 10 mL/min), the HCl recoveries were erratic (ranging from 40-105%) and tended to be low, even when using Teflon lines directly from the gas cylinder. The erratic results did not appear to be caused by analytical errors, problems in collection efficiency, gas metering errors, or losses in the Teflon lines. Rather, there appeared to be erratic adsorption/desorption processes occurring upstream from the outlet of the regulator, despite the precautions taken to select a regulator with nonreactive components (internal parts constructed mostly of Monel, with Kel-F and Teflon for the critical sealing and seating surfaces). After increasing gas flow rates to 100 mL/min or more, good precisions for HCl recoveries were obtained.

In other tests, the HCl gas mixture was passed through the testing apparatus. A total of about 25 tests were performed using gas flow rates ranging from 100-500 mL/min and sample line temperatures of either 25 or 200°C. At the elevated temperatures, tests were also performed with and without about 50% water present in the gas stream. Overall, HCl recoveries averaged

85 ± 5 %. The best precision and recoveries were observed for the tests where water vapor was present, in which case the HCl recovery averaged 92 ± 3%.

In subsequent work, tests were performed in which HCl gas was mixed with other gas components (including CH₄, CO, CO₂, COS, H₂, H₂S, NH₃, and HCN) and passed through the testing apparatus. The gases were heated to about 200°C and did not contain added moisture. Good HCl recoveries were obtained in the absence of NH₃. However, difficulties were encountered in obtaining acceptable HCl recoveries in the presence of NH₃ due to the formation and deposition of solid NH₄Cl in sections of the sample line that were not heated (i.e., the connecting line between the testing apparatus and the collection solution).

HCl TRANSPORT THROUGH CATALYST BEDS

Tests were performed to determine whether HCl gases could be passed through a heated, commercially available Pt catalyst. The catalyst was the same as that discussed in the “Gas Conditioning” section of this report and was a beaded (1/8-inch) catalyst containing 1% Pt on an alumina substrate (catalyst G-97B from United Catalysts). A nitrogen stream containing several hundred ppm HCl was passed through 100 cm³ of the catalyst while the catalyst temperature was slowly increased from 100 to 450°C. Each intermediate temperature was held for 10 minutes, and the final temperature was held for one hour. Gases exiting the catalyst tube were bubbled into deionized water to collect the chloride, and the water was subsequently analyzed by IC to determine the amount of chloride exiting the catalyst tube. In those tests, results indicated that little or no HCl exited the catalyst tube, even after one hour at 450°C. When the gases were bubbled directly (bypassing the catalyst) into water at room temperature and then analyzed by IC, full HCl recoveries were obtained.

Follow-up tests were performed to determine whether the HCl losses were due to the Pt itself or to the catalyst substrate (alumina). As before, gases were bubbled into water and then analyzed by IC to determine the amount of HCl exiting the catalyst tube. Because of the possibility that the HCl losses could be partially attributable to the large surface area of the catalyst, the catalyst tube was greatly downsized to hold about 2 cm³ (instead of 100 cm³) of catalyst. Also, the heating system was redesigned to provide more uniform heating. Whereas a heating tape was used previously, the new heating method involved using a rod heater embedded in an aluminum block containing the catalyst tube.

For the tests with 2 cm³ of catalyst and catalyst substrate materials, a standard gas containing 100 ppm HCl in a nitrogen balance was used. When the gases were bubbled directly (bypassing the catalyst) into water at room temperature and then analyzed by IC, full HCl recoveries were obtained. The HCl recoveries were about 90% when the gases passed through an empty catalyst tube at 475°C prior to bubbling the gases into water. This indicates that the walls of the catalyst tube and the associated hardware were not a significant source of HCl losses. Next, the HCl was passed over the Pt catalyst as well as just the catalyst substrate. The catalyst temperature was maintained at 475°C. Results of the IC analyses indicated that the HCl recoveries were low when using the catalyst and catalyst substrate materials. The tests were

repeated at 250°C, with similar results. Therefore, this catalyst material was not considered further for the oxidation of gasifier streams prior to HCl analyses.

Because of the problems encountered in passing HCl through the commercially available Pt catalyst, tests were performed to determine if HCl could be effectively passed over a hot Pt wire. For those tests, about 60" of 0.01" diameter Pt wire was pressed into a 1-inch long section of a 1/4-inch OD quartz tube. The Pt bed was maintained at a temperature of either 250° or 450°C using a small tube furnace. A stream of 100 ppm HCl in nitrogen was passed over the Pt bed and the gases exiting the tube were bubbled into water for subsequent chloride analyses by IC. The IC analyses indicated that nearly quantitative recovery of HCl was obtained at both temperatures. Thus, this type of Pt catalyst bed appears to be suitable for passing gas streams containing 100 ppm HCl without significant HCl losses.

Several revisions were made in the design of the catalyst module. In the current version of the catalyst system, Pt wire at 900°C was placed between two alumina beds at 900°C. Tests were performed with that catalyst module to determine whether low levels of HCl in a simulated gasifier stream could be successfully passed through the oxidation catalyst. The simulated gasifier stream consisted of 50% CO, 15% CO₂, 25% H₂, 8% CH₄, and 2% H₂S. For those tests, 500 mL/min of simulated gasifier stream was blended with 1 L/min of air and 50 mL/min of 100 ppm HCl. This gave an HCl concentration of 10 ppm_v in the simulated gasifier stream prior to blending it with air. Gases exiting the catalyst tube were bubbled into 100 mL of deionized water for 60 minutes to collect the HCl, and the water samples were then analyzed for chloride using IC. Results of the IC analyses on the water used to collect HCl while bypassing the catalyst indicated that 100% HCl recoveries were being obtained. Results of IC analyses on the solutions used to collect HCl passing through the heated catalyst bed indicated that HCl recoveries were 100-110%. Thus, low levels of HCl were successfully passed through the heated catalyst while using a simulated gasifier stream.

HCl TRANSPORT IN NAFION DRYERS

Moisture removal is a critical gas conditioning step. Gasifier streams can contain up to 50% moisture by volume, but existing monitoring systems are not generally able to operate with such high moisture contents. This is often because the sample cells or other hardware components can not be heated to the temperatures necessary to prevent moisture from condensing. Thus, it was necessary to incorporate a drying system into the CEMs which would remove most of the moisture without affecting ppm levels of HCl.

Common approaches for moisture removal prior to analysis of effluent gases include the use of condensers and desiccants. However, those approaches would not be suitable for this application because of the loss of analyte that would result from their use. As an alternative, the use of Nafion (a chemically selective membrane) was investigated for moisture removal. In that approach, the sample gas is transported with a Nafion tube, which is housed inside another tube. A countercurrent purge gas stream flows over the Nafion through the secondary (outer) tube and draws moisture through the walls of the Nafion while theoretically retaining HCl in the sample gas stream.

The Nafion has a maximum operating temperature of 150°C. Since the moisture content of gasifier streams can be very high, the gases will need to be heated to at least 110°C to ensure that no condensation occurs. Therefore, the maximum temperature of 150°C provides an adequate temperature range to work with. However, drying efficiency will decrease as the gas temperature into the drying system increases. Another consideration in using the Nafion dryer is that it does not necessarily have to remove all of the moisture from the gas stream. If Nafion is used to dry sample gases prior to analysis by IMS, the dryer only has to remove enough water to prevent condensation of water vapor in the sample stream at a temperature of about 50°C, which is the maximum inlet gas temperature of the IMS system. However, the sample stream flowing into the IMS unit should have a fairly constant humidity in order to reduce analytical uncertainties.

