CONTINUOUS EMISSION MONITOR FOR HYDROCHLORIC ACID

Tunable Diode Laser Test Report
Unisearch LasIR S Series

1022083

Final Report, December 2011

EPRI Project Manager
C. Dene

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

University of California at Riverside

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc.

Copyright © 2011 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This report was prepared by

University of California at Riverside
Center for Environmental Engineering and Technology
Bourns College of Engineering
1084 Columbia Avenue
Riverside, CA, 92507

Principal Investigators
J. Pisano
T. Durbin
K. Bumiller

This report describes research sponsored by the Electric Power Research Institute (EPRI).

This publication is a corporate document that should be cited in the literature in the following manner:

Continuous Emission Monitor For Hydrochloric Acid: Tunable Diode Laser Test Report, Unisearch LasIR S Series. EPRI, Palo Alto, CA: 2011 1022083.

ACKNOWLEDGMENTS

The following organization(s), under contract to the Electric Power Research Institute (EPRI), prepared this report:

University of California at Riverside
Center for Environmental Engineering and Technology
Bourns College of Engineering
1084 Columbia Avenue
Riverside, CA, 92507

Principal Investigator
J. Pisano
T. Durbin
K. Bumiller

This report describes research sponsored by EPRI. <In most cases, reports should indicate EPRI only as the "sponsor." If there is a desire to acknowledge funders, insert the following sentence: EPRI would like to acknowledge the support of the following organizations: [list]>.

The authors would like to thank Christopher Brown, Business Manager and Co-Owner of Energy Research Consultants (ERC) for their support of this project. ERC provided UCR with their Unisearch TDL based HCl instrument for the evaluation. ERC also gave us access to their laboratory to conduct preliminary investigations. Their proximity to UCR and kind loaning of the instrument as well as the IR detector helped us successfully interface the Unisearch TDL system into the UCR laboratory. Special thanks go to Ulises Mondragon, Senior Research Engineer and Jonathan Bastiaans, Research Engineer both of ERC for their help in doing the preliminary tests conducted at the ERC facility. This included audit cell verification and initial background response tests. Considering the issues we faced with the HCl delivery in the UCR laboratory, this project would not have been done in as timely a manner without their assistance.

ABSTRACT

In the United States, consent decrees, state laws and the proposed federal Maximum Achievable Control Technologies (MACT) standards for coal-fired plants drive the need for robust, accurate, and certifiable continuous emissions monitors (CEMs) for mercury, particulate matter (PM), acid gasses. Under current rules hydrochloric acid (HCl) is not continuously measured at most plants. However, as the MACT has been proposed it is likely that many plants will elect to monitor HCl. The level of HCl expected at plants with highly controlled emissions levels are expected to be much less than 5 ppm. With such low emission levels, it is important to understand the limit of detection and any potential measurement interferences. This work describes work done to verify the instrument detection limits of tunable diode laser base analyzers for measurements and test potential interfering species.

EPRI initiated a project with the University of California to use an existing laboratory facility for simulating in-situ measurements of NH_3 via tunable diode laser spectroscopy for investigating acid base gasses, as HCl, HF and HBr. The laboratory was modified to be able to measure these types of gasses but the flue gasses that were required to be simulated needed to be at the exhaust of the stack, where temperatures are normally lower at 100-200 °C. Also the sensitivity and reproducibility requirements for the evaluation measurements were more stringent as unlike the NH_3 measurements which serve as a process measurement, the acid gas measurements were for CEMS (continuous emission monitoring) applications and ultimately would need to meet EPA requirements. This work documents the limits of detection and precision of TDL monitors for measurement of acid gasses in flue gas.

CONTENTS

1 **INTRODUCTION 1-1**

2 **TECHNOLOGY DESCRIPTION 2-1**

Tunable Diode Lasers 2-1

Tunable Diode Laser Spectroscopy 2-1

Tunable Diode Laser Spectroscopy Signal Analysis Via Fast Scan Averaging 2-2

System Description 2-5

3 **TESTING PROTOCOL AND QUALITY ASSURANCE 3-1**

Test Configuration 3-1

Sample Cell 3-1

Calibration and Gas Delivery System 3-3

Water Delivery 3-4

Temperature Control System 3-6

System Temperature Measurements 3-7

Test Plan 3-7

Quality Control 3-8

Checks of HCl Delivery System vs. Reference TDL vs. ISE Method 3-9

Calibration Methodology 3-12

Mass Flow Controllers 3-12

Temperature Sensors 3-13

Checks of Water Content 3-13

4 **TESTING RESULTS 4-1**

TDL Laboratory Installation 4-1

Agreement with Standards and Temperature Correction 4-3

Audit Cell Verification of System Calibration 4-4

System Response Tests 4-6

IR Spectroscopy of Typical Coal Combustion Flue Gases 4-7

Investigation of IR Spectroscopy of Typical Coal Combustion Flue Gases in the Region where HCl Absorbs 4-10
Interference Tests 4-16
Data Analysis Moisture and Temperature Effects 4-19
Linearity 4-22
Precision 4-22
Zero Drift and Minimum Detection Limit 4-23

***5* SUMMARY 5-1**

***6* REFERENCES 6-1**

***A* APPENDIX A-1**
System Applications A-9
Specifications A-9
Company Information A-10

LIST OF FIGURES

Figure 3-1 Shows a Schematic Layout of the Laboratory Constructed to Conduct these Tests; Note the Laboratory was Constructed for NH_3 TDl Measurements to Simulate Process Temperatures (up to 400 ºC) and was Modified for these HCl Tests as Described in Section 3.4 3-2

Figure 3-2 Shows the Sample Cell with a Base Path of 1.0 Meters, has a Radiative Heater and White Insulation, Also Shows Setup for the Experiments Presented Here with Unisearch Optics Mounted and the Instrument Tested 3-3

Figure 3-3 Shows the Moisture Generation System which Consists of a Water Reservoir, a Graduated Burette, a Positive Displacement Pump, and the Water Heating System 3-5

Figure 3-4 Sample Cell with Light Path Flanges, Shows Gas Ports, Radiative Heating Assembly and Thermocouple Locations 3-6

Figure 3-5 Sample Cell Temperature Control System Schematic. 3-7

Figure 3-6 HCl Calibration Gas Cylinder 3-9

Figure 3-7 Teflon Tube Inserted into Sample Cell, Illuminated with a Visible Light for Better Viewing. Note, the Parralax View of the Teflon Tube is Due to the 7 Degree Angle that the Window Flanges are Constructed At 3-10

Figure 3-8 Teflon Tube Inserted into Preheater Cell which also was Converted to have a Radiative Heater, the Mixing Chamber was also Teflon Coated and Teflon Lines were Used for Transport to the Mixing Chamber 3-11

Figure 3-9 Teflon Tube Inserted into Preheater Cell which also was Converted to have a Radiative Heater, the Mixing Chamber was also Teflon Coated and Teflon Lines were Used for Transport to the Mixing Chamber 3-12

Figure 4-1 Single Pass Transmitter Assembly from Unisearch Mounted on UCR Laboratory Test Cell 4-1

Figure 4-2 Single Pass Receiver Assembly from Unisearch Mounted on UCR Laboratory Test Cell 4-2

Figure 4-3 LasIR Instrument Connected via Ethernet to Accompanying Laptop from Unisearch Mounted on UCR Laboratory Test Cell 4-3

Figure 4-4 LasIR Instrument, Configuration File at 373.3 K (100 ºC) 4-5

Figure 4-5 Audit Cell Verification of HCl Monitor Response Showing Audit Spike Value of 40.18 ppmV 4-6

Figure 4-6 Instrument Response Test over the Calibration Range 4-7

Figure 4-7 Graphical Representation of System Response over the Concentration Range at 100 ºC 4-8

Figure 4-8 Graphical Representation of System Response over the Concentration Range at 200 ºC 4-9

Figure 4-9 Typical Gaseous Infrared Spectra of Major Flue Gas Species Observed from Coal-fired Combustion Processes 4-10

Figure 4-10 Isotopologues Investigated for HCl in the 5500 to 6000 cm^{-1} Spectral Range 4-11

Figure 4-11 Resulting Hi Tran Database Spectra for HCl in the 5500 to 6000 cm^{-1} Spectral Range 4-12

Figure 4-12 Isotopologues Investigated for CO_2 in the 5500 to 6000 cm^{-1} Spectral Range 4-12

Figure 4-13 Resulting Hi Tran Database Spectra for CO_2 in the 5500 to 6000 cm^{-1} Spectral Range 4-13

Figure 4-14 Isotopologues Investigated for NO in the 5500 to 6000 cm^{-1} Spectral Range 4-13

Figure 4-15 Resulting Hi Tran Database Spectra for NO in the 5500 to 6000 cm^{-1} Spectral Range 4-14

Figure 4-16 Isotopologues Investigated for NH_3 in the 5500 to 6000 cm^{-1} Spectral Range, No Resulting Hi Tran Spectra 4-14

Figure 4-17 Isotopologues Investigated for CO in the 5500 to 6000 cm^{-1} Spectral Range, No Resulting Hi Tran Spectra 4-15

Figure 4-18 Isotopologues Investigated for SO_2 in the 5500 to 6000 cm^{-1} Spectral Range, No Resulting Hi Tran Spectra 4-15

Figure 4-19 Cylinder and Specification Sheet Containing CO, CO_2 and NO Used to Investigate for Possible Interferences of HCl in the 5500 to 6000 cm^{-1} Spectral Range 4-17

Figure 4-20 Graphical Representation of System Response over the Concentration Range at 0% Moisture at 200 ºC during the Interference Tests 4-18

Figure 4-21 Graphical Representation of the Percent Difference over the Three Groupings at Each of the Sampling Levels, Group 1: 100 ºC, Group 2: 200 ºC, Group 3: 200 ºC Interference Tests 4-21

Figure 4-22 Linear Regression of the measured response from the Unisearch S Series LasIR SM410 as compared tp the source calibration value. The measured responses are averaged from all 10 tests at each source calibration value that encompassed the range of moistures and temperatures used in this evaluation. 4-22

Figure A-1 Different Configurations of UnisearchLasIRTM S-Series Controller A-2

Figure A-2 Schematic of Fiber Coupled LasIR System A-3

Figure A-3 Front Panel of Unisearch S-Series Two Channel LasIR A-5

Figure A-4 Back Panel of Unisearch S-Series Two Channel LasIR A-5

Figure A-5 The Front Panel of an Eight Channel Multiplexed Rack Mounted S-Series LasIR and Two Channel Table mount Beamsplit S-Series LasIR with Dimensions and Channel Availability A-6

Figure A-6 Unisearch Optics that can go Single Path with an Emitter on One Side and a Detector A-7

Figure A-7 Unisearch Optics with a Transmitter/Receiving Assembly on One Side and a Retroreflector on the Other Side A-7

Figure A-8 Unisearch Optics Mounted in a NEMA4 Enclosure for Industrial Applications, Box Open A-8
Figure A-9 Unisearch Optics Mounted in a NEMA4 Enclosure for Industrial Applications, Box Closed, Two Sizes are Available A-8
Figure A-10 Unisearch Optics Mounted in a NEMA4 Enclosure Measuring HCl at an Incinerator A-9

LIST OF TABLES

Table 3-1 Lists the Quality Control Checks Conducted for the Laboratory Setup used in the Instrument Evaluation 3-14

Table 4-1 Results of Unisearch S Series LasIR SM410 for 1.0 Meter Sampling System at 100 ºC 4-8

Table 4-2 Results of Unisearch S Series LasIR SM410 for 1.0 Meter Sampling System at 200 °C 4-9

Table 4-3 Interference Testing Gas Concentrations 4-16

Table 4-4 Interfering Gas Test Results of Unisearch S Series LasIR SM410 for 1.0 Meter Sampling for NO, CO, CO_2, SO_2 and NH_3 at 0% Moisture and 200 ºC 4-18

Table 4-5 Lists the Average Percent Difference of the Measured Results Obtained with Respect to the Standard Gas Values Obtained with the Following Grouping: Group 1: 100 ºC, Group 2: 200 ºC, Group 3: 200 ºC Interference Testing 4-20

1
INTRODUCTION

In the United States, consent decrees, state laws and the proposed federal Maximum Achievable Control Technologies (MACT) standards for coal-fired plants drive the need for robust, accurate, and certifiable continuous emissions monitors (CEMs) for mercury, particulate matter (PM), acid gasses. Under current rules hydrochloric acid (HCl) is not continuously measured at most plants. However, as the MACT has been proposed it is likely that many plants will elect to monitor HCl. The level of HCl expected at plants with highly controlled emissions levels are expected to be much less than 5 ppm. With such low emission levels, it is important to understand the limit of detection and any potential measurement interferences. This work describes work done to verify the instrument detection limits of tunable diode laser base analyzers for measurements and test potential interfering species.

EPRI (The Electric Power Research Institute) has contracted the University of California at Riverside to construct a laboratory facility for simulating in-situ measurements of NH_3 via tunable diode laser spectroscopy. The role of the laboratory was to verify the response of various TDL (tunable diode laser) based instrumentation over temperature ranges and moisture levels that are representative in typical flue gasses at coal-fired power plants. The flue gasses were those past the economizer but prior to the air heater and are typically 300-400 °C and up to 12% moisture. The laboratory was constructed and finalized in 2007 and has been used to successfully evaluate 8 different TDL instruments and 6 manufacturers for NH_3. Results from these tests can be found on EPRI reports (xxx).

EPRI then approached the University of California for the possibility to utilize the same facilities for investigating acid base gasses, as HCl, HF and HBr. The laboratory was then modified to be able to measure these types of gasses but the flue gasses that were required to be simulated needed to be at the exhaust of the stack, where temperatures are normally lower at 100-200 °C. Also the sensitivity and reproducibility requirements for the evaluation measurements were more stringent as unlike the NH_3 measurements which serve as a process measurement, the acid gas measurements were for CEMS (continuous emission monitoring) applications and ultimately would need to meet EPA requirements.

The levels chosen to conduct the evaluation were chosen to be most representative of typical exhaust gas levels for the species of gasses investigated. For HCl it was determined that levels should be in the range of 0.5 to 5 ppmV. Since most exhaust stacks are around 5 meters, and a cross duct version of optics is required for the in-situ monitoring, the levels chosen are then 2.5 to 25 ppmV-m, as TDL sensitivity is nominally reported in ppmV-m, where the levels are multiplied by the path length. Since our sampling cell is only 1 meter long, the values chosen for the evaluation were 2.5, 5, 10, 15 and 25 ppmV, which yielded levels of 2.5, 5, 10, 15 and 25 ppmV-m similar to the requirements at coal-fired power plant flue gasses.

Also since this data evaluation is for CEMS applications, further investigation from other gasses present in the exhaust stream which may cause interferences or in any way bias the TDL measurements needed to be conducted. The possible interfering species were identified from typical known constituents of gasses in coal-fired power plants exhaust streams, these being H_2O, CO, CO_2, NO and SO_2. Also with the prevalence of SCR and or SNCR technologies being employed for NOx control, possible interference from NH_3 was required to be evaluated as well.

This report provides the evaluation of one TDL instrument, that being from Unisearch Associates Inc., their LasIR 410 S-Series. This instrument was chosen for two reasons:

1. they already have one coal-fired power plant site where their technology is being used for continuous HCl measurements
2. their instrumentation performed satisfactorily during the EPRI sponsored NH_3 evaluations

2
TECHNOLOGY DESCRIPTION

Tunable Diode Lasers

Tunable diode lasers (TDLs) are fabricated on a tiny piece of semiconductor material typically only 0.5 mm square. The diode lasers themselves produce laser light at specific wavelengths that can be continuously tuned over narrow wavelength intervals. Adjusting the device temperature enables tuning of the laser output, and even finer tuning can be achieved by adjustment of the laser operating current (Schiff et al., 1992). The development of diode lasers themselves has been rapid over the past few years, especially for application in communications transmission. Diode lasers with outputs ranging from visible to mid-infrared wavelengths are commercially available.

Tunable Diode Laser Spectroscopy

TDLs offer significant advantages when applied to spectroscopic systems. As a light source, they provide the highest available power density in a spectrally narrow window. The fundamental, vibrational absorption bands in the infrared region (IR) contain a number of discrete rotational lines, the width and shape depending on temperature and pressure. For some gases the lines are well separated; for others, pressure broadening results in overlapping lines. Larger molecules often possess so many closely spaced lines that thermal or Doppler broadening is sufficient to cause line overlapping (Fried et al., 1991). This inhibits most conventional forms of IR spectroscopy. However, TDLs have spectral resolutions smaller than Doppler line widths, and advantage can be taken of this inherent property (Cooper et al., 1987) because the fundamental, vibrational absorption bands in the IR contain a number of discrete rotational lines but the width and shape of which depend on temperature and pressure. For some gases the lines are well separated under normal atmospheric pressures and temperatures. For other molecules pressure broadening results in overlapping lines, and the pressure in the sampled air can be reduced to minimize this effect. Larger molecules often possess so many closely spaced lines that thermal or Doppler broadening is sufficient to cause line overlapping. Reducing the temperature is not a practical solution to this problem. Even though tunable diode lasers (TDLs) have spectral resolutions smaller than Doppler line widths, advantage can be taken of this property only if the Doppler line width of the molecule is smaller than the separation between adjacent lines.

The fraction of light intensity transmitted through a gas is given by the familiar Beer-Lambert law:

$$P/P_o = \exp(-\sigma(\upsilon)NL)) \qquad \textbf{Equation 2-1}$$

Where P and Po are the transmitted and incident powers respectively, L is the absorption path length in centimeters and N is the concentration of the absorbing molecules in number of molecules per cubic centimeter. $\sigma(\upsilon)$ is the wavenumber dependent absorption cross section in square centimeters per molecule

Tunable Diode Laser Spectroscopy Signal Analysis Via Fast Scan Averaging

Most companies use modulation techniques for improving signal to noise when evaluating the IR absorption signal. Unisearch had originally used a technique to fabricate a commercial tunable diode laser that employed two-tone FM modulation (TTFM). The principle of FM-Spectroscopy employing this type of frequency modulation technique has become well known from its application to communication transmission, which employs high frequency engineering. The development of this technique was done by Cooper et al: under EPRI and NASA funding.

