

DOE/MC--96002110

Development of Mercury and Chloride Monitors for Coal Gasifiers

Authors:

William H. Buttermore
Glenn A. Norton
Colin D. Chriswell

Dave E. Eckels
Rachel E. Peters
William H. Buttermore

Contractor:

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Contract Number:

93MC30024

Conference Title:

Advanced Coal-Fired Power Systems '95 Review Meeting

Conference Location:

Morgantown, West Virginia

Conference Dates:

June 27-29, 1995

Conference Sponsor:

U.S. Department of Energy, Morgantown Energy Technology Center
(METC)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

JK

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

6B.5

**Development of Mercury and Chloride
Monitors for Coal Gasifiers**

CONTRACT INFORMATION

Contract Number W-7405-Eng-82 (Ames)
93MC30024.000 (METC)

Contractor Ames Laboratory
Iowa State University
Ames, Iowa 50011

Contractor Project Manager William H. Buttermore

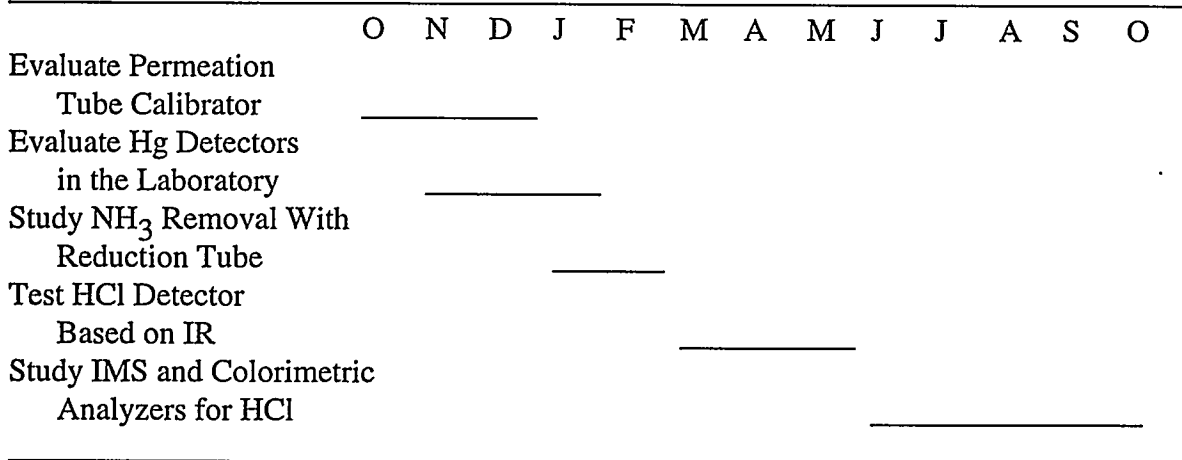
Principal Investigators Glenn A. Norton
Colin D. Chriswell

Contributing Authors Dave E. Eckels
Rachel E. Peters
William H. Buttermore

METC Project Manager Margaret A. Kotzalas

Period of Performance October 1, 1994 - continuing

Schedule and Milestones
FY95 Program Schedule



OBJECTIVES

Ames Laboratory will develop an integrated sampling and analysis system suitable for on-line monitoring of mercury (Hg) and hydrogen chloride (HCl) in advanced coal-based gasifiers. The objectives of this project are to 1) summarize current technology for monitoring Hg and HCl in gaseous effluents, 2) identify analytical techniques for such determinations in high-temperature, high-pressure gases from coal-based systems for producing electrical power, 3) evaluate promising analytical approaches, and 4) produce reliable on-line monitors which are adaptable to plant-scale diagnostics and process control.

BACKGROUND INFORMATION

The capability to continuously monitor and effectively control critical effluents must be developed in order to implement new clean coal technologies. Although Hg and HCl concentrations in hot, high-pressure gases from power producing systems are of environmental and technological concern, instruments suitable for determining Hg and HCl in those environments have not yet been sufficiently developed and tested. On-line analysis is more complex for such systems than for more conventional coal-based power producing systems because of the high temperatures (up to 500°C) and pressures (up to 300 psi) involved. In addition, the different gas compositions in emerging coal-based power producing systems relative to those present in conventional combustors can pose special analytical problems. Concentrations of Hg are anticipated to be in the range of 2 - 200 ppb_w in the raw gas. Concentrations of HCl are anticipated to be in the range of 50 - 500 ppm in the raw gas and less than 1 ppm after the flue gas is treated (1-3).

PROJECT DESCRIPTION

In previous work (4), commercially available instrumentation suitable for monitoring Hg and HCl in coal gasifiers was reviewed. Also, pertinent literature was assessed to obtain additional information on methods which could potentially be used. For Hg, the techniques selected for further consideration were atomic absorption and atomic fluorescence. For HCl, non-dispersive infrared absorption, a dry colorimetric procedure, and ion mobility spectroscopy were selected for testing in the laboratory.