Tests were performed with the gas drying system from Perma Pure (see Figure 3 on page 20) to see if HCl streams could be passed through the system. In order to simplify these initial tests and to reduce the number of experimental variables, only dry gases were used. Gas streams consisting of 100 ppm HCl in nitrogen were passed into the dryer and then bubbled into water (an HCl gas analyzer was not yet available). The sample gas flow rate was 100 ml/min. The absorbing solutions (water) were subsequently analyzed by IC to determine the amount of chloride exiting the dryer over a given amount of time. After 10 minutes or less, HCl concentrations in the sample gas stream exiting the gas dryer were within 80-100% of the theoretical concentrations. Similar results were obtained when the tests were repeated using a sample gas flow rate of 1000 ml/min. The countercurrent purge gas was also analyzed in the same manner. In the first few minutes of sampling, low concentrations of HCl were found in the purge gas. However, after 5 minutes, no HCl was detected in the purge gas stream. The initial low HCl readings are probably from sample line contamination during earlier experiments involving the transport of HCl. More work on passing HCl through large-scale Nafion dryers is needed, including tests with humidified gas streams.

CALIBRATION DEVICES

PRELIMINARY ASSESSMENT OF PERMEATION TUBES

A variety of HCl CEMs are available for analyzing gaseous effluent streams. As with any emission monitor, the accuracy of the instrument calibration is a crucial component in the accurate determination of the analyte in process streams. Verification of the HCl output from calibration systems is important for evaluating HCl analyzers and for performing accurate calibration of those analyzers. Consequently, numerous tests were performed with a VICI Metronics Model 340 Dynacalibrator (see Figure 36) using aqueous HCl (azeotropic 20.2% solution) permeation tubes. Those tests were performed to check for the proper operation of the calibrator and to check the accuracy of HCl permeation tubes from that vendor.



Figure 36. VICI Metronics Model 340 Dynacalibrator.

Two different HCl permeation tubes were used. The two different tubes had nominal emission rates of 510 and 1,200 ng HCl/min ($\pm 15\%$). The total mass loss rate from the permeation tubes was also checked to determine if it was within the range specified by the vendor. This was done by performing a gravimetric analysis on the tube after using the tube in the heated permeation chamber for several days. In addition, span gases from the calibrator were bubbled directly into a series of three water traps for several days, and the collection solutions were then analyzed titrimetrically and by IC to determine the amount of chloride collected. Additional tests were performed in which multiple collection solutions were used (in series) and then analyzed to ensure that HCl was not breaking through the first collector. Results of those tests indicated that essentially all (99% or more) of the HCl was being collected using a single collection solution. By using the IC data, the actual HCl emission rates from the calibrator were calculated and then compared to the theoretical emission rates. In addition to bubbling gases into solutions, calibration gases from the permeation tube calibrator were passed directly into a Teflon gas sampling bag. The gas in the bag was analyzed directly for HCl using a Sensidyne gas sampling pump with color-indicating HCl detector tubes (accurate to within $\pm 25\%$). As a final test, the calibration gases were analyzed directly by inserting color-indicating HCl detector tubes directly into the permeation chamber containing the HCl permeation tube.

Results of the gravimetric analysis indicated that the total emission rates from the permeation tubes were within the uncertainty range listed for each tube. If the total mass emission rates determined experimentally are used as the actual tube emission rates, then the HCl concentration detected in the Teflon sampling bag (using direct gas analysis with color-indicating tubes) was about 55% of the theoretical value, while the concentrations detected by withdrawing gases directly from the permeation chamber were about 45% of the theoretical

value. For the collection solutions, recoveries of about 15% and 25% were obtained by titration and IC, respectively. Although the HCl recoveries obtained by analyzing the gases directly were significantly higher than those obtained by bubbling the calibration gases into a collection solution, the collective analytical uncertainties for the permeation tubes and analytical approaches still can not explain why such low HCl recoveries were obtained for all of the approaches used. It is unlikely that all the methods gave erroneous results with respect to the fact that measured HCl levels were much lower than theoretical levels in all cases.

The Teflon line from the calibrator, which is about a foot long, was considered as a possible source of HCl losses. To check that possibility, a test was performed in which an extra nine feet of Teflon line were added between the calibrator and the gas sampling bag. No detectable change in HCl concentration in the sampled gas was observed, indicating that the Teflon line is probably not a source of any HCl losses. Consequently, it was concluded that the HCl calibration gases actually contained lower concentrations of HCl than predicted. Although the vendor had confidence in the accuracy of their equipment at that time, it is worth noting that the vendor's experimental verification of accuracy is based only on gravimetric determinations on the permeation tubes to check total mass loss rates. Although the permeation tubes are filled with an azeotropic solution of HCl, the emitted vapors from the tubes may have a lower HCl concentration for some unknown reason.

STUDIES OF DIFFERENT CALIBRATION SYSTEMS

In view of the accuracy concerns noted above for HCl permeation tubes, a variety of commercially available HCl calibration devices were investigated for possible use to calibrate our HCl emission monitor. The objective of this work was to assess the accuracy and response times associated with the overall calibration systems containing those devices. These evaluations were performed by using both direct gas analyses as well as analyses of collection solutions used to capture HCl emitted from the calibrators. Results of these tests are discussed below.

Gas Calibration Equipment

A variety of HCl calibration devices were studied, including an aqueous HCl permeation tube, two anhydrous HCl permeation wafers, and an aqueous HCl diffusion vial from VICI Metronics. In addition, an anhydrous "ULED" HCl permeation tube from KIN-TEK Laboratories was examined. There are no specific operating temperatures recommended by the manufacturers for those devices. Instead, certified HCl emission rates are provided by the manufacturer for a given operating temperature. The calibration devices and operating temperatures were selected such that each had a certified output of about 1000 ng/min of HCl. A summary of the HCl calibration devices, operating temperatures used in this study, nominal HCl emission rates, and nominal HCl concentrations in the gas stream exiting the calibrator are shown in Table 2. The reported accuracy of the certified emission values for the calibration devices ranged from $\pm 2\%$ to $\pm 5\%$. The certified values provided for the calibration devices from VICI Metronics were obtained using gravimetric determinations. That procedure involves taring the calibration device, heating it at a precise temperature for an amount of time sufficient to obtain an accurate weight loss, and then obtaining a final weight on the calibration device.

The weight loss per unit time is then calculated. The VICI Metronics calibration devices containing aqueous HCl contain an azeotropic solution of 20.2% HCl. Therefore, 20.2% of the weight loss from the calibration devices using that solution should be HCl. For the KIN-TEK system, the certified value was obtained by placing the permeation device in a vacuum and then measuring the pressure rise over time as anhydrous HCl was emitted at a specific temperature. The pressure rise is used to calculate the HCl emission rate.

Table 2. Summary of Calibration Devices from VICI Metronics and KIN-TEK Laboratories.