In the case of spectroscopy the modulation of laser light with RF frequencies generates sidebands shifted by the modulation frequency symmetrically to both sides of the laser frequency. The sidebands have the same amplitude but are exactly reverse in phase. When mixing the side bands on a detector, the sum signal compensates to zero. Without absorbing gases in the beam path, the result is a net-zero-signal on the detector. If one of the sidebands is tuned on the center of a trace gas absorption line in the absorption pass, the amplitude of this sideband reaching the detector is reduced. This results in a net detector signal at the modulation frequency. The amplitude of the detected signal is directly proportional to the absorption in the absorption path and therefore also proportional to the gas concentration. A subtraction between irradiated and transmitted light is not necessary with this method, because the difference between absorption and background signal is measured directly.

For example if the laser is a diode laser, it is operated with direct current from a current control module and is tuned with an additional ramp over the absorption line. The operation temperature and current of the laser subsequently control the radiation center wavelength. From a radio frequency generator of about 500 MHz, the RF is coupled into the laser via a Bias-T. After traversing the entire optical path length, the laser radiation is detected with a broadband Detector. The bandwidth of the detector is limited to several hundred MHz and therefore only the interference signal of the two sidebands is detected not the carrier frequency (500 MHz).

This signal is amplified, filtered through a high-pass filter and then supplied to a mixer. The mixer receives the necessary reference signal at via the phase shifter from the same RF-oscillator, with which the laser was modulated. Since the optical system will introduce phase anomalies of the signal, the phase of the signal needs to be adjusted to allow for maximum signal. The mixer-output signal is then amplified with an amplifier filtered with a low-pass filter and then supplied to the further data processing unit. The RF-Module in the instrument includes all components for the phase sensitive detection of a measuring and reference signal and two signal generators to measure in a TTFM (Two-Tone-Frequency-Modulation) mode. The resulting TTFM signal approximates second harmonic detection of the absorption signal which improves sensitivity by a factor of almost 50 as it reduces the impact of laser noise.

Presently Unisearch has developed commercial TDL instrumentation based on the Fast Scan Averaging Technique. Unisearch found from their preliminary investigations and trials using the fast scan averaging technique, four years ago, that they could approximate the same sensitivity of the TTFM technique yet obviate most of the disadvantages that the TTFM technique had. The fast scan averaging technique looks at the direct absorption response.

The fast scan averaging technique measures absorption spectra directly using rapid scan sweep integration, by measuring the absorption signal very fast and averaging the scans. The speed of the measurement is approaching the gigahertz range. By simply measuring the absorption signal many times and faster then can be done using TTFM, the signal to noise ratio is enhanced and detection limits approaching those by TTFM can be achieved. Experiments done by Unisearch for EPRI for Hydrochloric Acid (HCl) have shown that the minimum detection limits of the fast scan technique were only 2 times less sensitive than that by the TTFM technique.

Also since the measurement is very fast information on the laser power is retained, allowing direct, spectroscopic determination of concentration using predetermined line strengths, positions, and broadening coefficients. The result is an absolute measurement of the concentration of the trace gas. This spectroscopically derived concentration, not employing curve fitting routines, takes care of most of the problems that arose from the TTFM technique.

Basically the analyzer continuously oscillates the current applied to the laser. The wavelength of the laser's near infrared light changes when the analyzer changes the current applied to the laser. This allows the analyzer to detect light intensity across the entire absorption peak. The concentration of the target gas, in this case HCl, is calculated from Beer's law by using the intensity measurements to determine the area of the entire absorption peak.

The analyzer with fast scan averaging, is configured for the gas species at the wavelength of absorption for the specific species. The technique does not require calibration, but is verifiable in all configurations by use of an audit cell in the light path.

Although there are sources for span drift in any optical based device, such as changes in the output of the light source, mirror reflectivity, alignment dust levels and electronics contributions to noise the Fast Scan averaged measurement is independent of these traditional sources for span drift.

The fast scans takes the measurement from the left side of the HCl absorption peak, where there is no absorption, across the peak where there is absorption, and to the right side of the peak, where there is no absorption. This scanning process goes back and forth and is repeated thousands of times per second.

Continuously scanning on each side of the peak in the absence of absorption by HCl allows the analyzer to characterize the laser output and take it into account in determination of the area of the HCl peak.

This is a key as this technique continuously looks at the baseline on each side of the HCl peak where HCl doesn't absorb the laser's light.

Therefore, changes in the reflectivity of the mirrors, changes in alignment or dust loadings in the optical path, laser fluctuation or electronics contributions do have an affect on the quantity of signal detected at the detector, have no effect on the area of the moisture peak as it relates to the baseline measured.

Therefore the advantages are:

- Good sensitivity (typically approximates that of TTFM) when compared to normal direct absorption measurements
- Independent of radiation emissions from other sources as IR emissions from the boiler flue gas, as these other sources are compensated in the background measurement
- Very fast response as the technique implies.
- Subtraction between irradiated and transmitted light is also not necessary with this method
- Does not requires curve-fitting routines, as it a straight Beers law calculation
- Therefore the instrument does not need to be calibrated as it is a pure spectroscopic measurement and only needs to be audited for verification of system operation.
- The phase of the optical system which includes the optical elements and fiber cables does not affect the measurement
- The dynamic range of the measurement is no longer limited except to where signal saturation may occur, typically 5 orders of magnitude. Signal saturation effects only occur when the system reaches non-linearity, in a direct absorption mode, this typically occurs at 50% absorption of the total absorption which is far greater than modulation technique based signal analysis, which are normally non-linear at less than 5% absorption.
- Laser power differences of the return beam are no longer a problem unless the optical system becomes optically thick
- Relatively inexpensive as the fast scan technique does not require RF modulation electronics

However there are disadvantages with this technique, they are

- Although the technique does approach levels of sensitivity of the TTFM technique investigations show that it is still at least within a factor of 2 for HCl, meaning that the TTFM would be twice as sensitive but only under a much narrower range of response
- Since the TTFM technique narrows the absorption feature it is less impeded by background shifts and possible interferences than the Fast Scan Technique which has a wider sweep of the absorption feature
- Location of where to actually measure I_o on the fast scan technique can lead to anomalies with respect to power correction and will lead configuration of the instrument and temperature correction to likely be laser specific.

System Description

Unisearch has manufactured and marketed worldwide the LasIRTM line of gas analyzers based on near-infrared tunable diode laser spectroscopy since 1995 when they pioneered the NIR tunable diode laser measurement technique for HF measurements in the aluminum industry. They have introduced their next generation of gas analyzers in 2006 and have further developed their line with a complete revamp in 2010. These models are available as portable single-channel analyzer all the way up to a multiplexed 16-channel analyzer for monitoring multiple species and locations.

The instrument evaluated here is the Unisearch LasIR 410 S-Series for HCl, for a further description of the instrumentation available from Unisearch including different configurations and optical components refer to Appendix A.

3
TESTING PROTOCOL AND QUALITY ASSURANCE

The objective of this study is to document the response of the HCl monitor to a range of conditions from ambient to those most representative of flue gas from a coal-fired boiler. The purpose of this section is to provide an overview of the test conditions that the HCl monitor will be exercised over.

Test Configuration

Refer to Figure 3-1 which shows the layout of the laboratory constructed to conduct these tests. The layout is described in the following sections:

1. Sample Cell
2. Calibration and Gas Delivery System
3. Water Delivery
4. Temperature Control System

The sample cell is configured for interfacing optics provided by the manufacturer with standard 4 inch flanges, and has 2 inch diameter anti-reflective coated quartz windows on each side.

Sample Cell

The cell is 1.0 meters long and has an ID of 5.0 cm. This sample cell is typical of those commonly used to facilitate *in-situ* flue gas TDL measurements for HCl. Each end of the sample cell is equipped with 4” standard flanges; thus the operational path length of the cell is 1 meter. This cell provides sufficient diameter for a TDL beam to traverse a sufficient path length (1-meter) to detect values of HCl in ppmv-m.

Specifications

- Material The sample cell is made of 314 electro-polished stainless steel and is
- quartz lined
- Pressure The sample cell is maintained at atmospheric pressure
- Path length 1.00 m for single pass optics, 2.00 m for dual pass optics
- Temperature Range 300K-700K

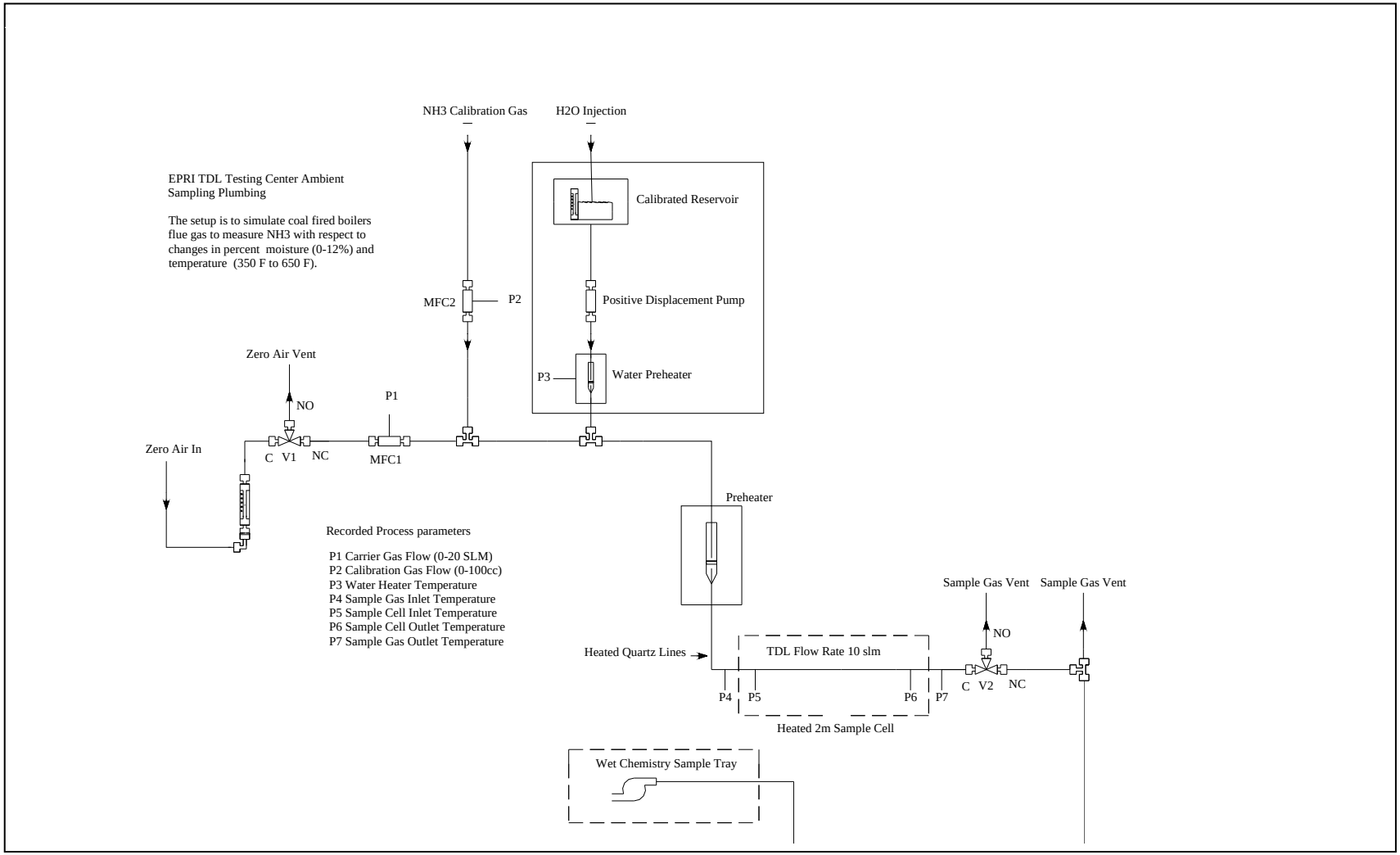


Figure 3-1
Shows a Schematic Layout of the Laboratory Constructed to Conduct these Tests; Note the Laboratory was Constructed for NH_3 TDl Measurements to Simulate Process Temperatures (up to 400 ºC) and was Modified for these HCl Tests as Described in Section 3.4

- Uncertainties

  Pressure - .01 atm

  Path length .025 m

  Temperature +/- 5 ºC

Refer to Figure 3-2 which shows the sample cell. The sample cell has a radiative heater and white insulation. It is mounted on a rigid assembly which is bolted to the structural beams of the laboratory.

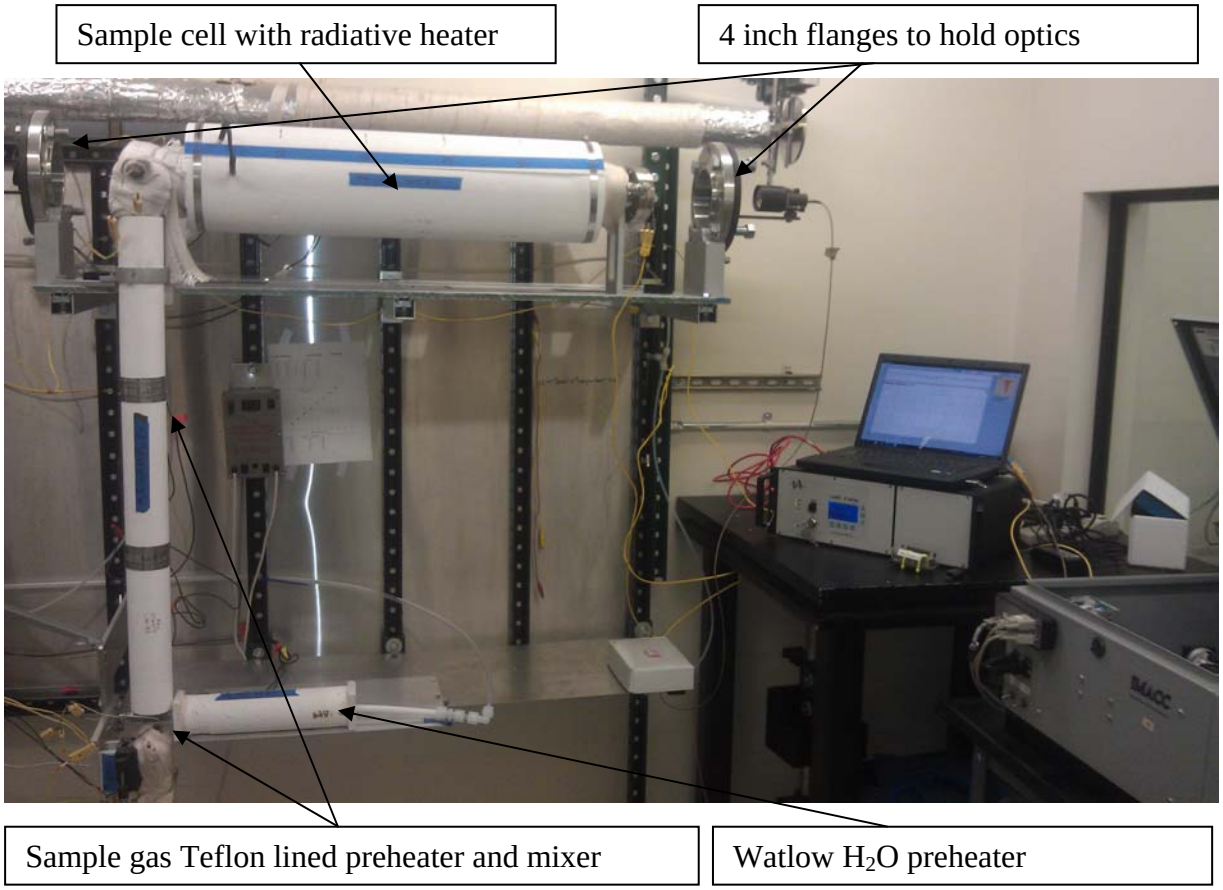


Figure 3-2
Shows the Sample Cell with a Base Path of 1.0 Meters, has a Radiative Heater and White Insulation, Also Shows Setup for the Experiments Presented Here with Unisearch Optics Mounted and the Instrument Tested

Calibration and Gas Delivery System

(The Laboratory employs a TECO -146C Dynamic Gas Calibrator)

The calibration system provides precise concentrations of the ammonia target gas by utilizing precision gas dilution.

In this case, a supply of "zero" air is required to dilute the higher concentration gases of ammonia in order to attain the necessary concentrations. Zero air refers to the purity of the diluent gas, indicating a non-detectable concentration of the pollutant under investigation. The zero air source used in the TDL laboratory is an Aadco which is also used for the zero air in the atmospheric chamber.

