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CHLORIDE AND MERCURY MONITORS FOR AIR TOXICS MEASUREMENTS

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DISCLAIMER

P21 Chloride and Mercury Monitors for Air Toxics Measurements

CONTRACT INFORMATION

Contract Number	W-7405-Eng-82 (Ames) 93MC30024.000 (METC)
Contractor	Ames Laboratory Iowa State University Ames, Iowa 50011
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Principal Investigators	Glenn A. Norton Colin D. Chriswell
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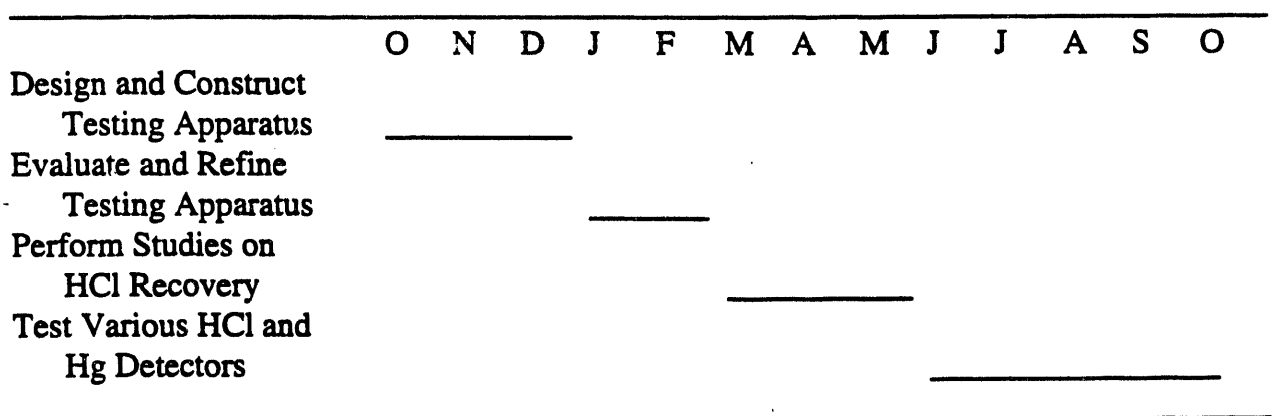
METC Project Manager	Margaret A. Kotzalas
Period of Performance	October 1, 1993 - continuing
Schedule and Milestones	

FY94 Program Schedule



OBJECTIVES

Ames Laboratory will develop an integrated sampling and analysis system suitable for on-line monitoring of hydrogen chloride (HCl) and mercury (Hg) in advanced coal-based gasifiers. The objectives of this project are to 1) summarize current technology for monitoring HCl and Hg in gaseous effluents, 2) identify analytical techniques for such determinations in high-temperature, high-pressure gases from coal-based systems of interest to METC 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 HCl and Hg concentrations in hot, high-pressure gases from power producing systems are of environmental and technological concern, instruments suitable for determining HCl and Hg 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 involved can pose special analytical problems. 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). Concentrations of Hg are anticipated to be in the range of 0.2 - 20 ppb in the raw gas.

PROJECT DESCRIPTION

In previous work (4), commercially available instrumentation suitable for the monitoring applications of interest was reviewed and evaluated. Also, pertinent literature was assessed to obtain additional information on analytical methodologies which could potentially be used. Based on the results of that work and our continuing review of available instruments, analytical approaches which appear to have the most potential for our monitoring applications were identified.

For HCl, the techniques currently being considered are infrared absorption, colorimetry, and ion mobility spectroscopy. For Hg, atomic absorption and atomic fluorescence techniques have been selected for testing in the laboratory.

Subsequent laboratory work will determine which analytical systems show the most promise for on-line analysis of HCl and Hg. Promising analytical instruments (or components of instruments) will be assembled and/or modified 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 systems themselves. After the laboratory studies have been completed, prototype instruments will be tested and evaluated in the field.