Calibration Device	Contents	Temp. (°C)	Emission Rate (ng HCl/min)	HCl Conc. (ppm _v)
Permeation Wafer #1	Anhydrous HCl	30	872	0.49
Permeation Wafer #2	Anhydrous HCl	30	1314	0.73
Diffusion Vial	20.2% Aqueous HCl	30	1242	0.69
VICI Permeation Tube	20.2% Aqueous HCl	100	1121	0.63
ULED Permeation Tube	Anhydrous HCl	30	1222	0.63

All of the calibration devices were used in conjunction with a corresponding calibrator from the respective companies participating in this study. Specifically, a VICI Metronics Model 340 Dynacalibrator (see Figure 36) and a KIN-TEK Laboratories Model 491M Gas Standards Generator (see Figure 37) were used. The calibrators were each fitted with 3 feet of virgin 1/4" OD FEP Teflon tubing at the calibrator outlet. The VICI Metronics calibrator was operated with ambient air, while the KIN-TEK unit was operated with compressed dry air, as recommended by the manufacturer of that unit. With both the VICI Metronics and KIN-TEK systems, HCl is emitted from the calibration devices and swept away by a carrier gas stream, which is then blended inside the calibrator with a dilution gas. For our tests, a carrier gas flow of 170 mL/min and a dilution flow of about 830 mL/min were used. Thus, the total gas flow rate at the outlet of each calibrator was about 1000 mL/min. Nominal HCl concentrations in the span gases from the calibrators were on the order of 1 ppm_v. For the VICI Metronics calibrator, the calibration devices (permeation tube, permeation wafer, or diffusion vial) are placed inside a chamber which has the carrier gas flowing through it. The KIN-TEK unit, on the other hand, does not involve the placement of a calibration device within a glass chamber that has a carrier gas flowing through it. Instead, HCl from the calibration device (ULED tube) enters directly from the permeation tube into the sample tubing (i.e., the HCl is not released into a chamber of any kind).



Figure 37. KIN-TEK Laboratories Model 491M Gas Standards Generator.

Testing Approach

Span gases from the calibrators were analyzed directly for HCl using the Molecular Analytics Model 20-HCl Stack Master IMS Analyzer discussed earlier in this report. HCl concentration profiles showing the IMS signal as a function of time were obtained. Also, the IMS readings were observed while switching back and forth between zero air (no HCl) and span gases. Those analyses provided information on memory effects and response times associated with each calibration system.

In addition to the direct gas analyses, HCl in the span gases was collected by bubbling the gases into 100 mL of deionized water in a 125-mL Erlenmeyer flask. For those tests, the 1/4" OD Teflon tubing at the calibrator outlet was connected to a short piece of 1/8" OD TFE Teflon tubing, which was inserted into the water in the flask. Sampling times ranged from 30-90 minutes. Before collecting HCl in the absorbing solutions, the IMS readings were used to help ensure that the calibrator was sufficiently equilibrated. Therefore, no samples were collected with the solutions until the IMS reading was constant (stable for at least several hours) for the calibration device being used. After constant IMS readings were obtained, span gases were bubbled into the absorbing solutions to collect HCl emitted from the calibrators. Three to five samples were collected for each calibration device.

As a check on the sample collection procedure with the Erlenmeyer flask, a series of tests were performed using a reduced flow rate to help ensure that the sampling procedure discussed above was valid. For those tests, gases were bubbled into 50 mL of deionized water in a 50-mL graduated cylinder at flow rates of 1000 mL/min and 170 mL/min. Using the graduated cylinder

increased the bubble path length by about a factor of two compared to using the 125 mL Erlenmeyer flask. If higher chloride recoveries were obtained using a greater depth of absorbing solution or a lower gas flow rate (170 mL/min versus 1000 mL/min), this would suggest that quantitative collection of chloride was not being obtained using the normal sample collection procedure. A test was also performed in which a backup chloride trap was used to check for possible breakthrough from the collection solution when using a gas flow rate of 1000 mL/min. For that test, the first trap was a 125-mL Erlenmeyer flask containing 100 mL of water and a 1/4" OD glass bubbler tube. The backup trap was an impinger containing 100 mL of deionized water and a fritted bubbler.

The water samples (absorbing solutions) for all of the tests discussed above were subsequently analyzed for chloride in duplicate or triplicate by IC at two different analytical laboratories. Analyses were performed in our own laboratories using a Dionex Model 2020i ion chromatograph system. In addition, samples were analyzed by IC at the Analytical Services Laboratory at Iowa State University using a Dionex DX 500 ion chromatograph system. Standards were prepared using either NaCl or KCl in water. Blanks and check samples were run routinely. Also, a 1.0 ppm aqueous HCl standard was prepared and submitted to the IC analysts as an unknown sample. Results of the IC analyses on the absorbing solutions were used to calculate HCl emission rates from the calibrator. Those values were then compared to the certified emission rates for each calibration device and served as an indicator on the accuracy of the overall calibration systems under the conditions employed in this study.

Although Dynacalibrators currently sold by VICI Metronics do not have a dial thermometer in the chamber containing the calibration device, the instrument used for this study was equipped with a dial thermometer with a stainless steel probe that was situated in the chamber. Therefore, tests with the Dynacalibrator (both direct gas analyses and collection of chloride in absorbing solutions) were performed with and without the dial thermometer installed while using the permeation tube and wafer devices. The diffusion vial could not be situated in the chamber in an appropriate position with the dial thermometer installed. Therefore, the effects of the thermometer on HCl output from the calibrator were not investigated while using the diffusion vial. In addition, direct gas analyses and the analysis of absorbing solutions were used to study the effects of the orientation (pointed upstream or downstream) and location of various VICI Metronics calibration devices in the chamber on the HCl output in the span gases. Those tests were necessary since there were no recommended procedures for the location and orientation of the VICI Metronics calibration devices in the Dynacalibrator chamber.

Results

For the IC analyses on the absorbing solutions, mean chloride values reported by each laboratory for a given solution were generally within 5% of each other. Similarly, for repeat analyses (2 to 3 injections per sample) of a given sample, the results were generally reproducible to within 5% for a given laboratory. For the 1.0 ppm aqueous HCl standard submitted as an unknown, each analyst reported a value within 10% of the theoretical concentration. Results of the IC analyses on the solutions used to determine the validity of the sample collection procedure (using absorbing solutions) indicated that the sample collection procedure was valid. In those tests, measured HCl emission rates from the calibrator (calculated from the IC results) at each

flow rate investigated (170 and 1000 mL/min) were within 5% of each other. Similarly, increasing the depth of the absorbing solution by using a graduated cylinder had little effect on chloride recoveries. Results of the IC analyses on the solutions used to check for HCl breakthrough indicated that the first solution contained 99% or more of the total chloride collected. Therefore, a single collection solution appears to be adequate when using the normal collection procedure. These collective results indicate that the gas sampling approach was valid.

Typical response times (based on IMS readings) are shown in Figure 38 for each of the calibration devices as the calibrators were switched from zero air to span gases and then back to zero air. A time of zero minutes represents the time when the calibrator was switched from zero air to span gas. These data were obtained after an initial equilibration period of one to two days for each calibration device (permeation tubes, permeation wafers, or diffusion vial). The KIN-TEK system with the ULED tube exhibited the best performance in terms of response times after switching to either span gas or zero air. With the KIN-TEK unit, 90% of the maximum span gas signal (on the IMS analyzer) was reached within 20 seconds, and the signal generally reached a steady value in less than 45 seconds. When switching back to zero air, the signal decreased by 90% within 20 seconds and returned to the original base line level in less than 60 seconds. Response times for all of the VICI Metronics devices were much longer.