After the analytical methods to be used for on-line analysis of Hg and HCl have been tested in the laboratory, they will be adapted for application to monitoring hot pressurized gases from coal gasifiers. Additional work will involve developing suitable gas conditioning and sample introduction systems. That work may be as important as the development of the analytical detectors themselves. After the laboratory studies have been completed, prototype instruments will be tested and evaluated in the field.

RESULTS

Mercury Studies

A Thermo Separation Products Model 3200 cold vapor atomic absorption (AA) detector and a Tekran Model 2500 cold vapor atomic fluorescence (AF) detector were received and evaluated in our laboratories. This evaluation included examining parameters such as dynamic range, detection limits, precision, baseline noise and drift, and general utility of the instruments for on-line monitoring applications.

In order to assess detector response, 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. By knowing the temperature and pressure within the flask, the Hg concentration in the air above the Hg pool was calculated from known Hg vapor pressure parameters. The Hg vapor was then manually injected into the carrier gas stream entering the detector. For comparative purposes, a series of injections was 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.

For the AA work, the carrier gas was either Ar or zero air. Research grade (99.9995% minimum purity) Ar was always used in the AF instrument to provide a continuous purge of the optical path. Research grade Ar was also generally used as the carrier gas for the AF tests. However, a series of tests was performed with the AF detector in which a variety of gases other than Ar were used for the carrier gas. These gases, which included CH₄, CO, CO₂, H₂, and N₂, were used to study 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. Because molecular gases can quench the fluorescence signal, the instrument is intended to be used with a gold trap for collecting and preconcentrating the Hg, followed by thermally evolving the amalgamated Hg in an Ar atmosphere.

In addition to manual injections of Hg vapor, a VICI Metronics Model 340 Dynacalibrator with elemental Hg permeation tubes was used to provide a continuous flow of gases containing known Hg concentrations in the range of 0.1 to 1000 ppb_w in air. All of the AA tests were performed using zero air as the carrier gas, except for one series of tests in which Ar was used as the carrier gas to allow better comparisons with data obtained by AF. Because of fluorescence quenching effects from molecular gases, Ar was used as the carrier gas for all tests using permeation tubes with the AF detector.

All data were collected on a strip chart recorder. The Hg responses were then obtained by measuring peak heights on the recorder output. For a given injection volume, three to six injections were made. When the permeation tubes were used, three sequential signals at each Hg concentration were recorded. Averages and relative standard deviations (RSDs) were then calculated from those data.

Results of the tests with the AA and AF detectors, a comparison of those two analytical techniques for monitoring Hg in coal gasification effluents, and work related to the accuracy of the permeation tube calibrator are discussed separately below.

Atomic Absorption. For the AA tests, baseline drift was less than 1×10^{-4} AU/hr. An AU reading of 1×10^{-4} is equivalent to a Hg concentration of about 0.5 ppb_w in air or an injection of several pg Hg. Minimal baseline noise was observed, even for flows up to 1000 mL/min. However, changes in the gas flow rate into the detector for gas flows ranging from 200 to 1000 mL/min caused significant changes in baseline absorption values. The magnitude of change in baseline absorption values for a flow rate adjustment of about 200 mL/min was typically equivalent to a signal that would be

observed from a Hg concentration of 1 ppb_w or less in a gas stream.

Results from Hg injections indicated that the detector could easily detect less than 3 pg Hg. A detection limit of 0.3 pg was calculated by comparing the peak height to the magnitude of the background noise for a 3-pg injection. The instrument response was linear in the range of 3 to 50,000 pg. The RSDs were typically $\pm 1-5\%$ for injections of 25 pg or more and were typically $\pm 10-15\%$ for injections of lesser amounts.

Results of tests with the permeation tube calibrator indicated that the dynamic range was excellent and spanned at least four orders of magnitude (from 0.1 to 1000 ppb_w) in Hg concentration. A typical signal for a Hg concentration of 0.5 ppb_w is shown in Figure 1. As can be seen, an excellent signal is obtained at that concentration. When a 0.1 ppb_w (0.01 ppb_v) Hg stream, which is near the minimum detectable concentration, was passed through the detector, a distinct signal was observed. For Hg concentrations ranging from 0.1 to 1000 ppb_w, RSDs for the sequential measurements at a given concentration were $\pm 5\%$ or better. For concentrations above 10 ppb_w, RSDs did not exceed $\pm 2\%$.

Atomic Fluorescence. The baseline drift for the AF unit was typically on the order of 0.5 mV/hr. A signal of 0.5 mV is roughly equivalent to the signal produced from injecting about 1 pg Hg. Flow rate changes for gas flows in the range of 10-1000 mL/min generally did not affect the baseline signal level or baseline noise.

Excellent peaks were observed for 3-pg injections of Hg. A detection limit of 0.1 pg was calculated by comparing the peak height with the magnitude of the baseline noise. The RSDs were $\leq 5\%$ for injections of 25-5,000 pg and 5-25% for injections of 2-25 pg.