RESULTS

Testing Apparatus

A laboratory apparatus was designed and constructed to blend, heat, and deliver gases to simulate gasifier streams. That apparatus will be used to study sample delivery and to evaluate various detectors. The basic design consists of a Teflon gas mixer for blending metered gases, a

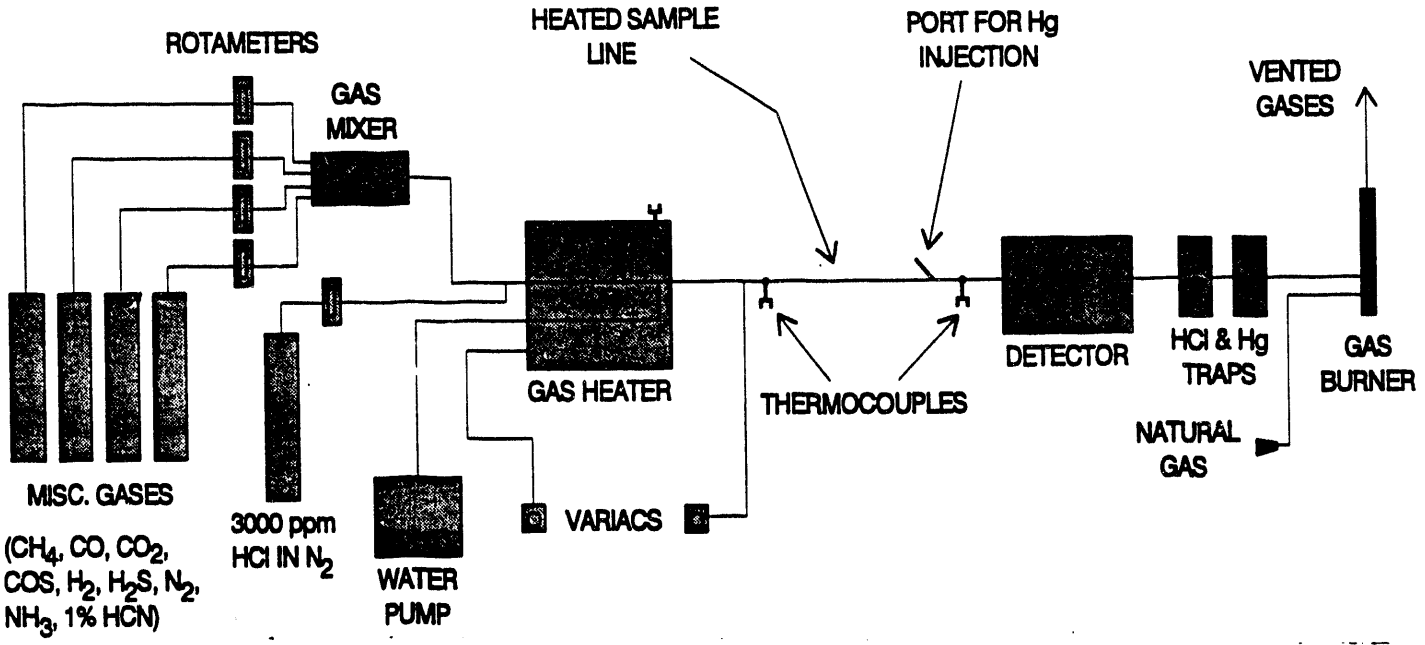


Figure 1. Testing Apparatus for Evaluating HCl and Hg Analyzers

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 the other gas lines are made of stainless steel. A schematic diagram of the current testing apparatus is shown in Figure 1.

After assessing the overall operation of the initial system, modifications or alternate approaches 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. 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 (LC). The LC 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.

HCl Studies

Preliminary studies were initiated to determine whether a known amount of HCl can be reliably delivered to a detector. Initial tests involved recovering HCl directly from a cylinder containing a HCl gas mixture (3000 ppm_v in nitrogen). Recoveries were determined by bubbling the gas into an absorbing solution and then titrating the solution to determine the amount of chloride collected. Erratic results and low recoveries were obtained at relatively low gas flows (e.g., 10 cm^3/min), even when using Teflon lines directly from the gas cylinder. The erratic results do not appear to be caused by

analytical errors, problems in collection efficiency, gas metering errors, or losses in the Teflon line. Rather, there appears to be erratic adsorption/desorption processes occurring upstream from the regulator outlet, despite the precautions taken to select a regulator with nonreactive components. Good precision for HCl recoveries was obtained by increasing the gas flow rates to 100 cm^3/min or more.