The TECO 146C Calibrator employs a central processor unit (CPU) and controlled precision mass flow controllers (MFC). A Linde certified gas cylinder, containing HCl gas in an inert (nitrogen) carrier, provide precise gas concentrations through a precision, low flow MFC. The gas supply consists of one certified 100 ppmV HCl cylinder, which is mixed with zero air in predetermined flow rates using mass flow controllers to achieve the desired concentrations. The dilution air and span gas mass flow controllers have nominal ranges of 0-10,000 and 0-500 cc/min, respectively. The nominal concentration of the cylinder was 100 ppmV HCl. These standards are certified by Linde Gases, and all gases purchased for this project include the supplier's certification sheets. After the HCl is mixed with dilution air, the effluent is heated to the desired temperature. Concurrently, relatively high flow rates of diluent zero air are supplied by a second precision MFC. Each MFC provides an electrical signal to the CPU. The CPU calculates the necessary flows to attain the desired pollutant concentration. The equation (Eq. 3-1) necessary to calculate the required zero air and pollutant gas flows is:

$$C_f = C_i * \{Q_{gas} / (Q_{gas} + Q_{air})\}$$ **Equation 3-1**

Where: C_f = final concentration of the diluted gas
C_i = source gas concentration
Q_{gas} = volumetric flow rate of the source gas
Q_{air} = volumetric flow rate of the zero air source

The MFC used to control the diluent air has a higher volume capability (approximately 5 standard liter per minute [slpm]) than the MFC used to control the source gas (approximately 100 standard cubic centimeters per minute [sccm], or 0.1 slpm). This allows the control system to develop various gas concentrations, ranging from trace amounts up to high concentrations, limited only by the concentrations available from the certified gas source. The low flow gas and the high flow diluent are mixed in an inert (Teflon®) chamber prior entering the exhaust manifold where the analyzers to be calibrated pull their samples from.

The uncertainty of the calibration source is dependent primarily on the accuracy of the TECO 146 C calibrator. The calibrator has a purported accuracy of better than 2% of full scale reading.

Water Delivery

Gaseous water is introduced into the blended HCl sample gas stream in order to provide the desired water content. The water generation system consists of a water reservoir, a graduated

burette, a positive displacement pump, and a heating system, refer to Figure 3-3. The pump speed can be adjusted to the desired flow rate, as measured by noting the change in volume in the burette over time. The water is drawn through the pump into a 1/8” stainless steel line, which is routed through a heated aluminum block to gasify the water.

The stainless steel line contains a particulate filter located inside the aluminum block. The gaseous water effluent from the block then enters the diluted HCl gas stream.

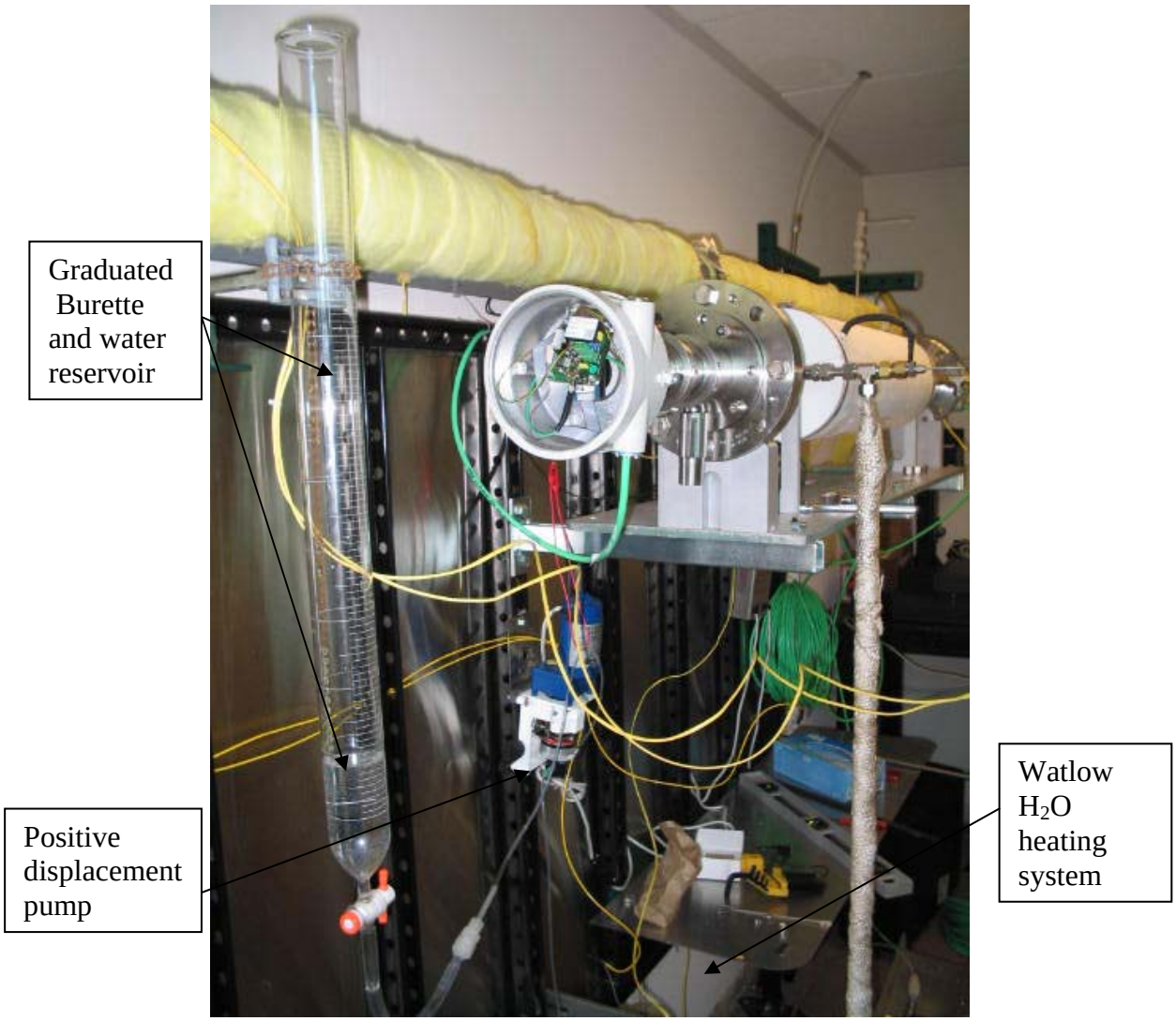


Figure 3-3
Shows the Moisture Generation System which Consists of a Water Reservoir, a Graduated Burette, a Positive Displacement Pump, and the Water Heating System

Temperature Control System

For the heating and control system for sample cell, the sample cell which is a 1.0 meter by 2.50 inch outside diameter stainless steel tube that can be heated to maintain a desired gas temperature up to 200º C within the cell path. A single radiative heater was custom ordered and fitted over the cell. The heater came with its own insulation.

The heater operates on 120 VAC and can deliver over 25 watt/inch^2 to the apparatus. Figure 3-5 shows the radiative heater as mounted on the sample cell.

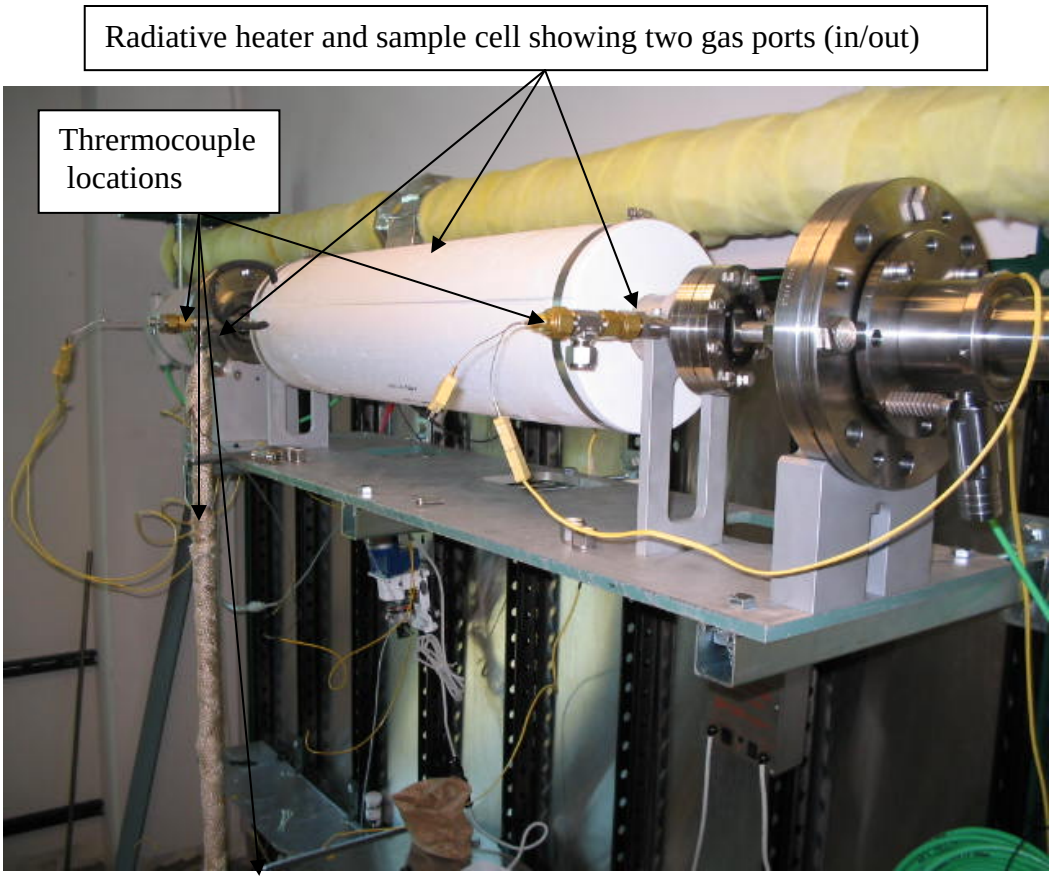


Figure 3-4
Sample Cell with Light Path Flanges, Shows Gas Ports, Radiative Heating Assembly and Thermocouple Locations

Temperature in either cell is regulated by thermocouple feedback to a PID temperature controller coupled to solid-state relays (SSR) as shown in Figure 3-6.

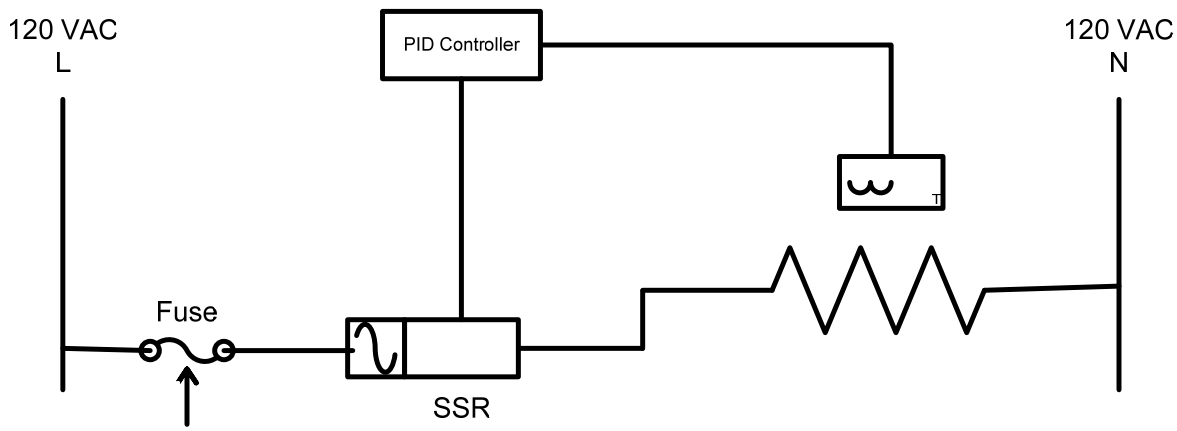


Figure 3-5
Sample Cell Temperature Control System Schematic.

System Temperature Measurements

Type K Thermocouples (TCs) are used for all temperature measurements in the system. All TCs are 0.0625 inch diameter, ungrounded junction in a stainless steel sheath and have a response time of approximately 0.25 seconds.

Standard wire type K thermocouples have a range from –200º C to 1250º C with an accuracy of ±0.75% or ±2.2º C (whichever is greater) above 0º C. Type K extension wire has an accuracy of ±2.2º C up to 277º C and ±0.75% above 277º C.

The temperature controllers used in the system are from Omega Engineering. These controllers have an input accuracy of ± 0.5º C and have cold-junction compensation with temperature stability of ±0.05º C.

An error analysis [Eq. 3-2] shows an overall system accuracy for temperature measurement of ± 3.15º C up to 277º C and ± 3.27º C at 315º C.

$$Accy_{Total} = \sqrt{Accy_{TC} + Accy_{Ext.} + Accy_{CNi} + Stby_{CJC}}$$ **Equation 3-2**

Test Plan

Overview of test procedure employed:

Initial Setup

1. We installed the diode laser system to manufacturers specifications. It was also ensured that the laser output from the diode laser in the instrument was as specified, this case laser power was 8.2 milliwatts.

2. We then mounted the optics and verified optical alignment to ensure that there were no optical artifacts as etalons or optical fringes that could have degraded or altered the optical signal. This was a very important and critical step as minimization of optical effects is an iterative procedure. For this it was required to have windows installed at seven degrees from parallel at each the entrance and exit of the sample cell as well as having windows with anti-reflective coating specific for the IR wavelength range measured. The windows were then rotated to generate as flat a background signal as possible.
3. Prior to measurement it was important to verify the stability of the alignment by recording the signal power for a 30 minute period. It was determined that if the standard deviation of the signal power was less than 10% of the signal power the alignment was stable.

The defined range was: 0 ppmV-m, 2.5 ppmV-m, 5.0 ppmV-m, 10 ppmV-m, 15 ppmV-m and 25 ppmV-m.

The test protocol was discussed with the manufacturer and they agreed to the procedures. The initial tests were done at ambient temperatures with no moisture over the defined range. For each test the instrument was configured for 1-minute measurements and the test number that resulted was the 15 minute integrated response showing this averaged number and the standard deviation of the one minute measurements over that 15-minute interval. Note that the test matrix is configured to complete all the tests at a specific temperature, varying the concentration of the target gas at each of the moistures investigated. Basically we measured the defined range at the 0% moisture first, then the defined range at 4% moisture.

The output signals from the two mass flow controllers and five thermocouples are recorded on a Campbell CR10 data logger in seven defined channels. This system provided instantaneous readouts, plus a one-minute average from each channel. The collected data from each test run were then converted to Excel files for data validation and interpretation. The HCl concentration as determined by calculation from the cylinder concentration, the span gas flow rate, and the dilution air flow rate are checked using a reference TDL.

Individual components of the laboratory system were tested and calibrated. These components included integrity checks and calibration of the mass flow controllers, calibration of the thermocouples, tests of the water delivery system for accuracy and precision, and tests of the heating systems.

Quality Control

Quality control (QC) is an organized set of activities that use defined standards to evaluate the attributes and/or performance of all critical components within a measurement system. These comprehensive and interrelated activities are designed to provide sufficient verification that all critical components of the measurement system are within established control limits. The QC activities employed in the operation of the TDL Test Laboratory are described in this section. The performance of these activities ensures that the measurement uncertainties are maintained within the established control limits, with the goal of achieving the project’s data quality

objectives. The control limits described in this section have been established to evaluate the results of the calibrations of the laboratory instrumentation.

Control over the handling, calibration and operation of the project instrumentation are continuously maintained by UCR. This section presents the types of controls that are incorporated into each project process. Where applicable, the instrument manuals and SOPs are followed.

Checks of HCl Delivery System vs. Reference TDL vs. ISE Method

At the time of the testing and before each test period the accuracy of the HCl generation system was tested against the Reference TDL.

The gas cylinder used was provided by Linde GASCO (pictured in Figure 3-6), certified to 100 ppmV of HCl in N_2.