The AF instrument response to Hg injections was nearly linear over at least two orders of

magnitude (from 3 to 300 pg), although a significant degree of non-linearity was observed over a wider range. The non-linearity may be a result of quenching effects related to the increased amounts of air associated with the increasing amount of Hg injected into the detector. It could also be partially due to the fact that peak heights rather than peak areas were used to measure instrument responses.

When studying quenching effects from molecular carrier gases, a 20-30% decrease in instrument sensitivity was noted after the use of CO. Instrument sensitivity was not recovered even after purging the sample cell for up to 24 hours with Ar. However, it was later observed that the sample cell had numerous black specks of unknown origin. When the specks were removed by washing the sample cell, the instrument was restored to its original sensitivity. Although this complicated assessing the magnitude of quenching effects, conclusions could still be drawn from the data. No quenching effects were observed for CH₄, but quenching effects were substantial for N₂ and were severe for CO₂, CO, and H₂. For Hg injections of 500 pg or less, the decrease in signal strength was roughly 75% for N₂ and was 99% or more for CO₂, CO, and H₂.

When the permeation tube calibrator was used, the detector could easily see an emission of about 20 pg/min of Hg into an Ar stream flowing at 170 mL/min. In Figure 2, results obtained using the permeation tubes are shown and compared to data obtained under identical conditions using AA with the Hg-containing Ar carrier stream. Unlike the Hg injections, nearly identical linearity was observed for AA and AF when the permeation tube calibrator was used. The use of the calibrator eliminated several experimental concerns, including peak broadening, quantifying peaks by peak heights, variable injection times, and quenching effects from air in the injected volumes.