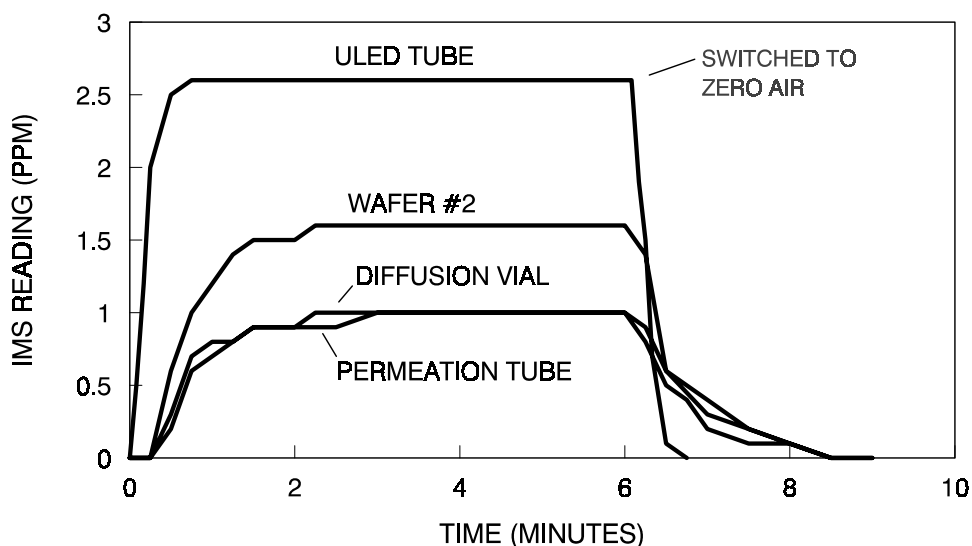


Figure 38. IMS Readings Versus Time for Different Calibration Devices.

When the dial thermometer was installed in the Dynacalibrator, results obtained by IMS and IC for the HCl permeation wafers were very low and indicated that HCl emissions from the calibrator were less than 25% of the expected values. This was true even after 60 hours or more of continuous operation. When the dial thermometer was removed from the Dynacalibrator chamber, the IMS reading and the HCl emission rate determined from the IC data increased by about a factor of two. Thus, when using wafers with anhydrous HCl, the absence of the metal stem of the dial thermometer greatly improved results. When using the VICI Metronics

permeation tube, the presence of the dial thermometer did not have a significant impact on the IMS signals.

To further demonstrate the effect of metal surfaces on HCl emission rates from the Dynacalibrator, it was experimentally determined that the location of the wafer in the Dynacalibrator chamber and the orientation (whether the membrane was pointed upstream or downstream) of the wafer both affected the IMS readings by as much as a factor of two. The highest HCl output from the calibrator was obtained when the wafer was centered in the chamber (see Figure 39) and when the wafer membrane pointed downstream (see Figure 40). When the wafer faced upstream, the stainless steel surrounding the permeation membrane became very greenish. Although this problem was also observed when the membrane was facing downstream, it appeared to be much less severe in that case. For the permeation tube, the location of the tube in the chamber affected the HCl output from the calibrator by 10% or less. Thus, the position of the calibration device was critical for the wafer, but not for the permeation tube.

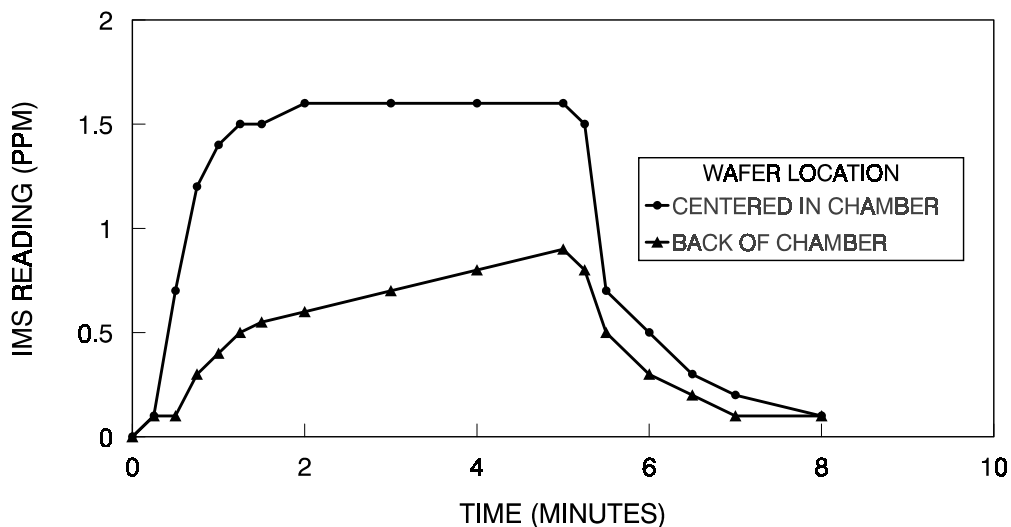


Figure 39. Effects of Wafer Location on HCl Output from the Calibrator.

Chloride emission rates determined from the IC data are shown in Table 3. As can be seen, the HCl outputs from all of the devices from VICI Metronics were found to be about 30-60% too low. The measured HCl emission rates were generally reproducible to within $\pm 5\%$ for each device. The second wafer device was one exception to this. Tests performed on different days with that device gave HCl emission values of 1094 and 763 ng HCl/min (average of 928 ng/min), even though the results were very repeatable on a given day. The reason for this experimental anomaly is unclear. However, the wafer devices tended to behave in a more erratic fashion (based on IMS readings) than the other calibration devices tested, and were also more sensitive to experimental conditions (e.g., location and orientation of the wafer in the permeation chamber).

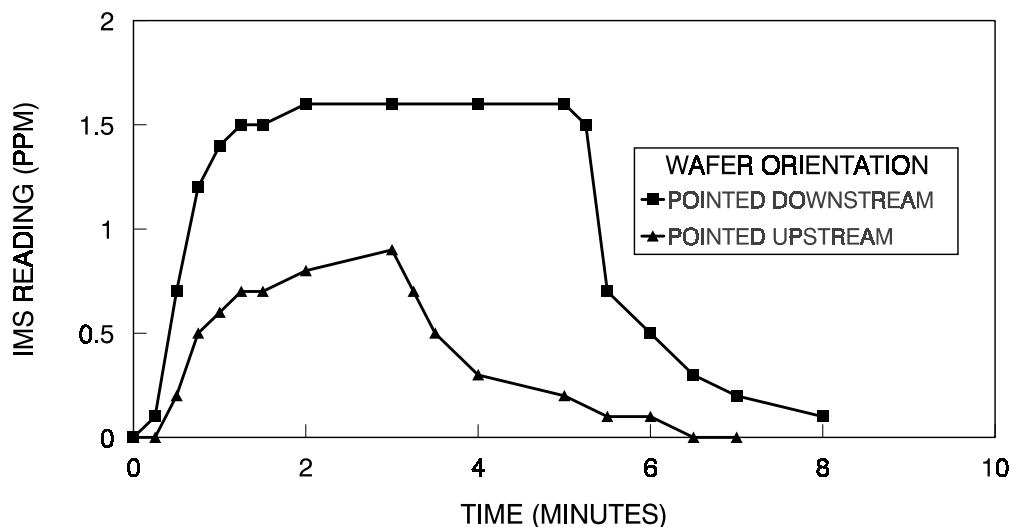


Figure 40. Effects of Wafer Orientation on HCl Output from the Calibrator.