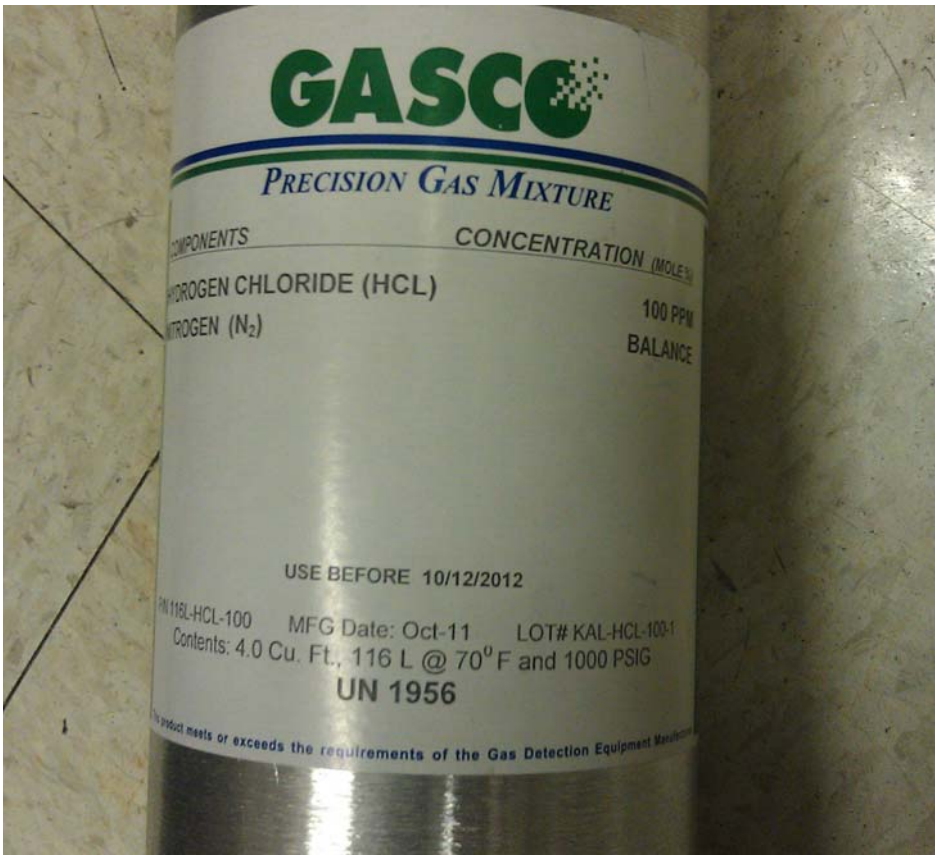


Figure 3-6
HCl Calibration Gas Cylinder

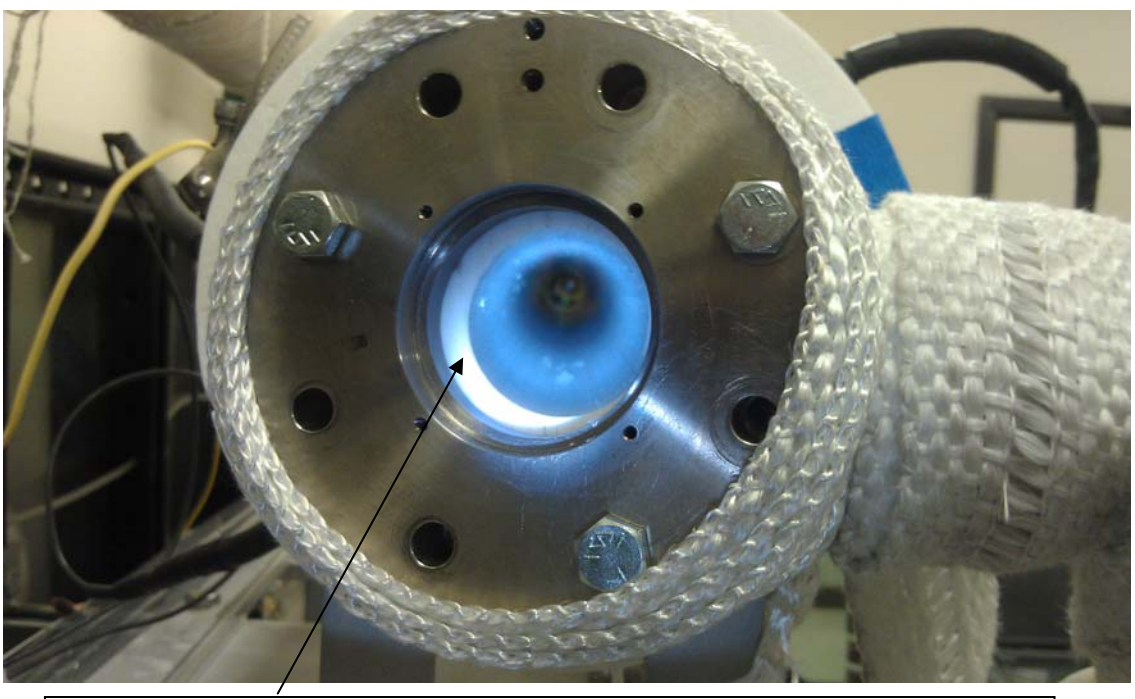
Each comparison test consisted of three runs at a single concentration of 10.0 ppm HCl at 25ºC and 0% H_2O. The result of this test was considered satisfactory if the percent difference between

the HCl concentration as calculated by the delivery system differs less than 5% from the Reference TDL.

Initial testing showed we were losing significant amounts of HCl through our sampling system and required considerable modification of the gas delivery system to minimize these observed losses. All of the lab gas interface material was initially quartz as that was what was used when we constructed the laboratory for NH_3 testing. Quartz was determined to minimize NH_3 interaction and subsequent losses in the calibration gas delivery. This was not the case for HCl as we experienced significant loss of the HCl calibration gas. It was decided that all surfaces that came in contact with the calibration gas needed to be Teflon (refer to Figures 3-7 to 3-9). The major losses were in the sample cell itself. To minimize these we machined a Teflon tube that was inserted into the sample cell. The tube inserted in the cell is shown in Figure 3-7.

The Teflon tube was constructed to parallel the surfaces of the SS sample cell tube and insert with a .002 inch tolerance to the sample cell walls. The tube was 0.187” thick and required us to recalibrate the thermal settings of the sample cell to ensure we achieved the required temperatures.

In Figure 3-7 the Teflon tube was illuminated with a visible light for better viewing, note the parallax view of the Teflon tube is due to the 7 degree angle that the window flanges are constructed at, this angle is specific to reduce etalon fringing of the transmission IR beam.



Teflon tube inserted into SS sample to minimize HCl calibration gas losses

Figure 3-7
Teflon Tube Inserted into Sample Cell, Illuminated with a Visible Light for Better Viewing. Note, the Parralax View of the Teflon Tube is Due to the 7 Degree Angle that the Window Flanges are Constructed At

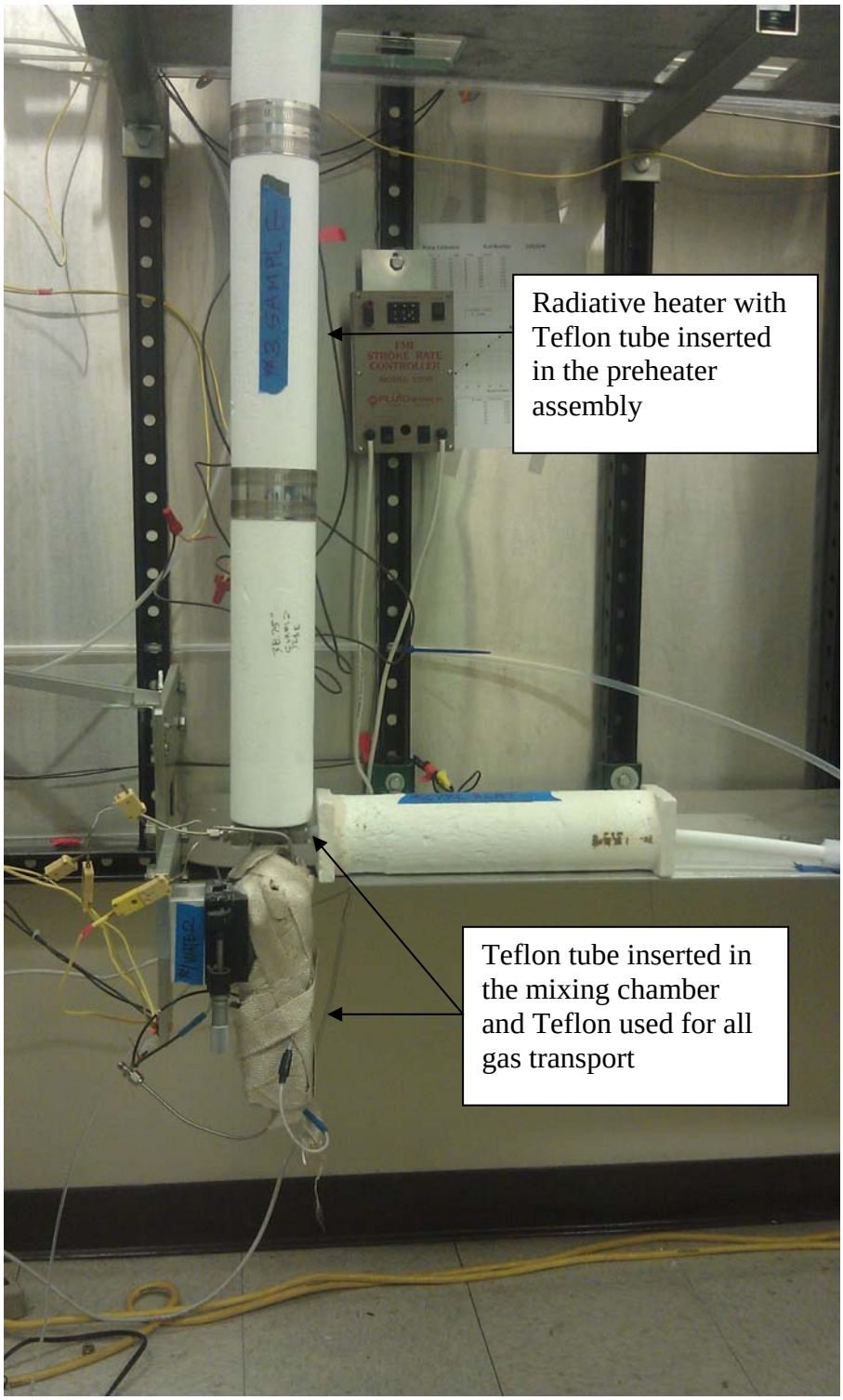


Figure 3-8
Teflon Tube Inserted into Preheater Cell which also was Converted to have a Radiative Heater, the Mixing Chamber was also Teflon Coated and Teflon Lines were Used for Transport to the Mixing Chamber

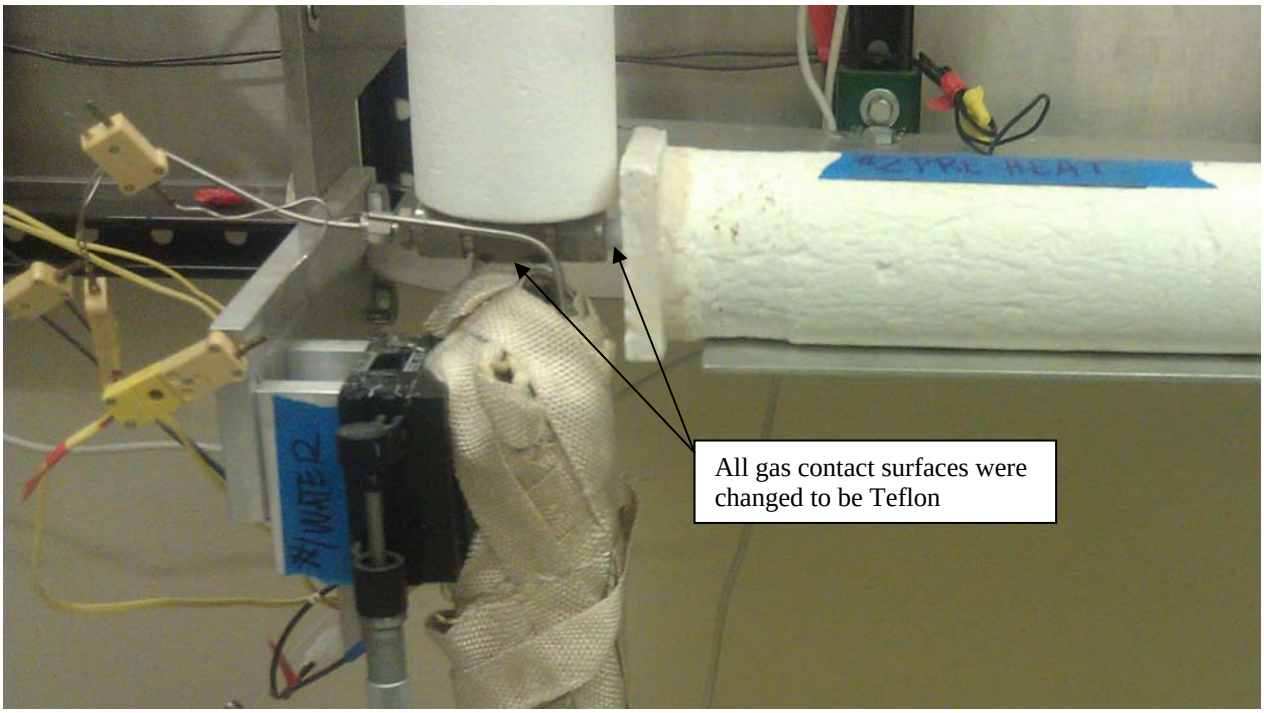


Figure 3-9
Teflon Tube Inserted into Preheater Cell which also was Converted to have a Radiative Heater, the Mixing Chamber was also Teflon Coated and Teflon Lines were Used for Transport to the Mixing Chamber

Calibration Methodology

Instrument calibrations are an organized set of activities that use defined and traceable standards to establish the initial accuracy of the equipment. Subsequent calibrations perform a twofold function: 1) They re-establish the accuracy of the equipment, and 2) They provide verification of the accuracy of the equipment since the time of the last calibration, thus providing a critical component of the data validation process described in Section 5.

The QC requirements described below provide the control limits for each instrument, which are used to evaluate the results of the calibrations. All calibrations described in this section are documented on hard copy and/or electronically. These records are then copied and archived.

Mass Flow Controllers

The accuracy of the flow rate calibrations of the dilution air and span gas mass flow controllers in the gas diluter are crucial in delivering accurate HCl concentrations to the test cell. These flow rate calibrations are checked before every test evaluation at all operational flow rates using a BIOS Meter, which is an authoritative flow rate standard.

The BIOS is certified by the manufacturer on a yearly basis. If the measured flow rate differs from the indicated flow rate by more than ±1%, a new multipoint calibration of the mass flow controller is performed.

Temperature Sensors

The thermocouples were calibrated at the target temperatures during the acceptance test of the laboratory system and on a yearly basis thereafter.

During the calibration the sensors were calibrated together so that they could be matched to one another, so that they were able to detect temperature gradients in the system during routine tests.

Checks of Water Content

At the time of the test and for each test period the water content as calculated by the spreadsheet will be compared to a measurement of the relative humidity at the effluent of the test cell using a certified Rotronics sensor.

Refer to Table 3-1 which lists the quality control checks conducted for the laboratory setup used in the instrument evaluation.

Table 3-1
Lists the Quality Control Checks Conducted for the Laboratory Setup used in the Instrument Evaluation

Device(s)	Measurement Component	Activity	Frequency	Criteria	Corrective Actions
HCl Gas dilutor	Mass flow controllers	Check flow rate calibrations	At acceptance test and each test period	±1% between measured and indicated flow rates	Perform new multipoint flow rate calibration
Standard Gas Cylinders	Certified HCl concentrations	Certification by supplier; crosschecks against one another	At acceptance test	±1.5% of the certified concentrations	Notify supplier and reject cylinders
Thermocouples	System temperatures	Check temperature calibration	At acceptance test	±10°F in accuracy; ±2°F difference between sensors	Correct thermocouple response as necessary
Water Injection System	Percent water in system	Check theoretical value using Rotronics sensor	At acceptance test and each test period	±1% in water content, by mass	Correct theoretical value to the measured value
Reference TDL	Reference for diluted HCl concentrations	Check against ISE method	At acceptance test and each test period	±10% in measured HCl concentration	Perform appropriate troubleshooting

4
TESTING RESULTS

TDL Laboratory Installation

The statistical methods used to evaluate the TDL instrument measured and the results are discussed in this section. Initially the equipment was mounted in the laboratory for evaluation. The equipment included a bi-static configuration with separate transmitter and receiver assemblies. The overall installation of this equipment in the laboratory can be seen in Figure 3-2. The individual components, transmitter, receiver and the LasIR instrument are shown and described in Figures 4-1 to 4-3 respectively.

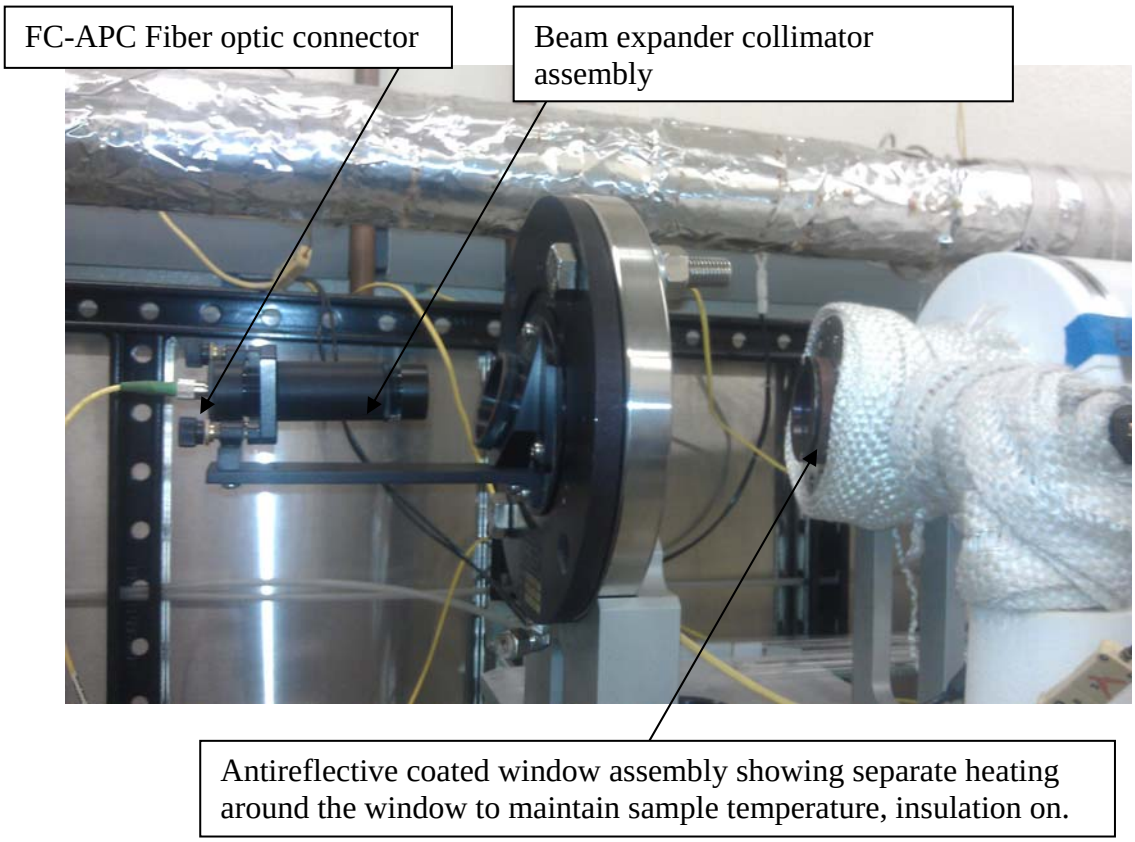


Figure 4-1
Single Pass Transmitter Assembly from Unisearch Mounted on UCR Laboratory Test Cell