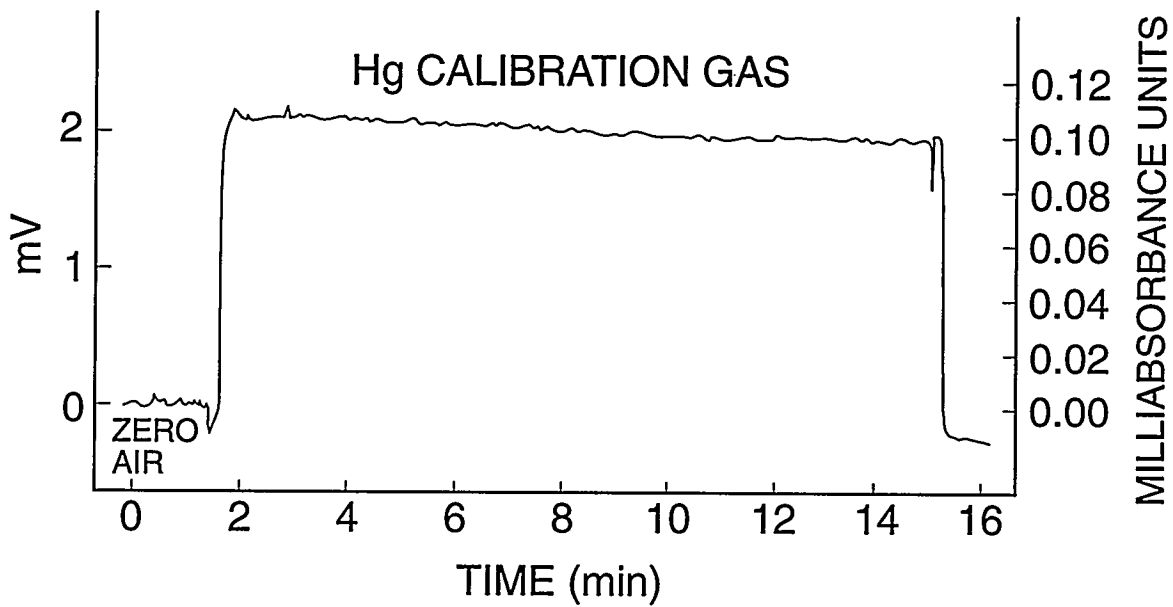


Figure 1. AA Signal Observed for 0.5 ppb_w Hg in Air

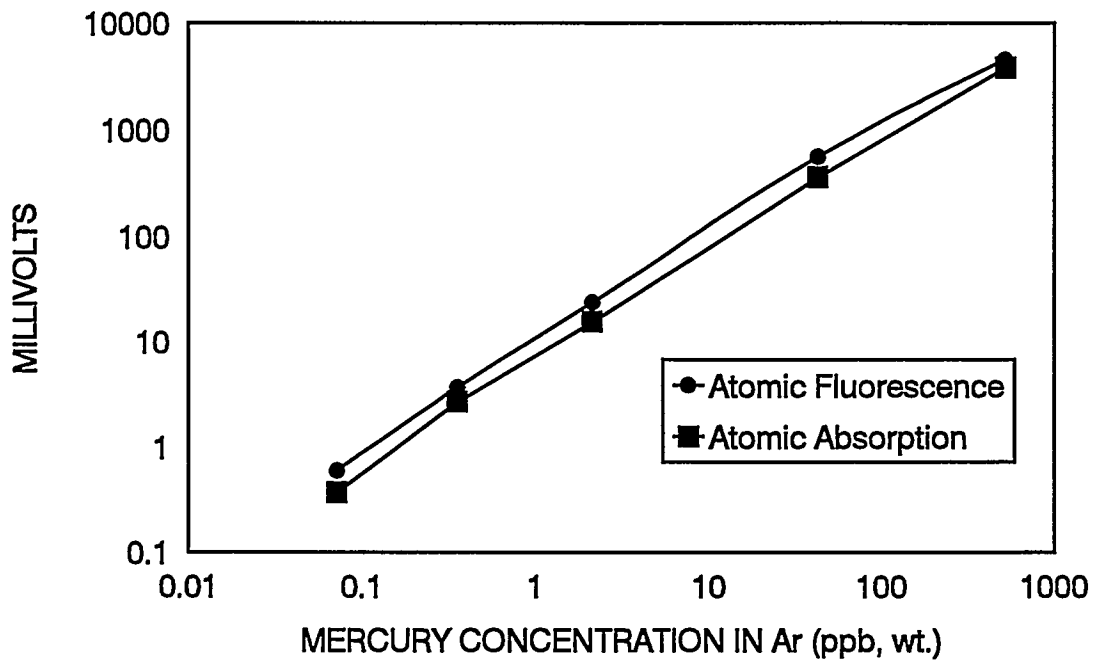


Figure 2. AA and AF Calibration Curves Obtained with a Permeation Tube Calibrator

Instrument Selection. We have carefully considered the AA and AF detectors for possible use in an on-line Hg monitor for coal gasifiers. Both detectors are compact, have minimal baseline noise, exhibit comparable precision, and require Hg to be in the elemental form for detection. In addition, they each offer rapid analysis, high sensitivity, low cost, and simplicity.

Because concentrations of Hg in gasifier effluents are anticipated to range from 2 to 200 ppb_w, both techniques should have sufficient sensitivity to measure total vapor phase Hg after all of the Hg has been converted to the elemental form for detection. Although the sensitivity of the AF unit appears to be somewhat better than that of the AA detector, there was less than a factor of two difference based on results from Hg injections and results obtained with the permeation tube calibrator.

The AF unit exhibited less baseline drift than the AA unit, although the amount of drift in the AA baseline was still acceptable in view of the Hg concentrations anticipated in gasifier streams. Unlike the AA unit, the AF baseline was not significantly affected by flow rate changes. Thus, at low Hg concentrations, small changes in flow rate during sampling would be less problematic.

As a result of the high sensitivity of the AF unit, the possibility existed that extensively conditioned effluent gases could be directly analyzed by passing those gases through the AF detector cell in spite of quenching effects. The gold amalgamation step would be eliminated along with the need for high purity Ar. Unfortunately, the extent of quenching from most of the major gases in a gasifier stream precludes the possibility of direct analysis at the anticipated Hg concentrations. The potential for passing conditioned effluent gases directly into the absorption cell is therefore an advantage to using

AA. Also, AA does not have the requirement for a high purity Ar carrier gas.

For many coals, it appears that the AA unit has a low enough detection limit that stream dilution (e.g., 10:1) could be used to lower the dew point of water in the sample gas to room temperature prior to passing the gases into the detection cell. However, if higher dilution ratios are needed, the detection limit may not be adequate. In this event, it may become necessary to capture the Hg by gold amalgamation for preconcentration prior to thermally evolving the Hg into a suitable dry carrier gas for detection by AA.

After weighing numerous considerations, we have decided to pursue the use of AA for an on-line Hg monitor. With AA, it may still be possible to pass conditioned gases into the detection cell without the additional step of gold amalgamation. However, for direct gas analysis, extensive gas conditioning may be required. In particular, coal tars will have to be eliminated. Also, it will be necessary to correct for or remove interfering compounds, such as H₂S and hydrocarbons.

Calibrator Accuracy. Checks on equipment vendors and proper instrument operation are an integral part of our research. This type of supporting work related to instrument development is crucial since it ultimately relates to the accuracy and reliability of our intended end product (i.e., on-line chemical monitors). In view of this, the operation of the Hg permeation tube calibrator was checked by bubbling Hg-containing gases from the calibrator into nitric acid absorbing solutions. The absorbing solutions were analyzed by conventional cold vapor atomic absorption spectroscopy. Recoveries of Hg were about 80%, which are very good in view of the uncertainties in the Hg emission rates (typically $\pm 15-25\%$ for uncertified tubes), gas flow rate, Hg collection

efficiencies, and Hg analysis by AA. When more precise instrument calibration is desired in later stages of this project, certified permeation tubes with reported Hg emission uncertainties of $\pm 10\%$ or better will be used.

Despite good Hg recoveries in our initial tests, subsequent work indicated that many 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. The vendor has since revised the emission rates and uncertainties for the uncertified Hg permeation tubes we had previously purchased.