Table 3. Measured and Certified (Provided by Manufacturer) HCl Emission Rates from the HCl Calibration Systems.

Calibration Device	Measured Emission Rate (ng HCl/min)	Certified Emission Rate (ng HCl/min)	Percent of Certified Rate
Permeation Wafer #1	400	872	46
Permeation Wafer #2	928 ± 214	1314	71
Diffusion Vial	492	1242	40
VICI Permeation Tube	550	1121	49
ULED Permeation Tube	1884 ± 45	1222	154

For the VICI Metronics calibration devices containing aqueous HCl, the hydrochloric acid-water system (20.2% HCl) is an azeotropic solution that has been used as a standard in quantitative analysis. As the solution is heated, the vapors should theoretically contain 20.2% HCl. However, the low HCl recoveries observed with the aqueous HCl may reflect possible changes in the equilibrium of the solution as the aqueous HCl is calibrated and used at different temperatures.

The HCl output from the KIN-TEK system using the ULED tube was about 50% too high. Analyses with absorbing solutions were performed on six different days over a period of several weeks, and similar results were obtained in each case. The mean value and standard deviation for those six days of testing are given in Table 3. As can be seen, the relative standard deviation

was about 2%. The consistency in data obtained with absorbing solutions while using the ULED tube was also reflected in the IMS values obtained for that tube. The same IMS reading was observed when passing span gases continuously into the IMS analyzer for a period of several days, and that same reading was obtained repeatedly on numerous days over the course of the work, which covered a two-month period. Personnel at KIN-TEK identified a probable source of their certification bias with the ULED tube and have determined approaches that are likely to correct the problem.

As shown in Figure 41, chloride emission rates determined from the IC data tracked well with the HCl concentrations determined by IMS, indicating that the IMS readings were a good indicator of relative HCl concentrations in the gas stream. Consequently, those readings were a good indicator of when the HCl calibration systems could be considered to be equilibrated prior to collecting HCl with the absorbing solutions. The IMS readings were always somewhat higher than the HCl concentrations determined from the IC data, which may reflect difficulties in performing IMS instrument calibrations at low HCl levels. The IMS unit had been calibrated at the factory using blended gases from compressed gas cylinders, and a recalibration was not performed prior to these tests. Therefore, the IMS readings were used primarily to track changes in relative HCl concentrations.

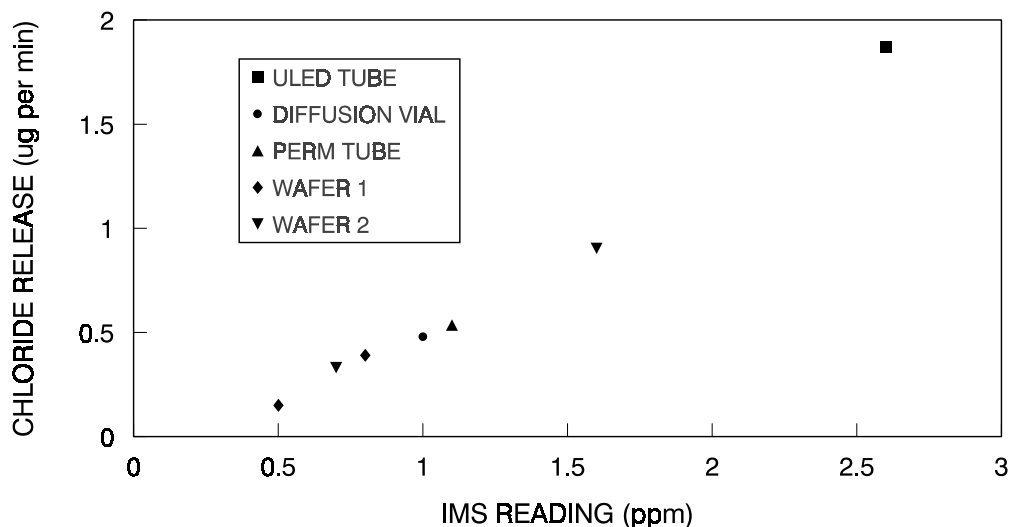


Figure 41. IMS Reading Vs. Calculated Chloride Release Rate from the Calibrators.

Discussion

In the results noted above, it must be kept in mind that data were obtained under specific experimental conditions, and results may be substantially different as changes in the experimental design are made. In this regard, some of the more important considerations include the gas flow rates, temperatures, and nominal HCl concentrations used. The magnitude of the deviation in experimentally determined HCl emission rates from the certified emission rates is larger than can be accounted for through the combined analytical and experimental uncertainties

involved. Also, it was observed that even minor procedural variations can significantly affect the HCl content of span gases from some calibration systems. It appears that additional work is needed in order to provide accurate calibration systems for trace levels of gaseous HCl. Caution should be exercised when using certified HCl emission values for a given calibration device in order to calculate nominal HCl concentrations from a calibration system. Downstream analyses of the calibrator output should be performed to verify HCl concentrations in cases where calibration accuracy is of great importance.

Follow-up Work with Diffusion Vial

Some follow-up work was performed with the VICI Metronics diffusion vial. Although the results discussed for the permeation devices were not disputed by VICI Metronics, personnel at VICI Metronics were puzzled by the low emission values determined experimentally for the diffusion vial. This was based on the fact that another laboratory was routinely getting higher results (85-98% of theoretical) with those vials, which was based on IC analyses of solutions used to collect the HCl emitted from their own Dynacalibrator. However, in their work, the vial was used at 70°C (as opposed to the 30°C we used) and the HCl concentrations were about 5-10 ppm rather than the 1 ppm levels used in our tests. In view of the discrepancy between their results and ours, we performed additional tests with the diffusion vial (containing aqueous HCl) using the Model 340 Dynacalibrator. In order to see if comparable results were obtained using a different calibrator, similar tests were also performed using a VICI Metronics field calibrator. However, because of temperature instabilities in the field calibrator below 35°C, the tests comparing the Model 340 Dynacalibrator with the field calibrator were performed at 35°C rather than the 30°C used previously.

In addition, a series of tests were performed under the conditions used by the other laboratory that was reporting higher HCl recoveries than we had observed. Specifically, a temperature of 70°C was used for the diffusion vial, which increased theoretical HCl emission rates by about a factor of ten. Those tests were performed to determine whether the differences in results obtained between us and the other laboratory could be explained by differences in experimental conditions used between the two laboratories. Before beginning our tests, proper gas flow rates were verified with a bubble flow meter, and chamber temperatures were verified using a reliable mercury thermometer. The calibrators were allowed to equilibrate with the span gases passing through the sample lines for a minimum of 24 hours before collecting samples (bubbling span gases into water). As before, absorbing solutions used to collect HCl were analyzed by IC. The IC data were then used to calculate actual HCl emission rates from the calibrators.

Comparable HCl emission results were obtained with the Dynacalibrator and the field calibrator at 35°C, indicating that there probably was not a problem with the Dynacalibrator. However, the calculated HCl emission rates were about 80% of the theoretical rates, as opposed to the value of 40% which was observed previously when using a temperature of 30°C. When the diffusion vial was used at 70°C in the Dynacalibrator, HCl emission rates calculated from the IC data were almost 95% of the theoretical emission rates.