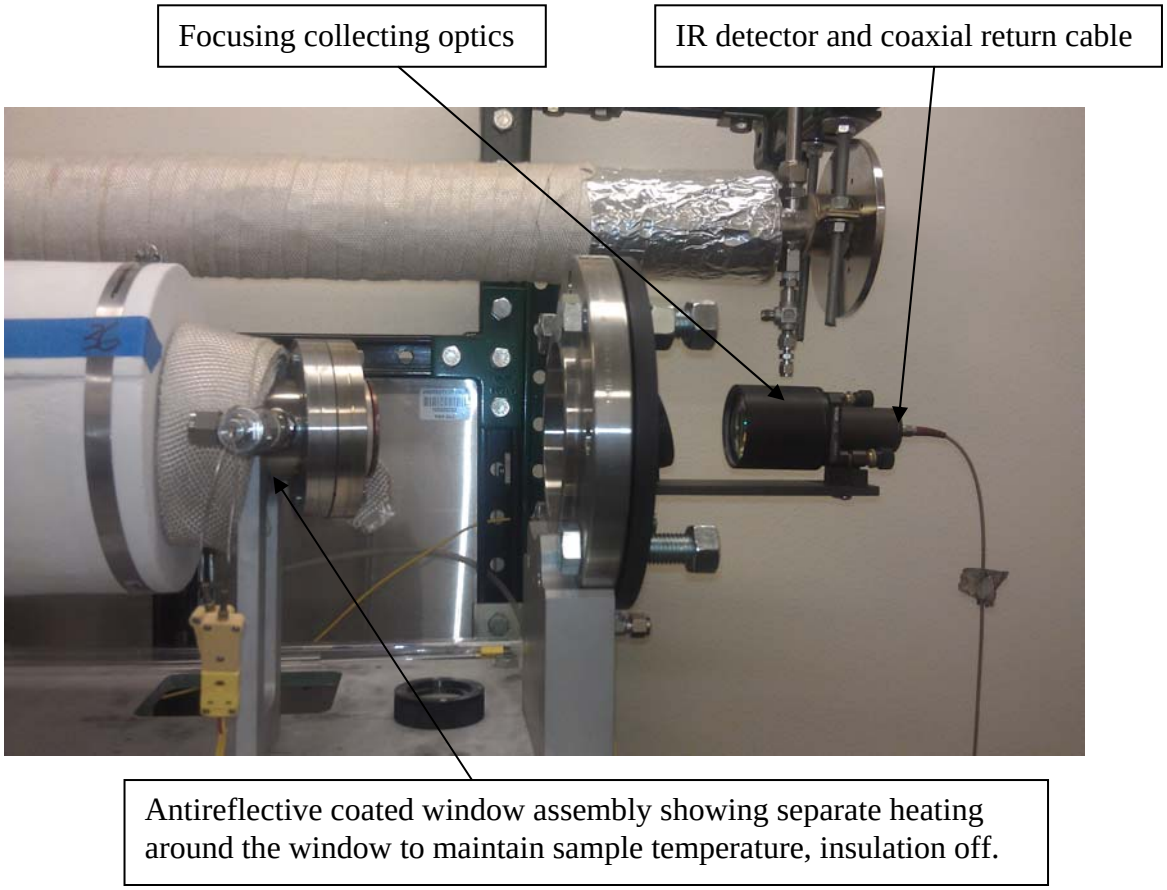


Figure 4-2
Single Pass Receiver Assembly from Unisearch Mounted on UCR Laboratory Test Cell

It was determined that the windows needed to be heated to maintain thermal integrity and were heated separately. The optical system was aligned with a visible 630 nm beam which simulated the optical traverse of the 1.742 µ IR beam. The optical system was adjusted to minimize background effects, specifically optical etalons, a single background signal was stored to evaluate background variability. Background levels were less than 0.1 ppmV for the 1 meter path at 25 ºC.

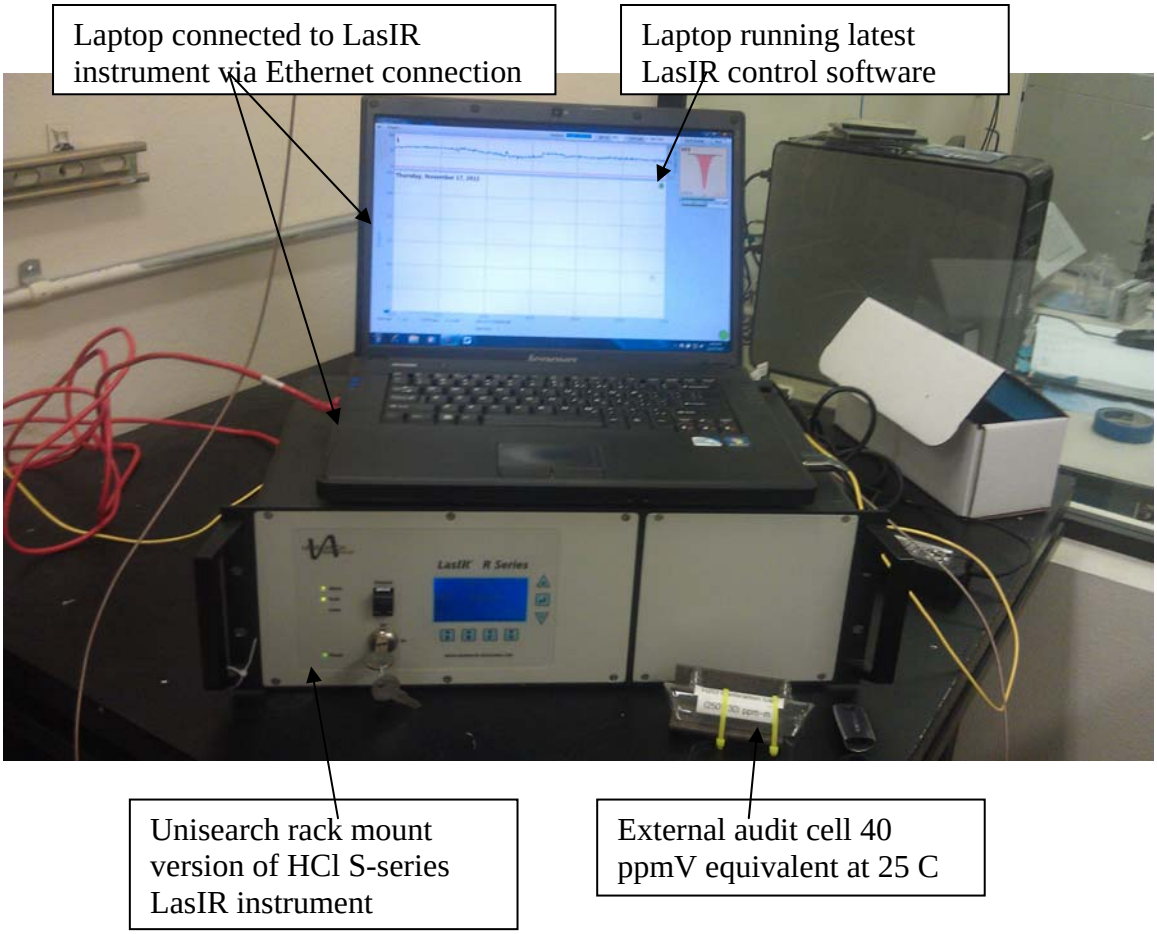


Figure 4-3
LasIR Instrument Connected via Ethernet to Accompanying Laptop from Unisearch Mounted on UCR Laboratory Test Cell

Agreement with Standards and Temperature Correction

The agreement of the Unisearch S Series LasIR SM410 with respect to the HCl gas standards was assessed by taking 15 one-minute averaged samples at each of the test matrix configurations. Therefore the values presented on data tables are 15 one-minute averages of the sample gas measurement already with the temperature corrected averaged concentration and the standard deviation of the 15 one-minute samples over the 15 minute sampling period. Temperature correction is required by all spectroscopic instruments as they all measure a mixing ratio, which is a ratio of the number of molecules of the measured species to the total number of molecules in a specific volume. As temperature changes the ideal gas law requires correction to maintain a standard volume size to that which the instrument was calibrated at, for example the number of total molecules at 25 ºC in one litre of sample gas is different than the number of total molecules at 200 ºC in one litre of sample gas.

Also most molecules are unsymmetrical and polyatomic so when the molecule becomes excited by absorbing energy, it will want to either vibrate or rotate. It is this tendency of the molecule to

absorb energy that leads to spectroscopic identification of the molecule by the wavelength of absorption and concentration of the molecule by how much of the energy is absorbed at that wavelength. However the ability to absorb energy for any unsymmetrical polyatomic molecule changes with temperature, so therefore the temperature correction algorithm for spectroscopic measurements must also deal with the effect of how the molecular absorption of the target molecule behaves under changes in temperature. This effect is called the line strength ratio, so temperature correction relates back to the instruments calibration temperature and corrects for both the ideal gas law change in temperature as well as the line strength changes.

For this evaluation, Unisearch calibrated their instrument at 25 ºC and would take input values in their software for 100 ºC and 200 ºC. The instrument is configured to read temperatures via a K type thermocouple and automatically correcting the values for temperature changes, these correction values incorporated both the ideal gas law as well as the line strength effects. Their instrument is capable of doing this continuously online with inputs from K-type thermocouples and an empirically derived algorithm which they employ for field installations but for our experiments we just input the values in the software since we were only at 3 discrete levels, 25 °C, 100 ºC and 200 ºC.

Figure 4.4 shows the configuration file for the LasIR instrument for temperature measurement at 373.3 K (100 ºC), note we only changed the fixed temperature values located on the screen setup files for different temperatures. The values used in kelvin, respectively were 298.3 K (25 ºC), 373.3 K (100 ºC) and 473.3 K (200 ºC). Also a manual background as indicated was taken at 25 °C and the system was left with the same manual background during the tests. The pathlength is shown at 1.0 meter. The integration time was chosen at 2 seconds but averaged for 1-minute, no running average was used and the response is as close to real time as was possible. Pressure was adjusted to atmospheric for each of the tests, in this 1013 mbar.

Since there are three separate temperatures, 25 ºC, 100 ºC, and 200 ºC and two distinct moisture levels for the enhanced temperatures, 0%, (2 tests) and 4%, this resulted in 3 different measurements for each of the target concentrations of 0 ppmV, 2.5 ppmV-m, 5.0 ppmV-m, 10 ppmV-m, 15 ppmV-m and 25 ppmV-m at each of the elevated temperatures. The 25 ºC sample was used as a control only. Note the units are not in ppmV but ppmV-m (parts per million x meters).

Audit Cell Verification of System Calibration

Since the instrument does not required to be calibrated as it is a direct absorption measurement, Unisearch recommends that an audit cell be purchased with the instrument to verify the calibration. The audit module was designed to allow the user to check the sensitivity of the analyzer without the need for calibration gas cylinders and flowing gas streams. The audit module concentration was warranted to be within +/- 5% of the stated value for a period of at least one year from date of shipment. The cell was expected to be stable for a minimum of 5 years for HCl. The HCl concentration measured on the monitor display represents both the HCl concentration in the measurement path plus the HCl in the audit cell. Thus, the audit module in effect introduces an HCl ‘spike’ to the measurement path, which can then be compared against a known response based on measurement and audit cell temperature, pressure, measurement path

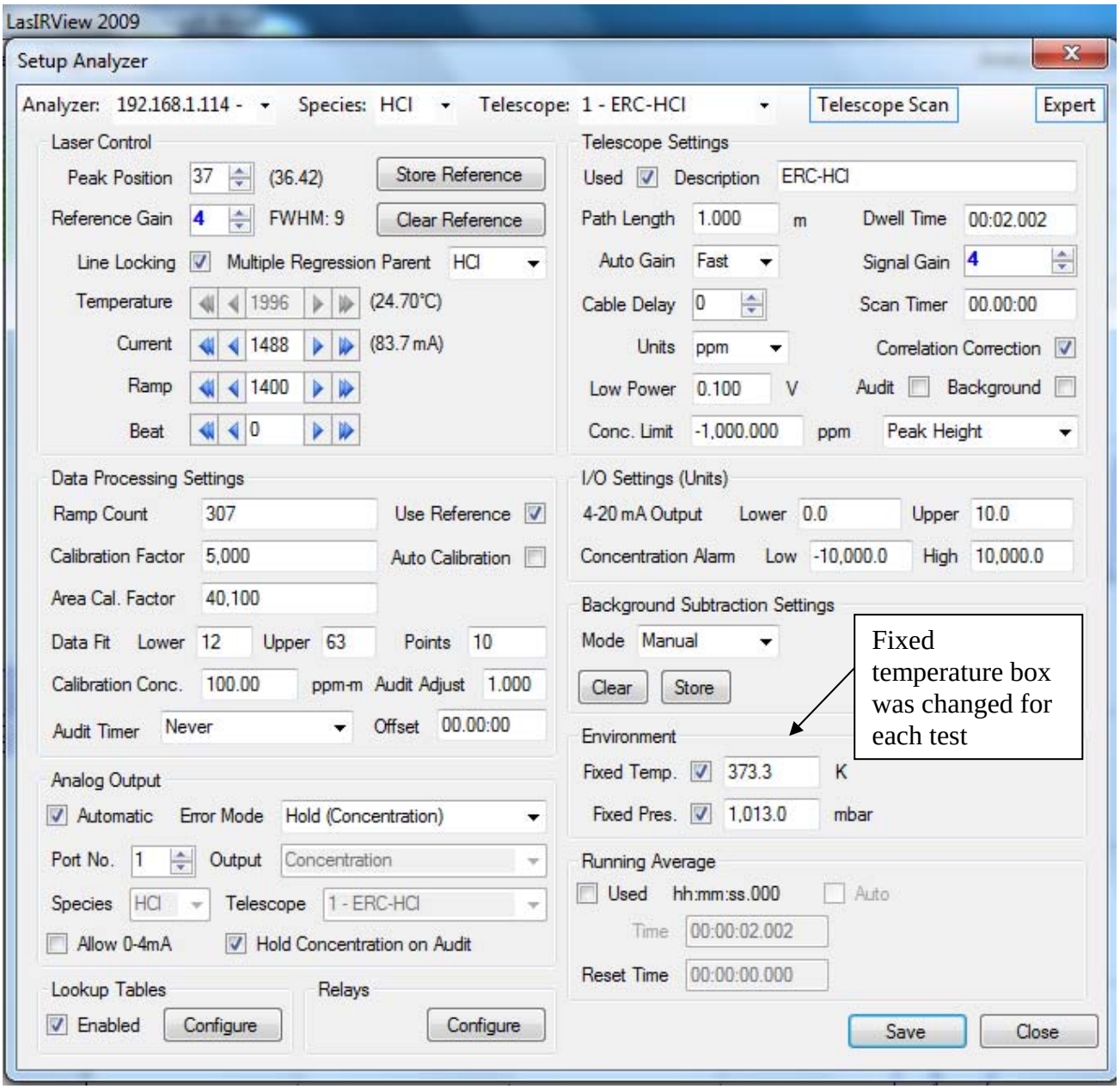


Figure 4-4
LasIR Instrument, Configuration File at 373.3 K (100 ºC)

length, and HCl concentration within the audit cell. The specification for the audit cell used yielded a value of approximately 40 ppmV-m, at 25 ºC and 1013 mbar with an error of +/- 5% (2 ppmV-m).

The HCl concentration value displayed on the HCl monitor with the audit cell inserted in series with the measurement path was then the sum of the concentration of the gas in the sample gas

stream plus the audit cell value, corrected to the same temperature, pressure, and path length. Thus, since the path length was 1-meter and the sample cell had zero air flowing through it at 25 °C, the total HCl concentration displayed with the audit cell inserted should be 40.0 ppmv.

The insertion of the audit cell in line does cause a loss in signal return power of approximately 30%. Audits were conducted at 25 ºC prior to each test and the value never varied greater than the 5% error specified with the audit cell. Simply the audit cell insertion never deviated greater than 2 ppmV on the 40 ppmV spike value. Figure 4-5 shows the system response with the cell inserted and zero air going through the sample cell, the audit spike value measured is 40.18 this test, well within the stated specifications of the audit cell and verified the calibration of the instrument.

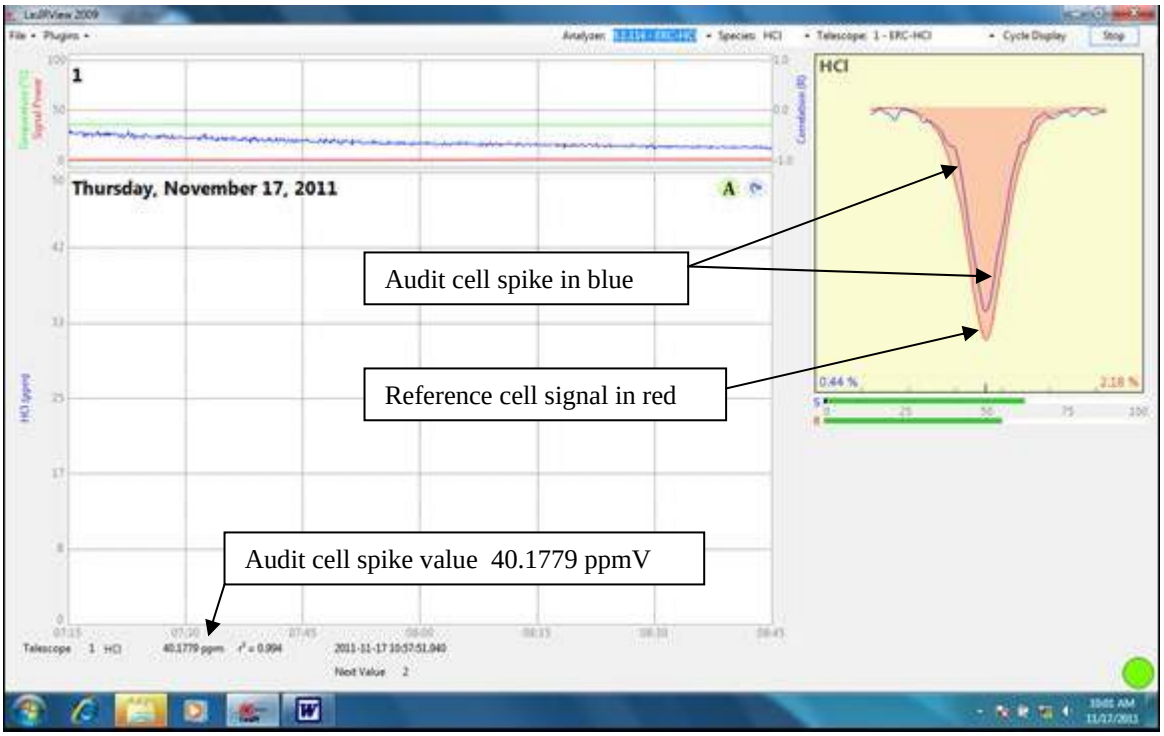


Figure 4-5
Audit Cell Verification of HCl Monitor Response Showing Audit Spike Value of 40.18 ppmV

System Response Tests

Figures 4-6 depicts the results obtained with the 1 meter sample cell, during a check of the calibration gas delivery, the sample tests are grouped by the source calibration value listed below as shown on the figure.