Hydrogen Chloride Studies

Gas Filter Correlation IR. We received a Thermo Environmental Instruments Model 15 Gas Filter Correlation IR (GFCIR) HCl analyzer on loan and evaluated the monitor in our laboratories. The sample cell for this instrument can operate up to about 50°C. Tests were performed at room temperature with HCl calibration gas (3000 ppm_v) in a nitrogen balance. Instrument readings were very stable and the calibration curve was linear in the range of about 50 to 3000 ppm_v HCl. At lower concentrations, particularly below 25 ppm_v, erratic responses were noted. It was suspected that memory effects due to sorption/desorption with sample line walls (noted even with Teflon lines) and dilution errors were at least partially to blame. Baseline fluctuations were minimal and were equivalent to the signal from only about 0.2 ppm HCl or less.

In addition to the above tests, a VICI Metronics Model 340 Dynacalibrator with HCl permeation tubes was used to provide a gas stream with HCl concentrations ranging from 0.2

to 2 ppm_v. The instrument response showed good linearity from about 0.5 to 2 ppm_v, as shown in Figure 3. Long equilibration times and pronounced memory effects were noted when passing low concentrations of HCl through the sample lines and flow meters. This could explain why many users of GFCIR for HCl have reported problems in differentiating between different concentrations of HCl below 10 ppm.

Tests were also performed to study the severity of the known interference from CH₄. For these 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 used. Results indicated that 300-400 ppm CH₄ gives a response equivalent to 1 ppm HCl. This has important implications on the analysis of gasifier streams using GFCIR. Concentrations of CH₄ can be as high as 15% in effluents from coal gasification. The equivalent HCl reading for this level of CH₄ is on the order of 400 ppm. Thus, if no CH₄ is removed prior to gas analysis, the magnitude of the error in the HCl concentration can be higher than the HCl concentration itself. Consequently, most of the CH₄ will need to be removed prior to analysis if GFCIR is used. Depending on the relative concentrations of CH₄ and HCl in the gasifier effluents, 75% to nearly 100% of the CH₄ will need to be removed prior to the HCl determination. Removing the CH₄ by oxidation is one approach that could be utilized.

In addition to our laboratory studies, personnel from several different companies who had both laboratory and field experience with the Model 15 GFCIR analyzer were contacted. They reported in discussions with us that the instrument generally works well. However, several of the instrument users noted that the analytical uncertainty is significant in the 1-10 ppm range and recommended "dampening" the

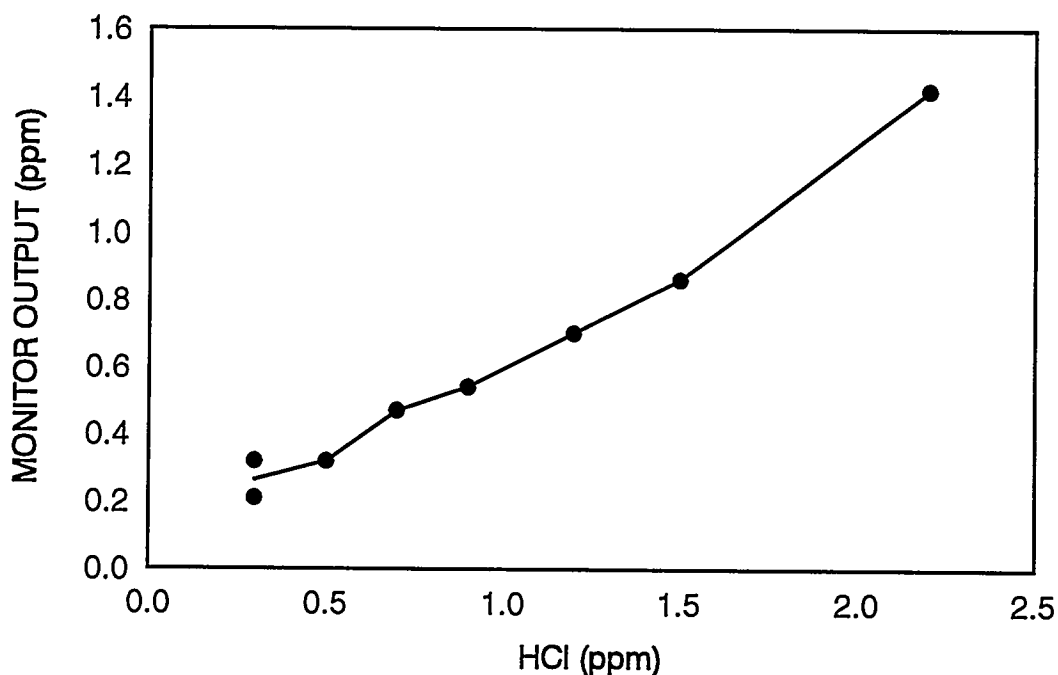


Figure 3. Calibration Curve for GFCIR Monitor Using Permeation Tubes

signal by taking 60-second averages. Baseline drift was also reported to be significant, which sometimes made it difficult to differentiate between 1 and 10 ppm.