Next, the tests performed in the Dynacalibrator with the diffusion vial at both 30°C and 70°C were repeated to see if the results were reproducible. However, unlike the previous tests, fresh 20.2% HCl was used at each of the temperatures studied. When the diffusion vial was at 30°C, HCl emission rates were 43% of theoretical values, which was in excellent agreement with the value of 40% reported for previous tests at that temperature. For the tests performed at 70°C, calculated HCl emission rates were 87% of the theoretical rates. Thus, it is clear that our results do not conflict with those from the other laboratory when similar conditions were used. It is also clear that the HCl output from the VICI Metronics Dynacalibrator is very low when using the diffusion vial at 30°C. It is interesting to note that HCl recoveries were about 40%, 80%, and 90% of theoretical values when using temperatures of 30°, 35°, and 70°C, respectively. It is not known whether the increased recoveries at higher temperatures are truly related to temperature or whether the HCl concentration is the primary issue. At any rate, these data again reflect the uncertainties involved with HCl calibration systems.

In view of results obtained with the various calibration devices, we are not comfortable with any of the HCl calibration systems that are commercially available for our HCl range of interest. Instead of using diffusion vials, we intend to use either a permeation tube or a diluted stream of a certified HCl gas in a compressed gas cylinder. In the first case, it was shown that HCl permeation tubes are not very accurate in the low ppm range. However, the HCl output from the permeation tube appeared to be consistent, and they are easier to use than diffusion vials. Therefore, if permeation tubes are used, the HCl output will be experimentally determined by bubbling span gases into solutions and analyzing the solutions by IC to calculate the HCl emission rate. In the case of diluting HCl standard gases from a compressed gas cylinder, this is difficult to do at extremely low HCl concentrations, but may be the most reliable approach overall.

ALTERNATE CALIBRATION APPROACHES

Another common approach for performing HCl calibrations is to use compressed gas cylinders containing known concentrations of HCl. Since HCl is generally believed to be unstable in gas cylinders at low concentrations (e.g., less than 10 ppm), higher starting concentrations are used and the gas is then blended to provide the desired final concentration. Some vendors believe this is an excellent way to perform calibrations at low HCl levels. However, the operator must be extremely careful of wall effects and the difficulties involved in accurately mixing gases to produce low HCl concentrations, as well as difficulties associated with HCl transport in general.

We briefly investigated an alternate approach for HCl calibrations whereby dilute aqueous solutions of hydrochloric acid were pumped at a known rate into a hot steam coil in our testing apparatus. The steam containing the HCl then entered the main carrier gas stream. This approach has the advantage of being able to accurately prepare the liquid HCl standard as well as the advantage of minimizing wall effects by pumping a liquid containing the HCl rather than using gases. By using this approach, good HCl recoveries at the exit of the testing apparatus were obtained in some cases. However, pumping problems were encountered when attempting to use the low flows necessary to attain both the desired moisture and HCl concentrations at the

total gas flow rate (about 1000 mL/min) being tested. No further work in this area was performed.

DESCRIPTION OF CEM

As noted earlier, the analytical detection system for determining HCl is a Molecular Analytics Model 20-HCl Stack Master IMS Analyzer. Thus, unlike the Hg analyzer, this is a commercially available detection system. The unit has programmable high and low alarms, built-in diagnostics, and two analysis ranges (0-20 ppm and 0-200 ppb) which are obtained by changing an internal membrane.

As with the Hg analyses, operation of the overall HCl CEM is based on the assumption that a properly filtered gas stream is available. Since filtering is not performed as part of the CEM operation, it should be performed upstream from the CEM using a suitable filtering device. Also, as with the Hg CEM, calibrations are nonautomated and are performed while bypassing the gas conditioning system. The issues discussed for calibrating the Hg CEM also apply to the calibration of this or any other HCl CEM. In addition, as discussed earlier in this report, commercially available HCl calibration systems tend to be unreliable at low HCl concentrations.

A picture of the overall gas conditioning and analytical system (all rack mounted) used for HCl is shown in Figure 42. The box on the floor next to the rack is the Hg analyzer, which uses the same gas conditioning system. The major components seen from the front of the equipment rack are 1) the control box at the top of the unit, which contains flow meters, temperature controllers, temperature displays, and Photohelic[®] pressure switch/gauges, 2) the IMS detection system for HCl, which is located underneath the control box, 3) a catalyst module (long rectangular box below the IMS unit) for the oxidative decomposition of NH₃ and tars, and 4) a large Nafion-based dryer for removing moisture from the sample stream prior to entering the detection system. The two Photohelic[®] pressure switch/gauges are used to monitor gas pressure as a safety feature in the event of a line plug. One of those switches has a relatively large range and is for positive pressures only. The other one has a relatively small range and is for both positive and negative pressures. The switch/gauge to be used depends on the specific monitoring application. The desired positive and negative pressure limits can be adjusted so that power to any of the analyzer components are automatically turned off if those limits are exceeded. This may be desirable if, for example, a line downstream from the catalyst plugs with ammonium chloride deposits because of problems with the catalyst module. Currently, the switch/gauges are for monitoring purposes only and have an automatic reset. However, by adding a manual reset switch, system components can be made to stay off until the problem causing abnormal pressure/vacuum conditions is corrected. Utility requirements for the overall CEM include two separate 20-amp circuits. It may also be desirable to have filtered house air available at 60-100 psi. If the addition of another compressor is desired, an additional circuit would be required.

A schematic diagram of the overall system is shown in Figure 43. A compressor is used to provide air for the oxidation catalyst, the purge gas for the Nafion-based dryer, and the instrument air for the IMS analyzer. Air from the compressor is first passed into a small Perma Pure 12-inch heatless dryer in order to meet dew point requirements for the IMS analyzer and to improve drying efficiency of the Nafion dryer. After reviewing a variety of options for

generating the necessary IMS instrument air (with a dew point requirement of at least -40°C), the 12-inch heatless dryer from Perma Pure was selected since it provides a dew point of -50°C . For field use, the heatless dryer could be coupled to an air compressor if house air is not available.



Figure 42. Gas Conditioning System and Analyzer for Monitoring HCl Emissions (Hg Analyzer Sitting on Floor Next to Rack).

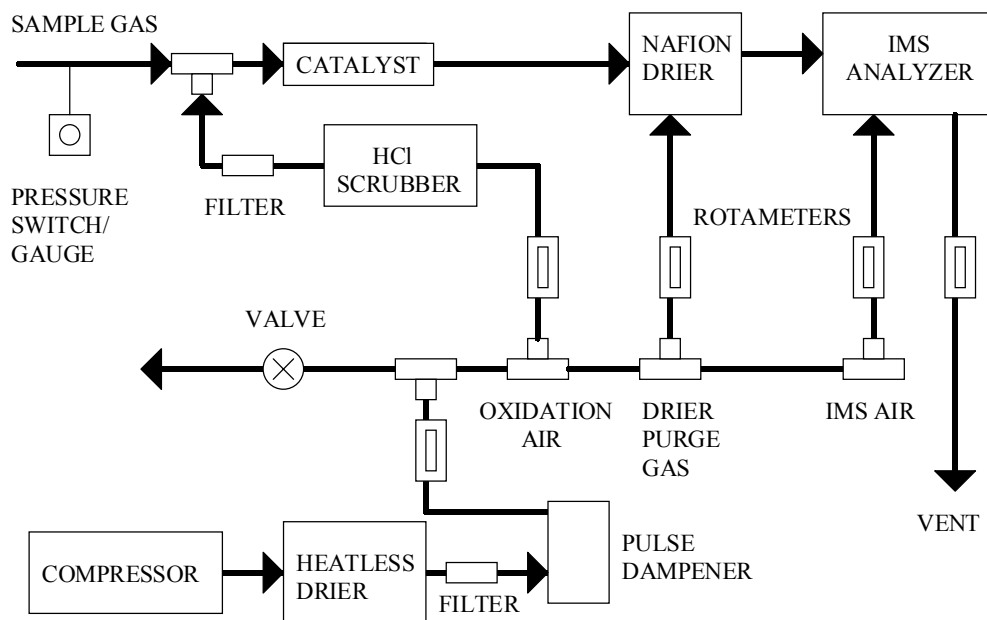


Figure 43. Schematic Diagram of Overall Gas Conditioning and Analysis System for HCl.