Subsequent tests involved passing the HCl gas mixture through the entire testing apparatus. Those tests were performed both with heated (180-200°C) and unheated gases. In the former case, tests were also performed with and without about 50% water present in the gas stream. A total of about 25 tests were performed using HCl/N_2 gas flows of 100-550 cm^3/min. Overall, HCl recoveries averaged 86 ± 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%.

An alternate approach for delivering known amounts of HCl was investigated. In that approach, a dilute aqueous hydrochloric acid solution is pumped at a known rate into a stainless steel coil in a hot sand bath. The hot coil vaporizes the HCl and water, which are then introduced to the primary gas stream in a heated sample line. By varying the water flow rate and the HCl concentration in the water, it should be possible to obtain both the desired moisture and HCl gas concentrations in the delivered gases. Good recoveries and precision were obtained in some cases. However, pumping problems were encountered when attempting to use the low flows necessary to attain both the desired H_2O and HCl concentrations at the total gas flow rate (about 1 liter/min) being tested. Efforts in this area have been discontinued since the HCl gas mixture appears to be working satisfactorily.

We have begun contacting various companies in an attempt to borrow the detectors of interest. These include one colorimetric detector and two different gas filter correlation IR units. In addition, we are now performing our final screening of Fourier transform IR detectors and ion mobility spectrometers. One or two detectors from each of the latter analytical approaches will also be selected for study.

Hg Studies

In preparation for later tests involving Hg determinations, some preliminary studies were performed to study potential problems in analyzing Hg using conventional instruments and standard procedures. One potential calibration technique is to inject Hg vapors (using gas-tight syringes) into the sample gas stream. The validity of using that approach was experimentally confirmed.

Studies were also performed using liquid Hg standards. Minor procedural variations were found to significantly affect the amount of Hg detected in those standards. In particular, when and how the standards are acidified during preparation were found to be important variables. By carefully controlling those and other variables, full recoveries of 100-ng quantities of Hg in liquid standards can now be consistently obtained. That work will be important when verifying the operation of a Hg permeation tube calibration system which will be used to compare different Hg detectors.

A final review of potential instruments for use in an on-line monitor was made. Measurements based on resistance changes in a gold film originally appeared promising. However, after continued discussions with company representatives, it became evident that the gold film approach is probably not a method of choice at this time. This is largely due to the costs and logistics associated with the frequent off-line calibrations which would be required for continuous analyses of gas streams. Consequently, that approach is no longer being

considered for on-line monitoring of coal gasifier streams.

Two atomic absorption detectors and one atomic fluorescence detector have been selected for study in our laboratories. Contacts with the pertinent companies have been initiated in an attempt to acquire the detectors of interest as short-term cost-free loans. Brief acquisitions of those instruments will allow us to make valid, direct instrument comparisons. This will in turn help us select the best instrument for use in an on-line Hg analyzer.

FUTURE WORK

Studies on the delivery of known amounts of HCl from our testing apparatus will continue. In this regard, the effects of gas temperature, gas stream composition, and flow rate on HCl recovery will be studied in more detail. HCl recovery will be examined while the entire testing apparatus is in operation and while all of the gases selected to simulate coal gasifier streams are flowing through the system. After those tests, our laboratory evaluation of selected HCl detectors will begin.

For Hg, a permeation tube calibration system and manual injections of Hg vapor (using gas-tight syringes) will be used to evaluate various detectors. Testing will be performed both with and without the use of gold amalgamation for collecting and concentrating Hg prior to analysis. A double gold amalgamation approach may also be integrated into the analytical system and tested as a possible approach for improving accuracy and precision.

For both HCl and Hg, 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 studied. Modifications of existing instruments will be made, as needed, for application to gasifier streams.

The severity of interferences from compounds such as H_2S, CH_4, HF, and H_2O on HCl and Hg determinations will 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. Ultimately, prototype analytical systems which appear to be acceptable based on results of laboratory studies will be integrated with the gas handling system and then tested in the field.