Ion Mobility Spectroscopy. The use of ion mobility spectroscopy (IMS) for process gas monitoring was discussed with several researchers experienced in the laboratory and field determination of HF or HCl by IMS. The IMS technology is still considered to be emerging and there are numerous uncertainties involved with its use. Advantages of IMS include high sensitivity and few occurrences of false positives (5). Problems encountered include large baseline drift, sensitivity to changes in temperature and pressure of sample gas, matrix dependency, and narrow dynamic range (about two orders of magnitude). We are currently attempting to arrange the loan of an IMS system to evaluate in the laboratory.

Colorimetric Method. An analyzer using the colorimetric "dot" method was tested in the field by other researchers about seven years ago at a MSW incinerator. Accuracy problems were encountered and it was suspected that those problems involved different levels of humidity between the sample and calibration gases. We contacted the manufacturer of the colorimetric analyzer to discuss the accuracy problems that had been encountered earlier. Technical experts with the company informed us that the relative humidity at room temperature of the gas delivered to the analyzer needs to be between 25 and 70%. HCl readings are too low if humidity levels are outside of that range. It was also noted that the sample gas temperature at the detector inlet must be at or below 50°C. They believe that their instrument will work for our application and that sample delivery will be the most difficult part. We are currently pursuing the loan of one of their process gas analyzers for evaluation in our laboratories.

Problems with Ammonia. In previous work, a laboratory apparatus containing Teflon and stainless steel (types 304 and 316) components was designed and constructed to blend, heat, and deliver gases to simulate gasifier streams (6). Good HCl recoveries were obtained by passing an HCl gas mixture (3000 ppm_v in nitrogen) through the testing apparatus using both heated (180-200°C) and unheated gases with flows of 100-550 mL/min.

In our recent 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 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 of solid NH₄Cl in sections of the sample line that were at room temperature. The formation of NH₄Cl has important sample delivery and analytical implications. For sample delivery, losses of chloride during sample transport must be avoided. Based on the vapor pressure of NH₄Cl as a function of temperature, it is evident that NH₄Cl can be kept in the vapor phase by proper heating of the sample line. However, since most of the HCl monitors to be evaluated are low-temperature (<100°C) analyzers and require the chloride to be present as HCl rather than NH₄Cl, the presence of NH₃ gases in the sample stream presents a problem.

Because it may be necessary to remove NH₃ gas prior to determining HCl in coal gasifier streams, tests were performed with a reduction tube consisting of a heated quartz tube containing about 100 mL of granular (minus 20 mesh) copper. Components of the reduction tube were purchased from Perkin Elmer, who manufactures the tubes for use in their CHN analyzers. Semiquantitative tests were performed using

color-indicating paper for NH₃ by passing 5% (molar) NH₃ in a nitrogen balance through the reduction tube at a flow rate of about 25 mL/min. Results of these tests indicated that the reduction tube needs to be at a temperature of about 800-900°C in order to effectively remove the NH₃ under the concentrations and flows employed. However, additional semiquantitative tests indicated that the removal of NH₃ decreased as the flow rate was increased beyond 25 mL/min.

To help quantify the decrease in NH₃ removal efficiency with increased flow rate, NH₃ concentrations exiting the reduction tube were measured using a Sensidyne gas sampling pump with color-indicating NH₃ detector tubes (accurate to within $\pm 25\%$). For these tests, 5% (molar) NH₃ in a nitrogen balance gas was passed through the reduction tube at about 950°C. For gas flows of 25 and 45 mL/min, final NH₃ concentrations were 200 and 600 ppm, respectively. This corresponds to a NH₃ removal efficiency of nearly 100% at 25 mL/min and about 99% at 45 mL/min.

Another series of tests was performed in which higher flow rates and lower initial NH₃ concentrations were used. When 5% NH₃ flowed through the tube at 100 and 500 mL/min, NH₃ removal efficiencies at 950°C were $\geq 99\%$ and 90-95%, respectively. When 1% NH₃ was used, NH₃ removal efficiencies were 100% and 95% at flow rates of 500 and 1000 mL/min, respectively.

Tests were also performed to determine whether anticipated concentrations of HCl in a gasifier can pass through the hot reduction tube without being affected. This was studied by passing a 300 ppm HCl stream in a N₂ balance through the reduction tube, which had been previously exposed to NH₃, as the temperature was increased from ambient to 950°C. Results of these tests and results from NH₃ removal tests obtained previously are depicted in Figure 4. The reduction tube appears to effectively remove NH₃ only at temperatures at which the analyte (HCl)