Pressure surges in the dried air from the heatless dryer were observed as the dryer cycled back and forth between two drying chambers. These pressure pulses caused fluctuations in the IMS instrument air (nominally 2 L/min) and the oxidation air (nominally 2 L/min) of up to about 0.5 L/min. Because of the pressure pulses, a pulse dampener was added to minimize downstream flow fluctuations resulting from the use of the heatless dryer. The pulse dampener, located immediately downstream from the heatless dryer, consists of a 1-gallon plastic jug fitted with Swagelock connectors. This reduced the magnitude of the flow fluctuations from 0.5 L/min to only 0.05 L/min. Although this effectively dampened the flow fluctuations in the IMS instrument air and the oxidation air, the jug is only intended as a very temporary solution since the fittings in the jug can not be considered as being secure in view of the pressures of up to about 75 psi that are being used.

It should also be noted that the IMS unit is very sensitive to fluctuations in the sample gas flow. Pressure fluctuations were not a problem in our laboratory work using compressed gas cylinders. However, during actual field sampling, it may be necessary to put in a suitable Teflon chamber upstream from the analyzer in order to minimize pressure fluctuations in the sample gas flow into the IMS unit.

The oxidation air passes through a soda lime scrubber to remove HCl prior to being mixed with the sample gas upstream from the oxidation catalyst (the soda lime is replaced with

activated carbon traps when Hg analyses are being performed). The sample gas is blended with the oxidation air using about 1 L/min of sample gas and 2 L/min of air. That stream then enters the oxidation catalyst for removal of NH₃ and tars. Next, the gases enter a large Nafion-based dryer to remove moisture from the gas stream. The dryer is a Perma Pure GASS™ (Gas Analysis Sampling System) designed to handle a 1-2 L/min gas flow with up to 50% (volumetric) moisture. That system contains two Perma Pure PD-1000-24AFS dryers with Nafion tubes as well as an internal Model FF-250-FG Filter Coalescer. After exiting the dryer, the gases enter the IMS analyzer for HCl determinations.

TESTING OF ENTIRE CEM IN THE LABORATORY

Laboratory testing was performed with the entire integrated (gas conditioner coupled to the analyzer) HCl CEM using a simulated coal gasification stream. The simulated gasifier stream, on a dry basis, consisted of 22% H₂, 13% CO₂, 7% CH₄, 1.7% H₂S, 44% CO, 0.25% NH₃, up to 100 ppm_v HCl, and a balance of N₂. In addition, moisture was added to give a water content of 20%. A single compressed gas cylinder containing blended H₂, CO₂, CH₄, H₂S, and CO was used. The NH₃, H₂O, and HCl were each added separately to the sample line just prior to the inlet of the gas conditioning system. Compressed gas cylinders were used for the NH₃ and HCl, while known amounts of water were fed into the gas stream by using a peristaltic pump. The sample line (316 stainless steel) into the gas conditioner was heated and maintained at 600°C, and the NH₃, H₂O, and HCl were added to the gasifier stream via union tees in the 600°C sample line. Type 316 stainless steel would not be the preferred choice of materials for the sample line during prolonged testing, but it was used here because of its low cost relative to other options and because extended testing of the CEM was not to be performed. Sections (about 8" each) of the NH₃, H₂O, and HCl lines into the union tees were heavily insulated to provide preheating of those gas stream components prior to entering the gasifier stream.

Testing was performed using about 1 L/min (dry basis) of gasifier stream blended with 2 L/min of oxidation air, which was preheated to 600°C and added to the simulated gasifier stream just prior to the oxidation catalyst. For comparative purposes, HCl streams in air were passed directly (bypassing the gas conditioner) into the IMS analyzer. Similarly, tests were performed in which HCl in air alone was passed through the entire heated gas conditioning system.

In the tests where streams of HCl in air bypassed the gas conditioner and passed directly into the IMS analyzer, the nominal HCl concentration was varied from 2 to 10 ppm. The IMS analyzer exhibited rapid response, reaching 90% of the full reading within 30 seconds and reaching a steady reading within 60 seconds. Also, the IMS analyzer was very sensitive to small (1 ppm) changes in the HCl concentration.

Next, streams of HCl in air were passed through the entire heated gas conditioning system. A variety of minor problems were noted during these tests. For example, it became apparent that the compressor being used to provide the IMS instrument air, oxidation air, and purge gas for the Nafion dryer was slightly undersized. Therefore, dry filtered house air was used instead of the

compressor. Also, it was noted that the overall operation of the CEM could be improved by a variety of modifications in the CEM design, many of which related to plumbing considerations.

When passing a 10 ppm HCl stream (in air) through the gas conditioner, the HCl concentrations reported by the IMS analyzer were about 20% lower than those obtained while bypassing the conditioner. This could be due to a variety of reasons. One possibility is that there were HCl losses due to sorption onto the walls of the sample transport lines and other gas conditioner components. Another possibility is that the countercurrent purge gas flow rate in the Nafion-based dryer may have required fine tuning. In previous tests with the Nafion dryer, low-level HCl streams were successfully passed through the Nafion dryer and there did not appear to be any losses of analyte into the purge gas stream. However, for HCl, the ratio of the purge gas flow rate to the sample gas flow rate is of great importance, and higher ratios are generally needed to prevent losses of HCl into the purge gas stream. Still a third possibility relates to the fact that the IMS analyzer requires sample gases to be at atmospheric pressure for proper operation. The pressure of the sample gases that bypassed the gas conditioner may have been slightly different than the sample gas pressure when going through the gas conditioner. If this is indeed the case, the problem can be easily corrected through minor design changes in the gas conditioning/sampling system. Additional work would be required to determine the reason for the 20% decrease in the IMS readout when going through the conditioner rather than bypassing the conditioner.

As expected, the signal lag times when switching back and forth between zero air (no HCl) and span gases (containing 10 ppm HCl) were substantially greater when going through the gas conditioner. Instead of reaching a steady signal within 60 seconds (as was the case when bypassing the conditioner), it took about 5 minutes when passing span gases through the conditioner. Similarly, due to apparent wall effects in the gas conditioner, it took a long time to purge residual HCl out of the system after turning off the HCl flow. Typically, it took several minutes just for a 50% signal reduction to be observed after switching from span gases to zero air. The response times can probably be improved considerably through a variety of improvements in the gas conditioning hardware.