ACKNOWLEDGEMENTS

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REFERENCES

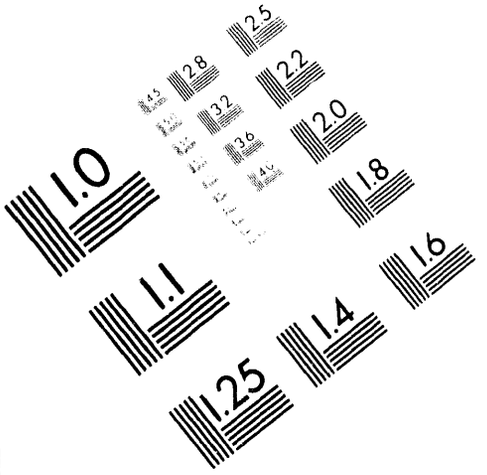
1. G. N. Krishnan, G. T. Tong, B. J. Wood, and N. Korens, "High Temperature Coal Gas Chloride Cleanup for Molten Carbonate Fuel Cell Applications," Final Report, DOE/MC/21167-2080 (DE87001041), November 1986, pp. 57-60.

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.



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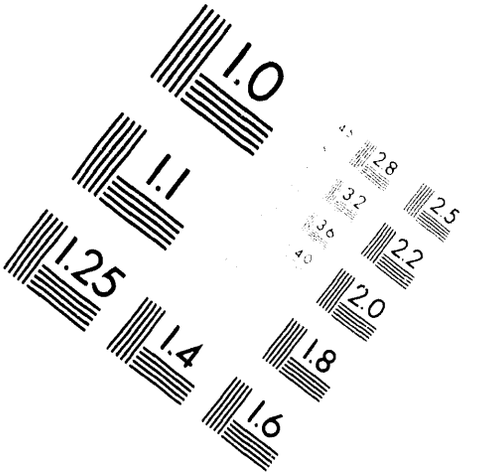

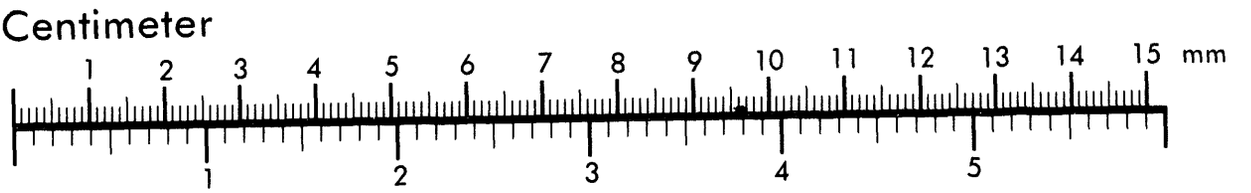

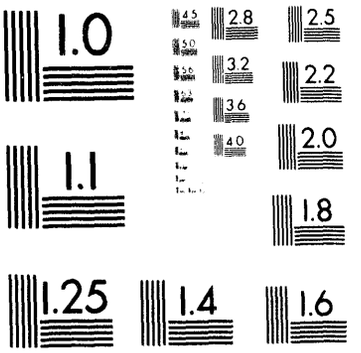

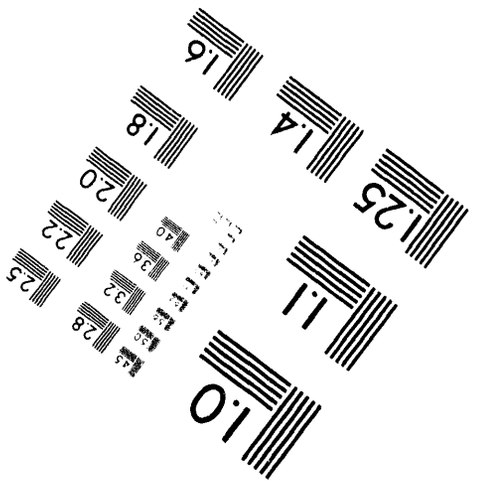

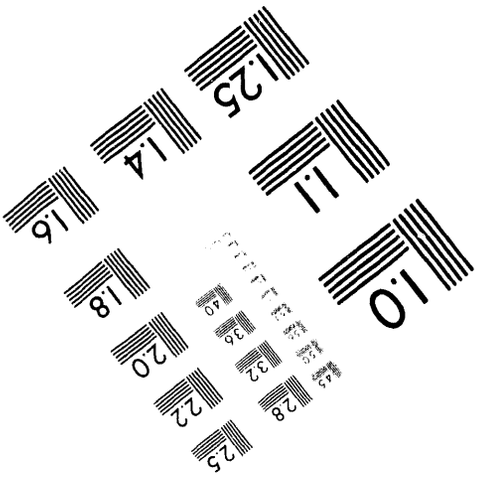

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