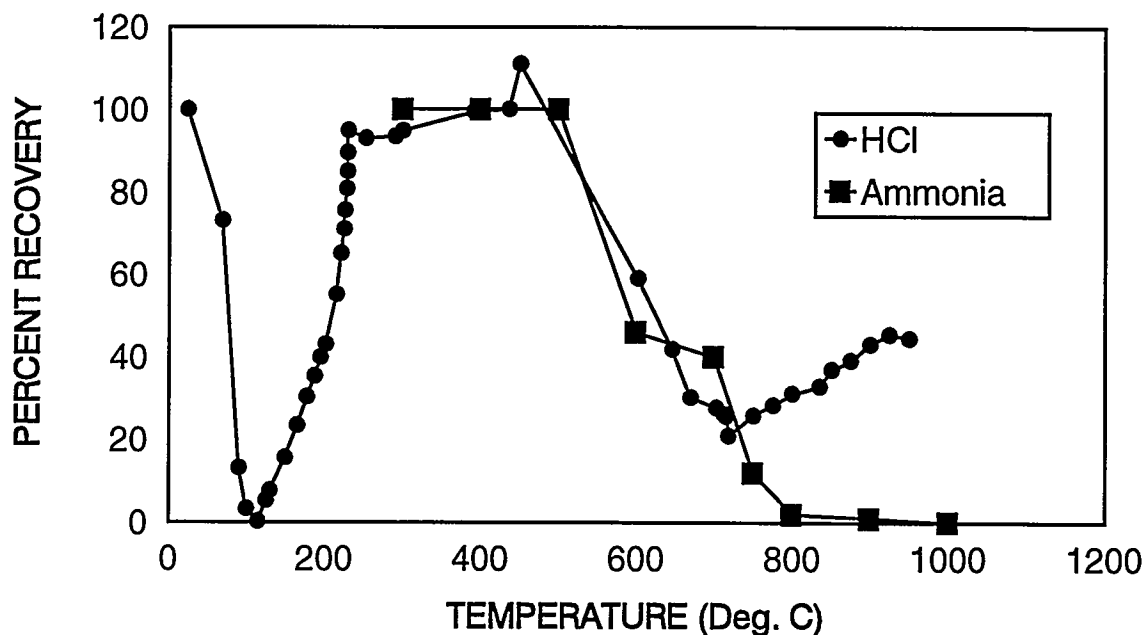


Figure 4. Percent Recovery of NH_3 and HCl Versus Temperature

does not pass through the tube without loss. Also, NH_3 is not permanently removed by the copper. At temperatures above 600°C , the decrease in HCl concentration is apparently due to the formation of NH_4Cl . The presence of NH_3 is due to previous tests involving NH_3 streams. Thus, this approach for removing NH_3 does not appear to be promising. Consequently, alternate approaches for NH_3 removal, including oxidation, are currently being considered.

Calibrator Accuracy. Verification of the HCl concentration output from the calibrator is important for evaluating HCl analyzers and for performing accurate calibration of those analyzers. Consequently, numerous experiments were performed to test the correct operation of the calibrator and to check the accuracy of permeation tubes supplied by the manufacturer. The permeation tubes used in our studies are filled with an azeotropic 20.2% solution of hydrochloric acid.

Calibration gases from the permeation tube calibrator were bubbled into a series of collection solutions for several days. The solutions were then analyzed titrimetrically and by ion chromatography to determine the amount of chloride collected. In addition, calibration gases were passed directly from the calibrator into a Teflon gas sampling bag. The gas in the bag was analyzed 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 in the permeation chamber were analyzed directly with the Sensidyne sampling pump and detector tubes. The total mass loss rates from the permeation tubes were also checked to determine whether they were within the range specified by the vendor (i.e., $\pm 15\%$). This was done by performing gravimetric analyses on the tubes after using the tubes in the heated permeation chamber for several days. All of the above tests were performed with two

different permeation tubes with nominal emission rates of 2500 and 6000 ng/min of 20.2% HCl.

Results of the gravimetric analyses indicated that the total emission rates were within the uncertainty listed for the tubes. The HCl concentration determined by analyzing the gases directly using the Sensidyne pump and detector tubes was about 50% of the nominal value. Results of the analyses of the collection solutions by titration and ion chromatography indicated that the solutions contained only about 20% of the HCl expected based on the nominal HCl emission rates from the permeation tubes. It is unlikely that all of the different collection and analytical techniques are erring on the low side. Consequently, we suspect the HCl concentration of the gases from the calibrator are lower than expected.

The equipment vendor has confidence in the accuracy of their equipment. However, their experimental verification of proper HCl emissions from the tubes are based on gravimetric determinations of the permeation tubes to check mass loss rates. They have not determined HCl concentrations of gases emitted from the calibrator. Although the permeation tubes are filled with an azeotropic solution of hydrochloric acid, the emitted vapors from the tubes may have a lower HCl concentration. Also, it is possible that there are some HCl "wall losses" during transport of the calibration gases.

Gas Conditioning

In order to monitor Hg and HCl in actual gasifier streams, it is likely that the dew point of the gas stream will need to be decreased substantially by removing much of the water or by dilution. Potential methods for removing moisture from gasifier streams without affecting Hg or HCl concentrations are being evaluated.