1. Test 1 the source calibration value is 0 ppmV-m.
2. Test 2 the source calibration value is 2.5 ppmV-m.
3. Test 3 the source calibration value is 5.0 ppmV-m.

4. Test 4 the source calibration value is 10 ppmV-m.
5. Test 5 the source calibration value is 15 ppmV-m.
6. Test 6 the source calibration value is 25 ppmV-m.

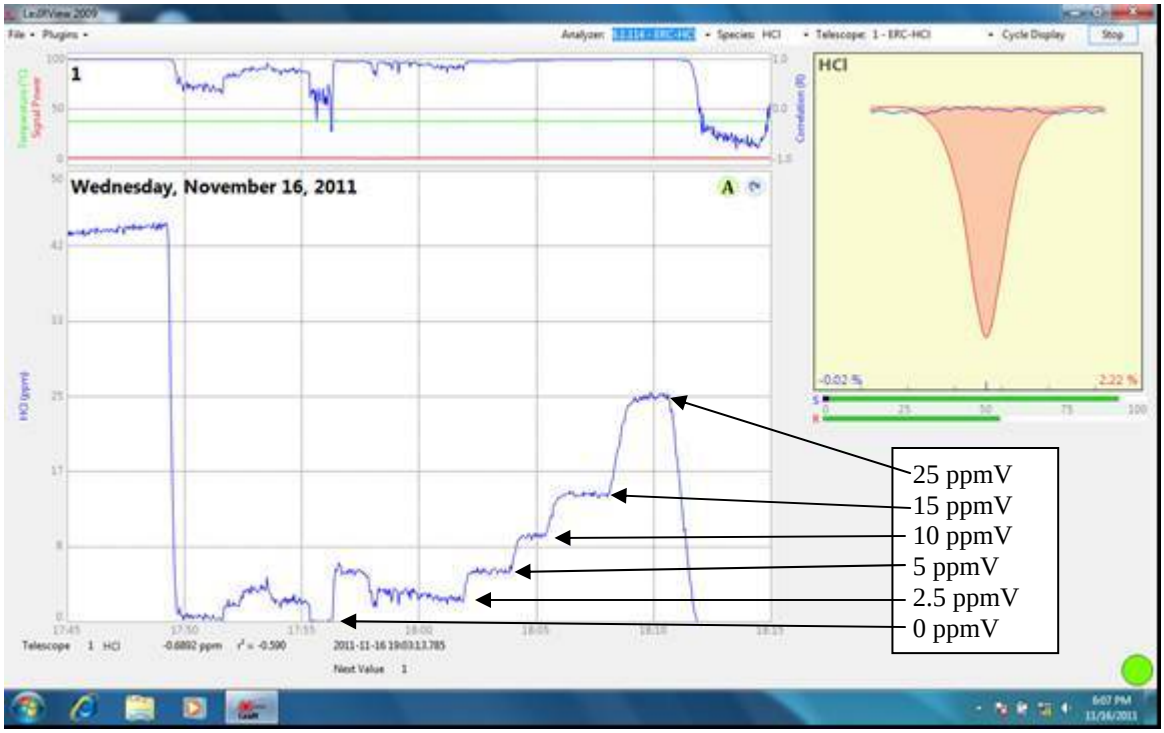


Figure 4-6
Instrument Response Test over the Calibration Range

Tables 4-1 to 4-2 lists the results obtained with the 1.0 meter cell, single pass configuration. Note the system was calibrated at 25 ºC and left on each plot as the control, the temperature tests at 0% moisture were repeated so there are two tests at that moisture level for each of the elevated temperatures, the tests at 4% moisture were conducted once at each level. The figures below each table, Figures 4-7 and 4-8 respectively, are a graphical representation of the system response for the set of tests at each of the two temperatures investigated.

IR Spectroscopy of Typical Coal Combustion Flue Gases

Combustion applications generate high amount of water vapor and CO_2. Typically, their absorption spectra strongly overlap with other species of real interest for the combustion analyses. The difference of the concentration levels of water vapor and CO_2 with respect to other combustion products can range from 1 to 5 orders of magnitude. The high-intensity spectral features of gaseous water and CO_2 at high concentrations work like narrow band pass filters, which block significant amounts of the available light in the spectral regions they occupy.

Table 4-1
Results of Unisearch S Series LasIR SM410 for 1.0 Meter Sampling System at 100 ºC

HCl		Temperature 1			Temperature 2 test 1 and 2 and 4% moisture					100 C						
ppmV-m		Moisture	25 C			Moisture				Moisture				Moisture		
(25 C)		0%	SD		Test 1	0%	SD		Test 2	0%	SD			4%	SD	
0.0		0.09	0.05			-0.03	0.07			0.10	0.09			0.11	0.11	
2.5		2.50	0.07			2.88	0.14			2.42	0.23			2.34	0.25	
5.0		5.26	0.09			5.15	0.15			5.13	0.31			5.13	0.35	
10.0		9.76	0.05			9.60	0.28			10.47	0.37			10.00	0.40	
15.0		14.60	0.23			15.22	0.34			14.80	0.55			15.16	0.56	
25.0		25.20	0.24			25.10	1.02			25.78	0.64			25.89	0.83	

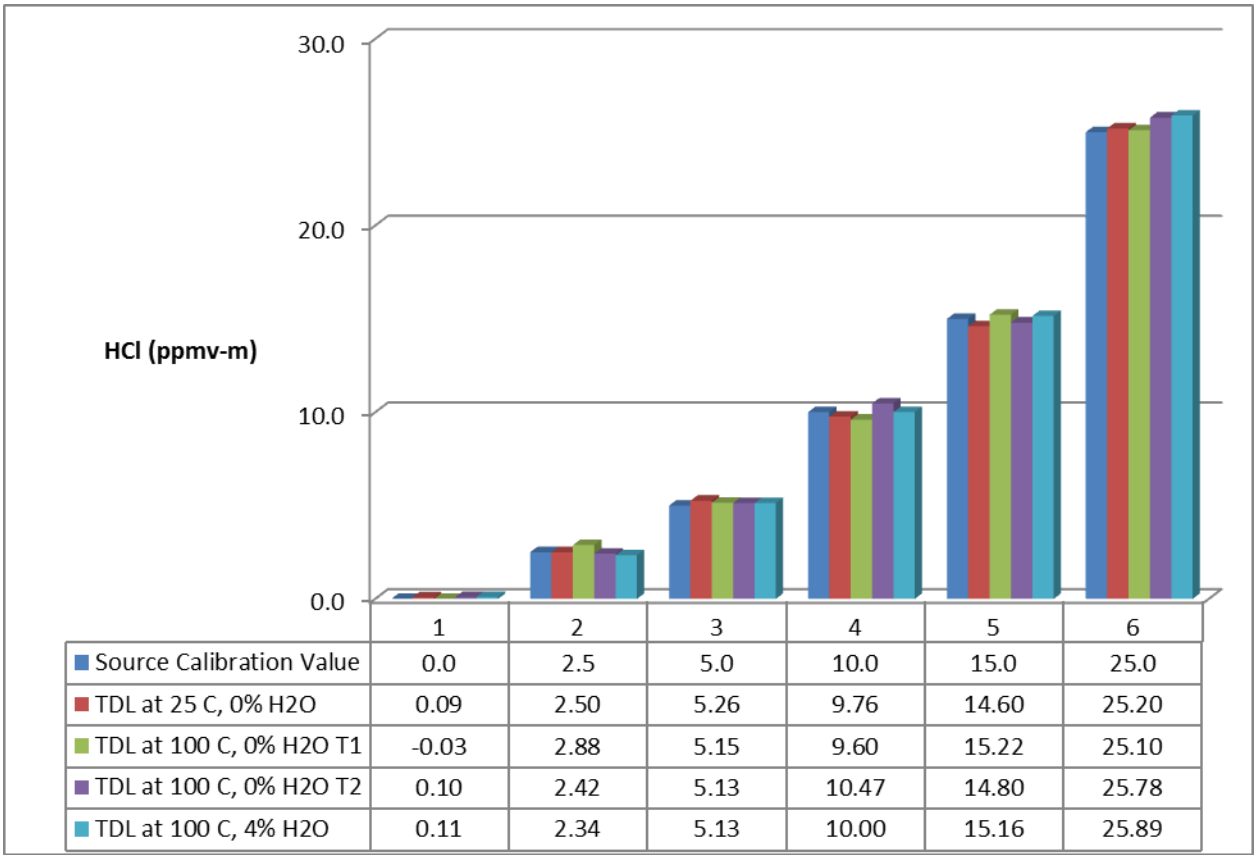


Figure 4-7
Graphical Representation of System Response over the Concentration Range at 100 ºC

Table 4-2
Results of Unisearch S Series LasIR SM410 for 1.0 Meter Sampling System at 200 °C

HCl		Temperature 1			Temperature 3 test 1 and 2 and 4% moisture					200 C						
ppmV-m		Moisture	25 C			Moisture				Moisture				Moisture		
(25 C)		0%	SD		Test 1	0%	SD		Test 2	0%	SD			4%	SD	
0.0		0.09	0.05			0.04	0.08			0.11	0.09			0.12	0.11	
2.5		2.50	0.07			2.28	0.33			2.36	0.37			2.33	0.38	
5.0		5.26	0.09			5.11	0.27			5.02	0.39			5.15	0.36	
10.0		9.76	0.05			10.30	0.30			10.67	0.39			10.61	0.36	
15.0		14.60	0.23			14.77	0.55			14.97	0.64			15.14	0.57	
25.0		25.20	0.24			25.26	0.85			25.33	0.74			25.61	0.79	

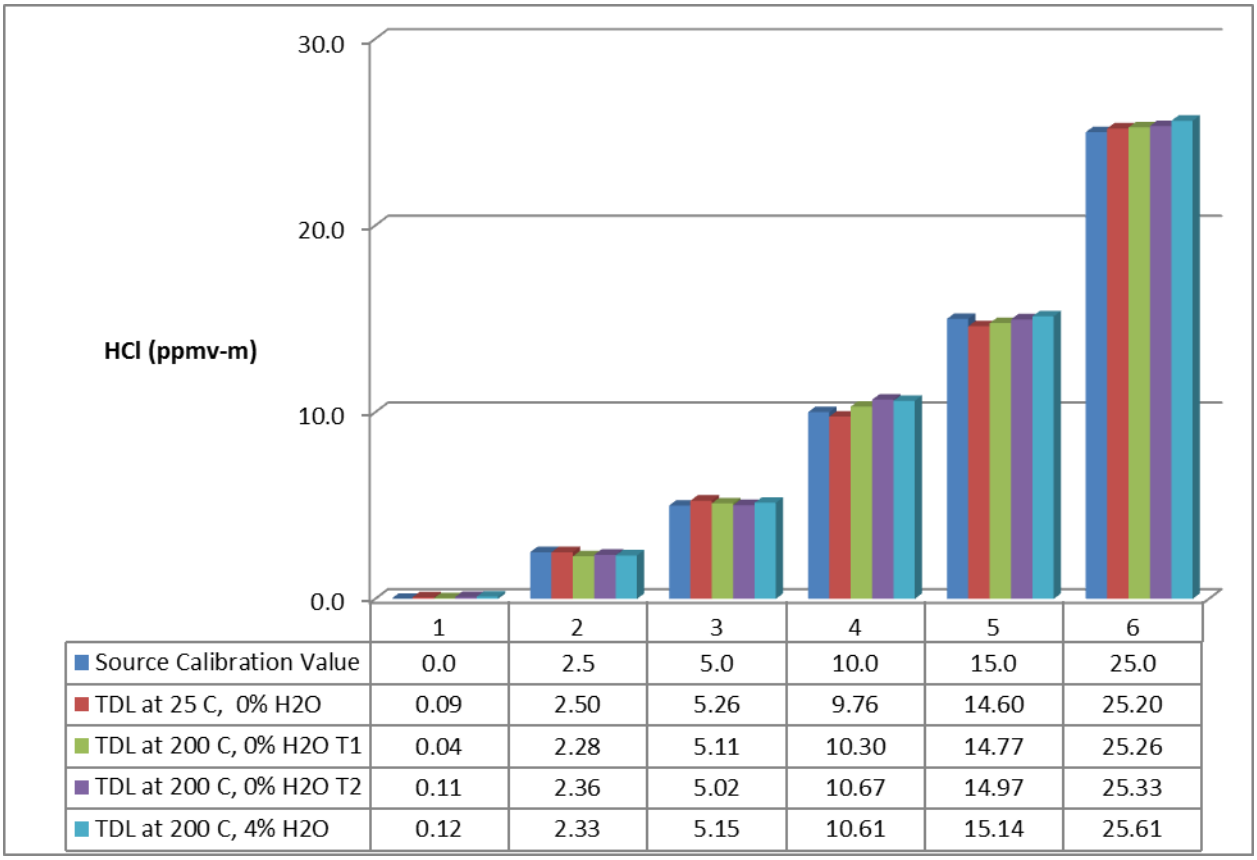


Figure 4-8
Graphical Representation of System Response over the Concentration Range at 200 ºC

The less intense features of water and CO_2 that overlap with other combustion species will normally show a non-linear behavior in their absorption spectrum. Clearly the best for a target species is to find suitable lines that are not perturbed by either the high concentrations of water and CO_2 but other gases as CO, NO, NH_3 and SO_2.

Figure 4-9 shows typical gaseous infrared spectra of major flue gas species observed from coal-fired combustion processes. Temperatures of these spectra are around 200°C (392°F). Since most of the reported HCl absorption lines are between 5500 and 6000 cm-1, it is likely possible that only CO_2 could interfere as the other gasses of interest have much weaker absorptions past 4000 cm-1. However, most of the CO_2 lines weaken considerably at these wavelengths. To investigate which of the HCl lines are less likely interfered with from combustion gas processes, and identify the interferences Hi Tran database spectra were generated for the each of the species including HCl over the 5500 and 6000 cm-1.

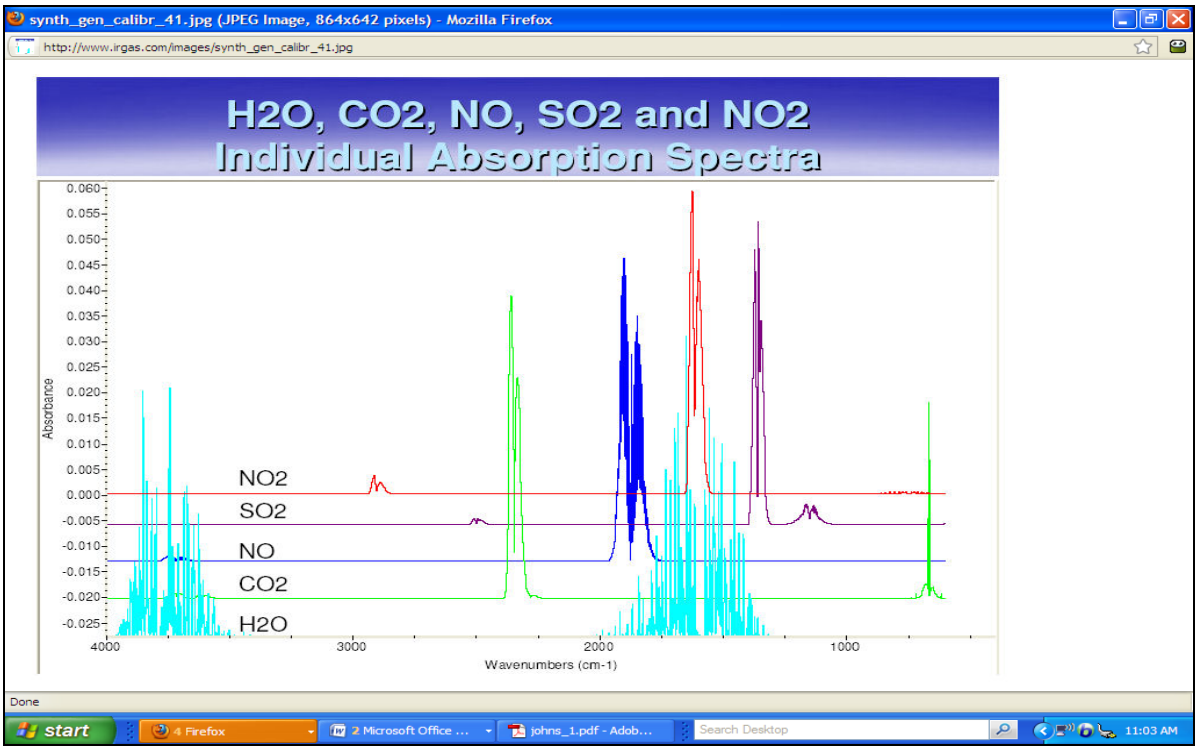


Figure 4-9
Typical Gaseous Infrared Spectra of Major Flue Gas Species Observed from Coal-fired Combustion Processes

Investigation of IR Spectroscopy of Typical Coal Combustion Flue Gases in the Region where HCl Absorbs

The goal of this section is to explore specifically the IR spectra of the possible interfering species from combustion applications and use this to first determine theoretically if they is any possible interferences that may result from the possible other combustion gasses to the HCl measurements, and secondly to actually conduct interference testing of the species. Note water is

not discussed here as we have already tested for water interferences with the moisture tests done earlier.