In other tests with HCl streams (in air) passing through the gas conditioning system, HCl concentrations of 2, 4, 8, and 10 ppm in the span gases were used after first equilibrating the system with a 10 ppm HCl stream. The HCl concentration was then decreased sequentially to lower levels. In a relative sense, the IMS reading tracked well with the changing HCl concentrations. However, a specific percentage reduction in the nominal HCl concentration did not result in the same percentage reduction in the IMS reading. The decrease in the IMS reading was always somewhat less than expected based on the magnitude of the decrease in theoretical HCl concentrations in the gases entering the gas conditioning system. This could reflect a possible need for some routine maintenance of the IMS analyzer, or could reflect the extended lag times observed in the signal responses when passing sample gases through the conditioner. Another possibility is that some of the HCl was being removed from the gas stream due to wall losses. In that event, the magnitude of the changes in theoretical HCl concentrations could easily be greater than the magnitude of the changes in the IMS reading as the HCl concentration was varied. This is particularly true in view of the fact that sorption/desorption equilibrium may change with changing HCl concentration.

Next, tests were performed in which a simulated gasifier stream (excluding NH_3) containing 10 ppm HCl was passed through the gas conditioning system prior to the IMS analyzer. For these tests, 2 L/min of air was blended with 1 L/min of gasifier stream (dry basis) prior to entering the catalyst tube in the gas conditioner. This resulted in a nominal HCl concentration of about 3 ppm in the final blended gas stream. The reading reported by the IMS analyzer for these tests was about 2.5 ppm. This is in excellent agreement with the theoretical value of 3 ppm in view of the collective experimental uncertainties involved.

Unlike the tests using streams of only air and HCl through the conditioner, fairly rapid response times were observed with the simulated flue gas stream when going from zero air to span gases. Specifically, steady signals were obtained by the IMS analyzer within 60 seconds when passing the simulated gasifier stream through the conditioner. Although the signal rise time was short, it took five minutes or more to clear the HCl out of the system when returning to zero air. This shows that there are significant wall effects in the gas conditioner and/or steel sampling lines. The greatly improved signal rise times observed while using the simulated flue gas instead of the air/HCl streams is probably related to the high moisture content of the simulated gasifier stream, as opposed to the dry gases used in the tests with only air and HCl. The moisture probably resulted in a flushing effect which helped transport the analyte through the system. However, the added moisture did not seem to help purge HCl out of the system very quickly.

With the simulated gasifier stream, the IMS readings tracked well with changes in the HCl concentration as the HCl concentration (prior to blending with air for catalytic oxidation of the gas stream) was varied from 2 to 10 ppm. However, as was the case with passing air/HCl streams through the conditioner, the magnitude of the changes in the IMS readings for different HCl concentrations was somewhat less than anticipated based on the magnitude of the changes in the nominal HCl concentrations entering the gas conditioner. Since signal lag times were not an issue in the tests with simulated gasifier streams (i.e., rapid responses were observed), the fact that the changes in IMS readings were somewhat less than expected may reflect HCl losses during sample transport. Alternatively, as noted earlier, the analyzer may require some routine maintenance in order to exhibit peak performance.

In the next series of tests, NH_3 was added to the simulated gasifier stream after a steady IMS signal was obtained for a gasifier stream containing 10 ppm HCl (prior to dilution with oxidation air). When the NH_3 was added, the IMS reading quickly decreased and most of the HCl signal on the IMS analyzer disappeared. When the NH_3 flow was stopped, the IMS reading returned to nearly the same value that was observed before the NH_3 addition. This implies that the oxidation catalyst was not effectively destroying all of the NH_3 , in which case the NH_3 can easily combine with HCl to form ammonium chloride as the gases cool. Although laboratory tests indicated that the catalyst effectively destroys all of the NH_3 at the gas flow rates being used, those tests were performed with dry gases. The added moisture in the simulated gasifier stream substantially increased the volumetric flow rate, which in turn decreased the gas residence time in the catalyst zone. This problem can easily be circumvented by simply increasing the size of the catalyst zone.

The tests with NH₃ were repeated after adjusting some of the temperatures in the gas conditioner. This time, the introduction of NH₃ did not cause a decrease in the HCl signal. These results show how sensitive the critical NH₃ removal step is to various parameters in the gas conditioner. The effects of those parameters on the IMS readings require more thorough investigation.

The tests with the HCl CEM were successful in that low-level HCl streams could be successfully passed through the entire system (even in a simulated gasifier stream), and small changes (e.g., 1 ppm) in the HCl concentration could be observed. The catalytic oxidation component of the CEM worked well (although more work on NH₃ removal is needed), as did the Nafion-based dryer. However, additional work is required to minimize potential wall losses and to minimize residence times of residual HCl in the sample transport lines and the gas conditioning system.

CONCLUSIONS

The gas conditioning issues involved with coal gasification streams are very complex and do not have simple solutions. This is particularly true in view of the fact that the gas conditioning system must deal with tars, high moisture contents, and problems with NH₃ without affecting low ppb levels of Hg, low levels (low ppm or less) of HCl, or the successful operation of conditioner components and analytical systems. Those issues are far from trivial. Trying to develop a non-chemical system for gas conditioning was very ambitious in view of the difficult sampling environment and unique problems associated with coal gasification streams. Although a great deal was learned regarding calibration, sample transport, instrumentation options, gas stream conditioning, and CEM design options, some challenging issues still remain. Sample transport is one area that is often not adequately considered. Because of the gas stream composition and elevated temperatures involved, special attention will need to be given to the choice of materials for the sample line and other plumbing components. When using gas stream oxidation, there will be sample transport regions under oxidizing as well as reducing conditions, and each of those regions will require different materials of construction for sample transport. The catalytic oxidation approach worked well for removal of tars and NH₃ on a short term basis, but durability issues related to using the catalyst tube during extended testing periods still require study.

The Hg analysis system employing a D₂ background correction approach is promising, but is not yet fully developed. The primary complicating factor at this time is the fact that the required correction factor on the D₂ channel of the instrument changes slightly with changing levels of interfering gases. Additional work is required to resolve that issue. Since the analyzer is the first of its kind, it can probably be improved through modifications in the optical/electrical design as well as upgrades in the optical/electrical components. Such modifications should enhance base line stability, lower the detection limit, improve the accuracy of Hg readings in the presence of high levels of interfering gases, and minimize the importance of the D₂ correction factor. Passing low levels of elemental Hg through the gas conditioning system is very complex. Additional work is required to address sample transport issues through the gas conditioner.

Also, the formation and deposition of sulfate aerosols and the successful conversion of oxidized Hg (formed while passing over the oxidation catalyst) back to the elemental form (and keeping it in that form) are issues that still require further study. The overall gas conditioning system needs to be simplified to allow for more routine use.

The tests with HCl using simulated gasifier streams were generally successful, but it is clear that additional development is needed before it is ready for field use. Using the IMS analytical approach is attractive in view of its high sensitivity and lack of significant interferences. However, because of the low dynamic range, a dilution system would be needed to cover HCl concentrations in the range of 0 to 100 ppm. IMS is sensitive to pulsations in the sample gas flow and the sample gas must be at atmospheric pressure, but those issues are easily dealt with. As with Hg, additional work on transporting HCl through the gas conditioning system is required. The complete removal of NH₃ is critical to the successful operation of the HCl CEM, and more tests in that area should be performed using simulated gasifier streams.

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