Common approaches for moisture removal prior to analysis of effluent gases include the use

of condensers, desiccants, and selective permeable membranes. Condensers and desiccants are unsuitable for our purposes because of loss of analytes that would occur during gas conditioning. There is disagreement among the experts as to whether HCl would be retained by permeable membranes, and little information is available on the effects of those membranes on Hg vapor. The applicability of using permeable membranes to condition our sample gases requires experimental verification. Another possible gas conditioning approach for moisture removal is to use a special chemically selective membrane, such as Nafion, which reportedly has a higher moisture removal rate than permeation membranes and reportedly does not retain significant amounts of Hg or HCl.

FUTURE WORK

For Hg, problems associated with the use of AA will be investigated. The primary problem anticipated is the presence of interfering compounds (e.g., aromatic hydrocarbons and sulfur compounds) in actual gasifier streams. Future work will focus on studying approaches for either removing interfering compounds through gas conditioning or for performing suitable spectral background corrections during analysis of the gasifier streams. The best approach for use in an on-line analyzer for coal gasifiers will then be selected. Also, because AA analysis requires the Hg to be present as elemental Hg, approaches for converting Hg compounds (e.g., methyl mercury) to the elemental state will be investigated.

For HCl, the analytical method to be used for the on-line monitor will be selected. Studies on the delivery of known amounts of HCl will continue. In particular, the use and accuracy of permeation tubes and permeation tube calibration systems will continue to be investigated.

Methods for removing or destroying NH_3 in the sample gas prior to HCl analysis will be considered and tested.

For both Hg and HCl, subsequent testing will include determining the effects of gas temperature, pressure, and composition (including moisture content) on detection limits, dynamic range, precision, and accuracy. The effects of sample line composition will also be considered. Modifications to existing commercial instruments will be made in order to adapt those systems for use with gasifier streams.

The severity of interferences from compounds such as H_2S , HF, and selected hydrocarbons on Hg and HCl determinations will continue to be investigated. In addition, suitable sample handling systems will be developed. Gas conditioning steps which may be required include temperature and pressure adjustments, filtering particulate matter, and removing moisture and interfering gases. The amount and type of gas conditioning will be largely dependent on the analytical methodology employed. The effects of any necessary sample conditioning steps (e.g., moisture removal) on analyte concentrations will be examined. Ultimately, prototype integrated analytical systems which appear to be acceptable based on results of laboratory studies will be tested in the field.

ACKNOWLEDGEMENTS

We thank Laura Clifford for her research assistance in this study. We also thank Frank Schaedlich, President of Tekran Incorporated, for the loan of an atomic fluorescence Hg detector and for helpful discussions. In addition, thanks are due to Thermo Environmental Instruments for the loan of an HCl analyzer based on GFCIR and to Steve Schelwat of WESLINE Company for helping to arrange that loan. This work was performed with funds provided by the U.S.

Department of Energy through the Morgantown Energy Technology Center. Ames Laboratory is operated for the U.S. D.O.E. by Iowa State University under Contract No. W-7405-Eng-82.

REFERENCES

1. G. N. Krishnan, G. T. Tong, B. J. Wood, and N. Korens, "High Temperature Coal Gas Chloride Cleanup for Molten Carbonate Fuel Cell Applications," Final Report, DOE/MC/21167-2080 (DE87001041), November 1986, pp. 57-60.
2. G. L. Anderson, F. O. Berry, B. D. Harmon, R. M. Laurens, and R. Biljetina, "Development of a Hot Gas Cleanup System for Integrated Coal Gasification/Molten Carbonate Fuel Cell Power Plants," Final Report, DOE/MC/19403-1816 (DE86001589), October 1985, p. A-4.
3. T. Grindley and T. H. Gardner, "Trace Contaminants in Fixed-Bed Gasifier Gas," in Proc. Twelfth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Volume II, DOE/METC-92/6128, Vol. 2 (DE93000229), September 1992, pp. 479-497.
4. G. A. Norton, C. D. Chriswell, D. E. Eckels, and W. H. Buttermore, "On-Line Monitoring of Mercury and Hydrogen Chloride in Hot Gases from Coal Gasifiers," in Proc. Coal-Fired Power Systems 93 -- Advances in IGCC and PFBC Review Meeting, DOE/METC-93/6131 (DE93000289), June 1993, pp. 276-283.
5. V. Harris, "Field Validation of the Portable Ion Mobility Hydrogen Fluoride Continuous Emissions Monitoring Systems," presented

at Stationary Source Sampling & Analysis for Air Pollutants, XIX, Engineering Foundation Conference, San Diego, CA, March 26-31, 1995.

6. G. A. Norton, C. D. Chriswell, D. E. Eckels, and R. E. Peters, "Chloride and Mercury Monitors for Air Toxics Measurements," in Proc. Coal-Fired Power Systems 94 -- Advances in IGCC and PFBC Review Meeting, Morgantown, WV, June 21-23, 1994, 492-497.