First the HCl spectra were investigated and are found on Figures 4-10 to 4-11.

The following possible interfering species were investigated:

CO_2: Figures 4-12 and 4-13

NO: Figures 4-14 and 4-15

NH_3: Figure 4-16 (no resulting IR spectra in this range)

CO: Figure 4-17 (no resulting IR spectra in this range)

SO_2: Figure 4-18 (no resulting IR spectra in this range)

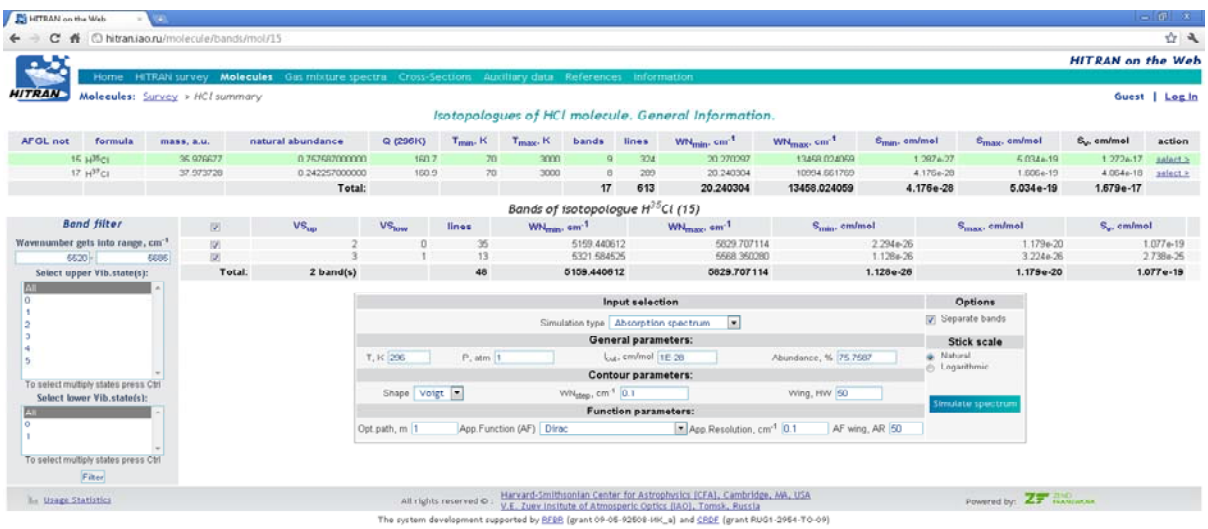


Figure 4-10
Isotopologues Investigated for HCl in the 5500 to 6000 cm^{-1} Spectral Range

The Hi Tran database spectra are provided listing first the particular isotopologues investigated for each of the possible interfering species and the resulting spectra if any that may lie in the measurement range.

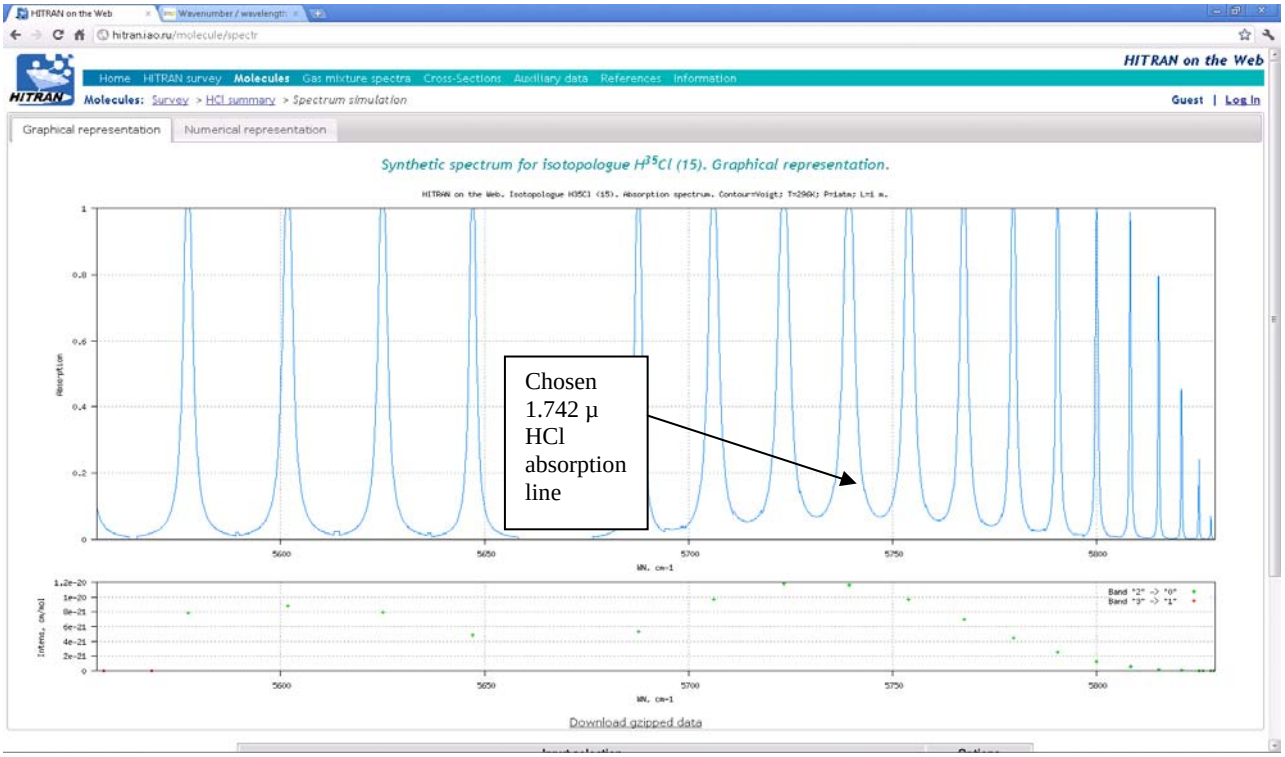


Figure 4-11
Resulting Hi Tran Database Spectra for HCl in the 5500 to 6000 cm^{-1} Spectral Range

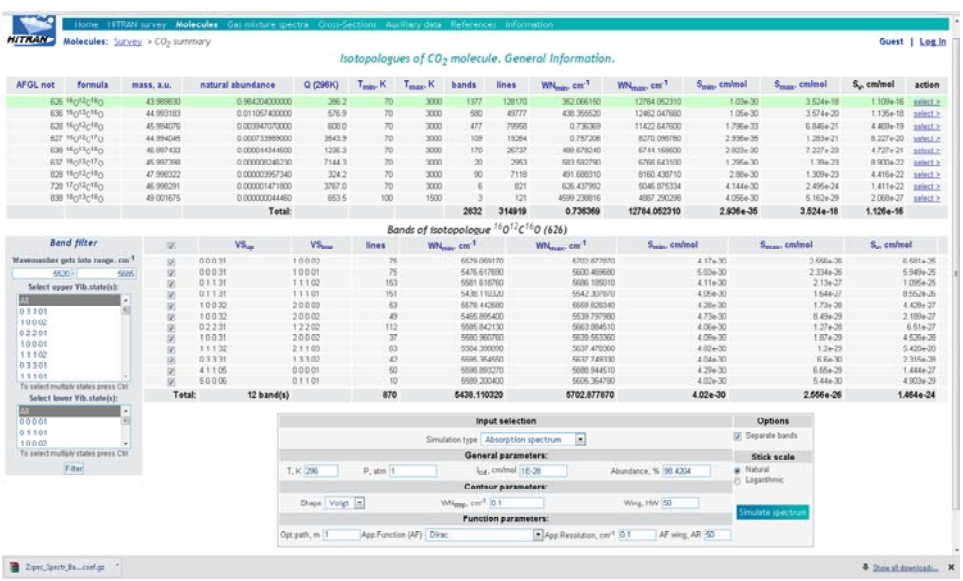


Figure 4-12
Isotopologues Investigated for CO_2 in the 5500 to 6000 cm^{-1} Spectral Range

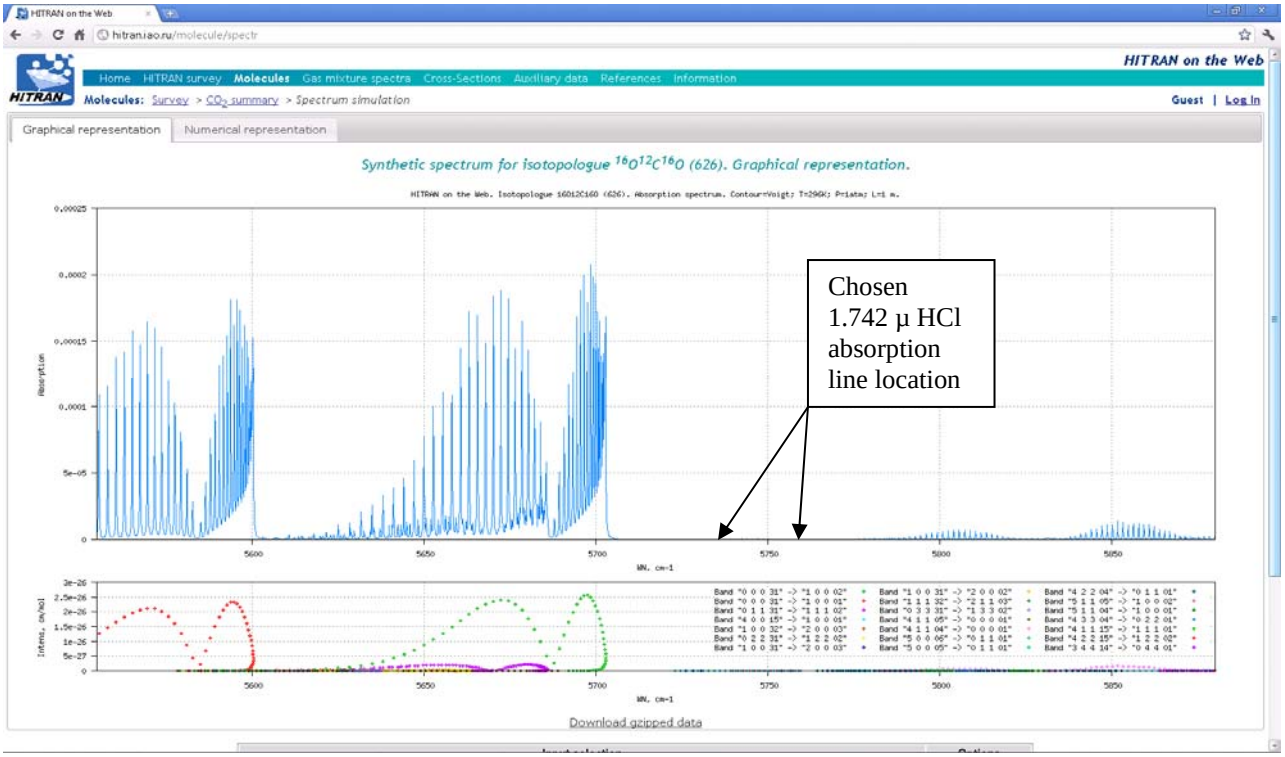


Figure 4-13
Resulting Hi Tran Database Spectra for CO_2 in the 5500 to 6000 cm^{-1} Spectral Range

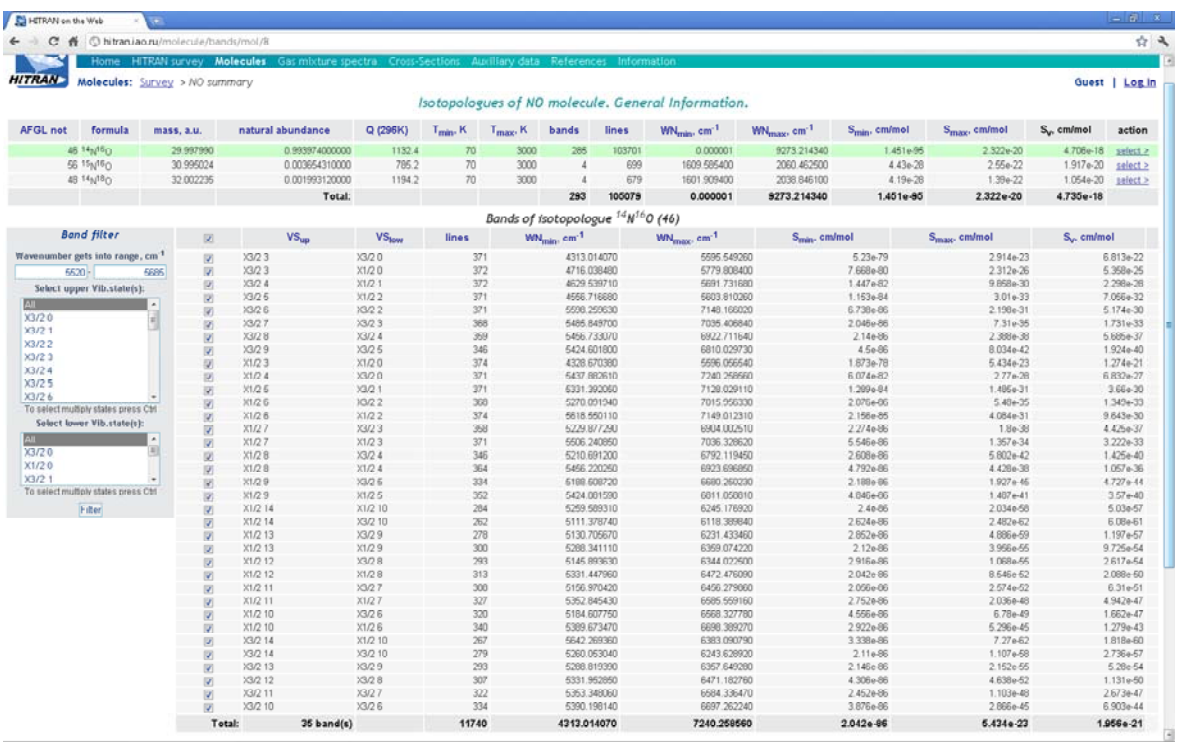


Figure 4-14
Isotopologues Investigated for NO in the 5500 to 6000 cm^{-1} Spectral Range

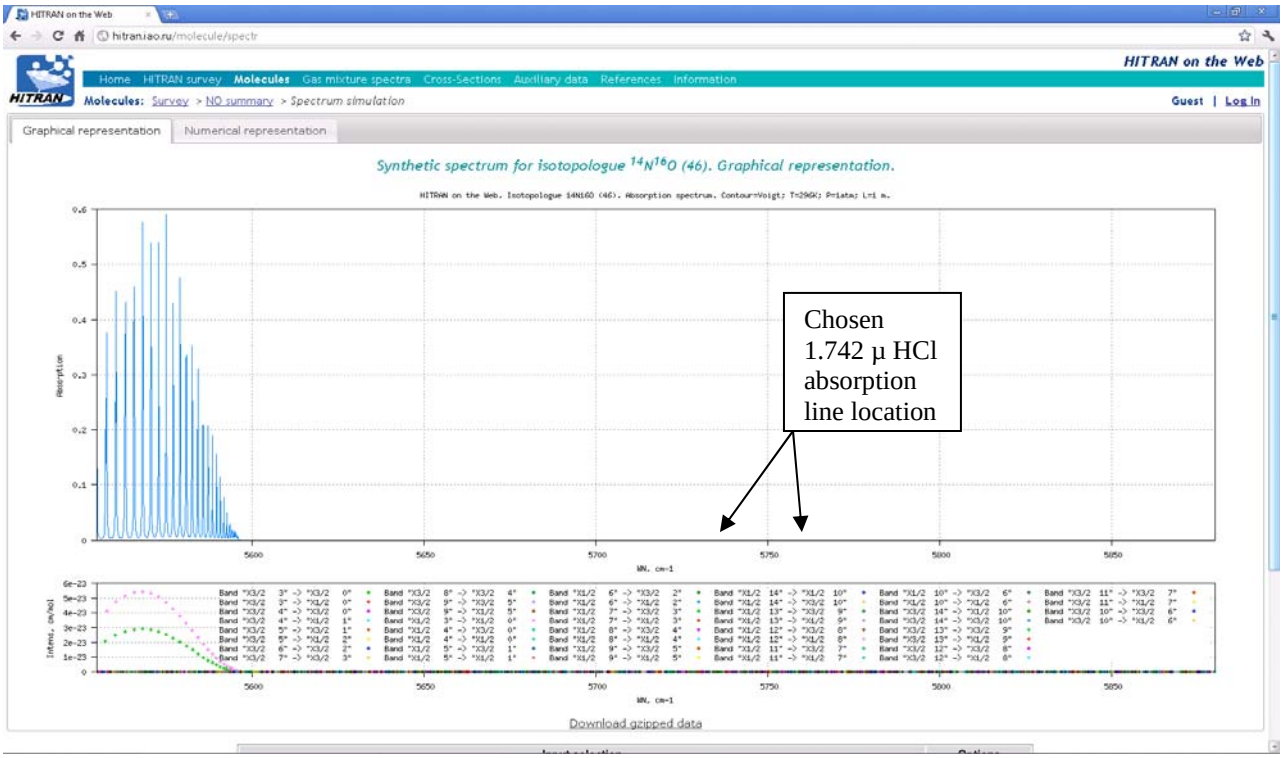


Figure 4-15
Resulting Hi Tran Database Spectra for NO in the 5500 to 6000 cm^{-1} Spectral Range

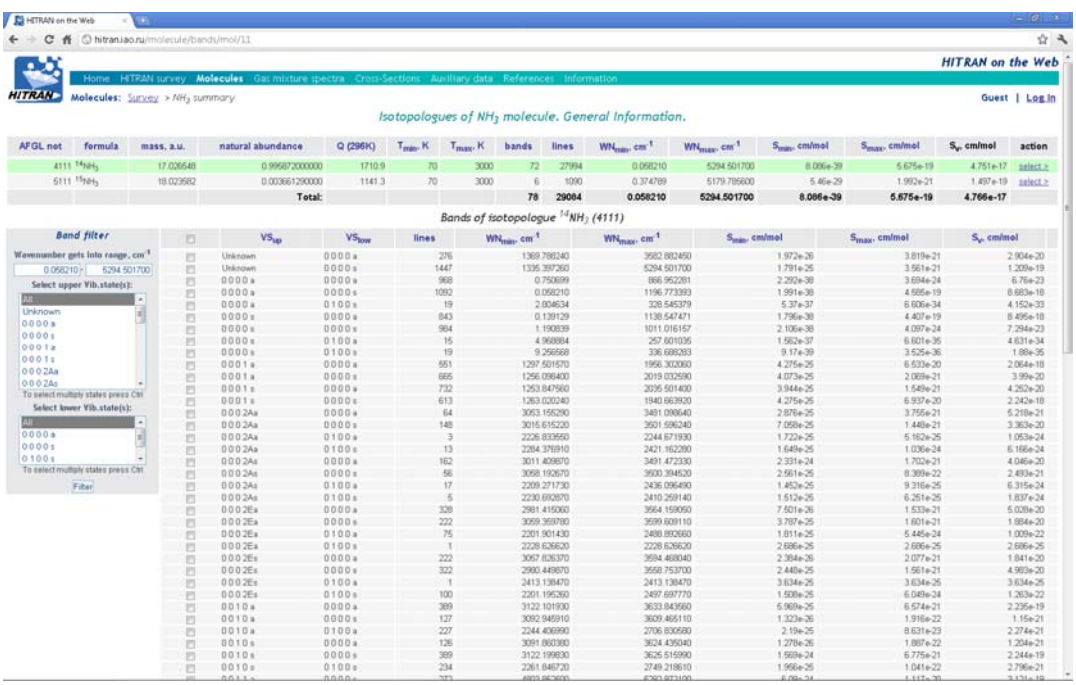


Figure 4-16
Isotopologues Investigated for NH_3 in the 5500 to 6000 cm^{-1} Spectral Range, No Resulting Hi Tran Spectra

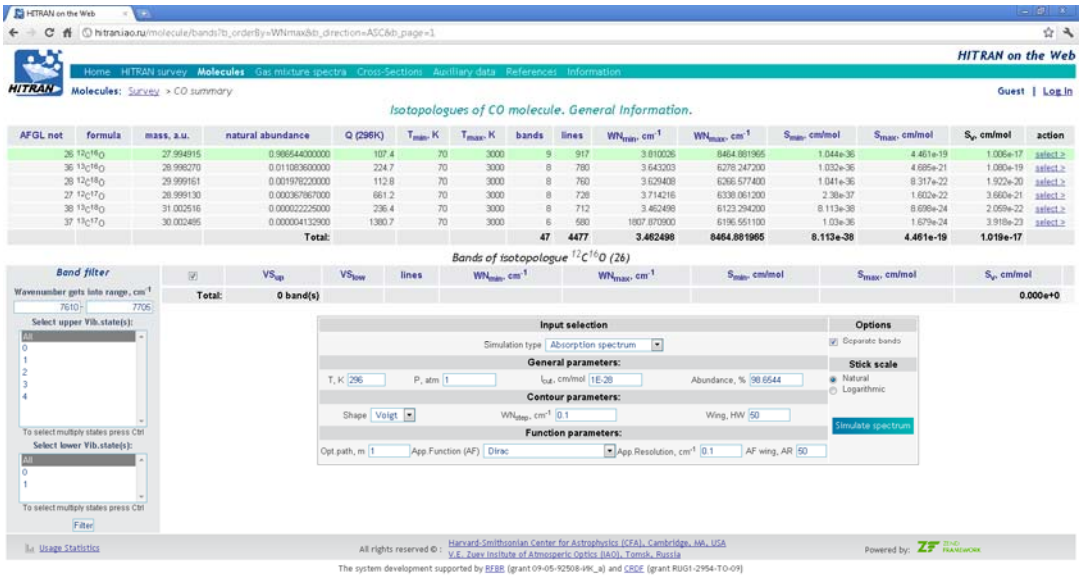


Figure 4-17
Isotopologues Investigated for CO in the 5500 to 6000 cm^{-1} Spectral Range, No Resulting Hi Tran Spectra

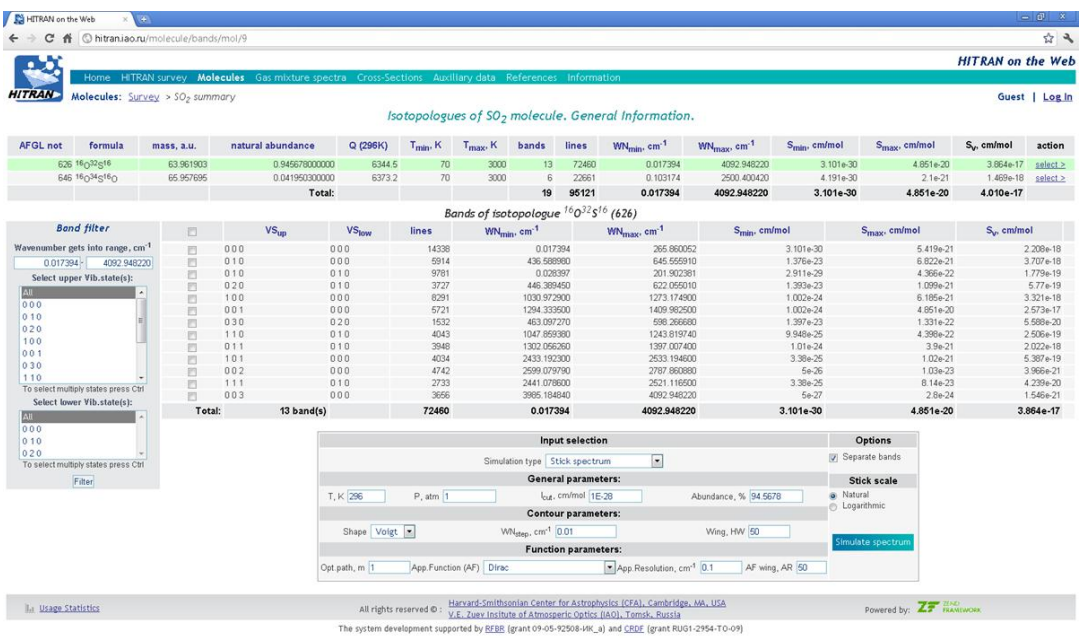


Figure 4-18
Isotopologues Investigated for SO_2 in the 5500 to 6000 cm^{-1} Spectral Range, No Resulting Hi Tran Spectra

The resulting spectra indicate where the HCl absorption line chosen by the manufacturer for their HCl instrument (1.742 µ) is, and is also indicated on the possible interfering species spectra where that line fits on any of the resulting spectra.

When doing the Hi Tran database evaluation of the possible interfering species only NO and CO_2 had resulting spectra in the same region where HCl spectra were determined.

From the Hi Tran database, the chosen 1.742 µ HCl absorption line appears to only have a possible interference from CO_2 (refer to Figure 4-12), although the CO_2 absorption is very weak at that wavelength.

Interference Tests

To verify that there were no interferences from other flue gas constituents, it was decided to use cylinders of gas that had concentrations similar to that known in coal-fired power plant flue gasses

The table below lists the gas concentrations used to check for interferences, to simplify matters, the gas in the cylinders (refer to Figure 4-19) were used as the carrier gas for the HCl into the sample cell instead of zero air which was used for the earlier tests. All tests were done at 200 °C but without moisture as those tests were conducted in the earlier investigations.

Table 4-3
Interference Testing Gas Concentrations

Interference		**NO= 1510 ppmV**
Testing		**CO= 1220 ppmV**
Gas		**CO2=11.9%**
Concentrations		**SO2=2050 ppmV**
		NH3=100ppmV

Tables 4-4 lists the results for the interference tests obtained with the 1.0 meter cell, single pass configuration. Note the system was calibrated at 25 ºC and the response at the ambient temperature was left on each plot as the control, the interference tests were done at 0% moisture at the 200 ºC temperature and were conducted only once at each level.

The figure below the table, Figure 4-20, is a graphical representation of the system response for the set of the interference tests for each of the possible interfering gasses investigated.

It is clear from these tests that the other gasses at concentrations typical to flue gasses in coal-fired power plants do not interfere with TDL HCl measurements at 1.742 µ, as there was no observed effect in the system response. The only gas that may have been of concern from the Hi Tran evaluation, CO_2 also did not affect the TDL HCl response at a concentration of 11.9% CO_2 in N_2.

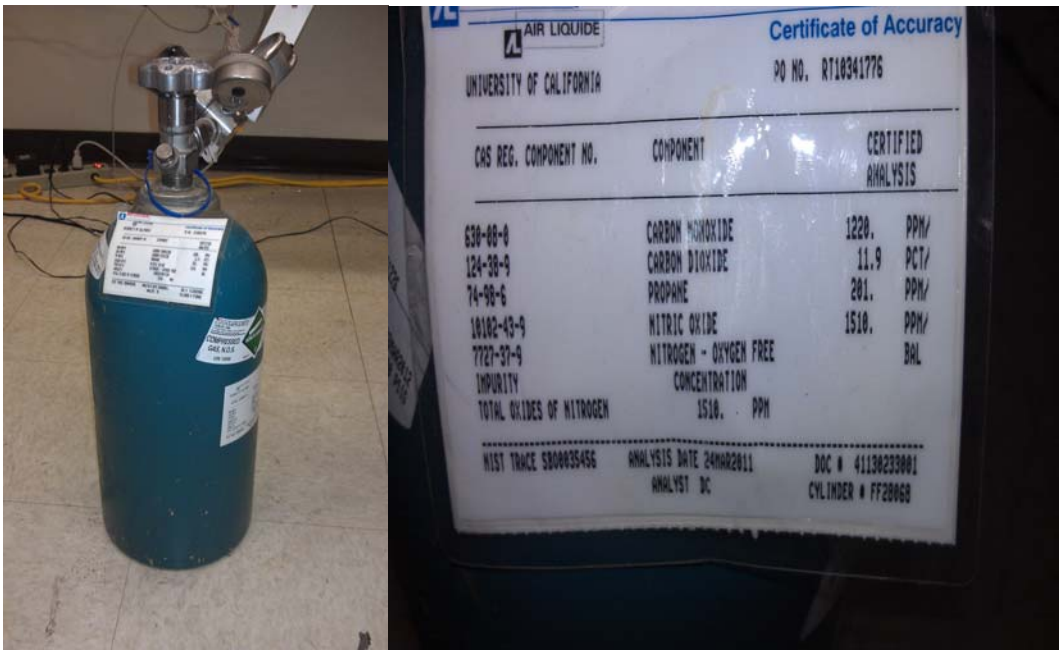


Figure 4-19
Cylinder and Specification Sheet Containing CO, CO_2 and NO Used to Investigate for Possible Interferences of HCl in the 5500 to 6000 cm^{-1} Spectral Range

Table 4-4
Interfering Gas Test Results of Unisearch S Series LasIR SM410 for 1.0 Meter Sampling for NO, CO, CO_2, SO_2 and NH_3 at 0% Moisture and 200 ºC

HCl	Temperature 1		Interference NO, CO, CO2 at 200 C		Interference SO2 at 200 C		Interference NH3 at 200 C	
ppmV-m	Moisture	25 C	Moisture		Moisture		Moisture	
(25 C)	0%	SD	0%	SD	0%	SD	0%	SD
0.0	0.09	0.05	0.18	0.12	0.14	0.09	0.16	0.11
2.5	2.50	0.07	2.45	0.34	2.23	0.23	2.33	0.34
5.0	5.26	0.09	5.15	0.14	5.14	0.36	5.35	0.44
10.0	9.76	0.05	10.23	0.38	10.48	0.46	10.38	0.54
15.0	14.60	0.23	15.21	0.24	15.16	0.55	15.25	0.87
25.0	25.20	0.24	25.27	0.52	25.07	0.86	25.36	1.20

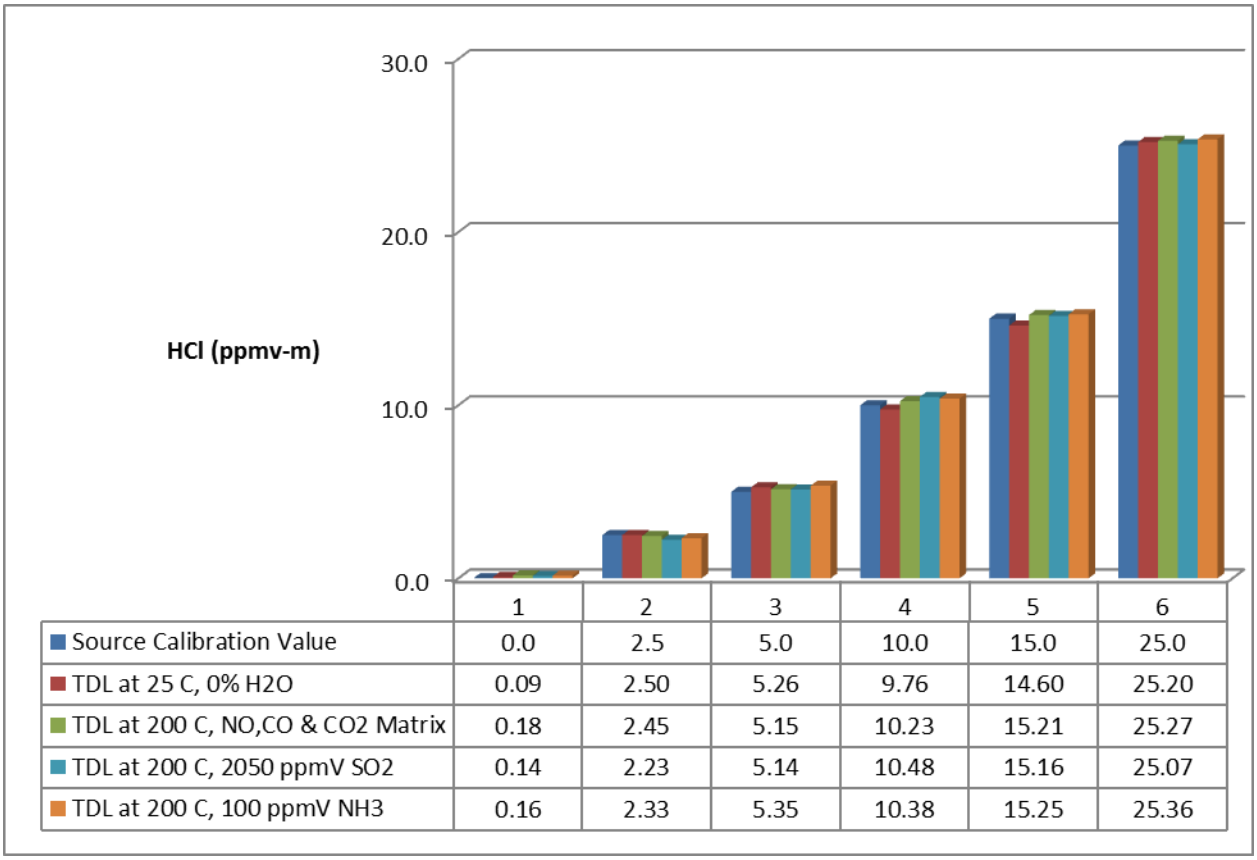


Figure 4-20
Graphical Representation of System Response over the Concentration Range at 0% Moisture at 200 ºC during the Interference Tests

Data Analysis Moisture and Temperature Effects

The data was then analyzed for both moisture effects and temperature effects, all data was used including the interference tests since they were part of total data set.

For moisture effects the average percent difference for each matrix point was determined by the following equation (Eq. 4-1)

$$< d(m)i > = \frac{\sum absolute\ (x_i - a_i)\ x\ 100\%}{(n)\ (x_i)}$$ **Equation 4-1**

where *d(m)j* refers to the average percent difference with respect to moisture between the expected ammonia concentration (x) from the calibrated standard source and the fifteen-minute average SM410 HCl reading (a_i) (corrected for the initial zero air background) during the sampling period, and *n* corresponds to the number of samples of different moistures at the same temperature (which is 4, 2 for each of the different water concentrations).

The average difference with respect to moisture was 3.33 %.

For temperature effects the average percent difference for each matrix point was determined by the following equation (Eq. 4-2)

$$< d(t)\,j > = \frac{\sum\ absolute\ (x_i - a_i)\ x\ 100\%}{(n)\ (x_i)}$$ **Equation 4-2**

where *d(t)j* refers to the average percent difference with respect to temperature between the expected HCl concentration (x) from the calibrated standard source and the fifteen-minute average SM410 ammonia reading (a_i) (corrected for the initial zero air background) during the sampling period, and *n* corresponds to the number of samples of different temperature at the same moisture (which is 9, 7 for zero moisture and 2 for 4% moisture).

The average difference with respect to temperature was 2.69 %.

Table 4-5 lists the average percent difference of the measured results obtained with respect to the standard gas values obtained from the 1 meter sample cell, single pass configuration with the following grouping.

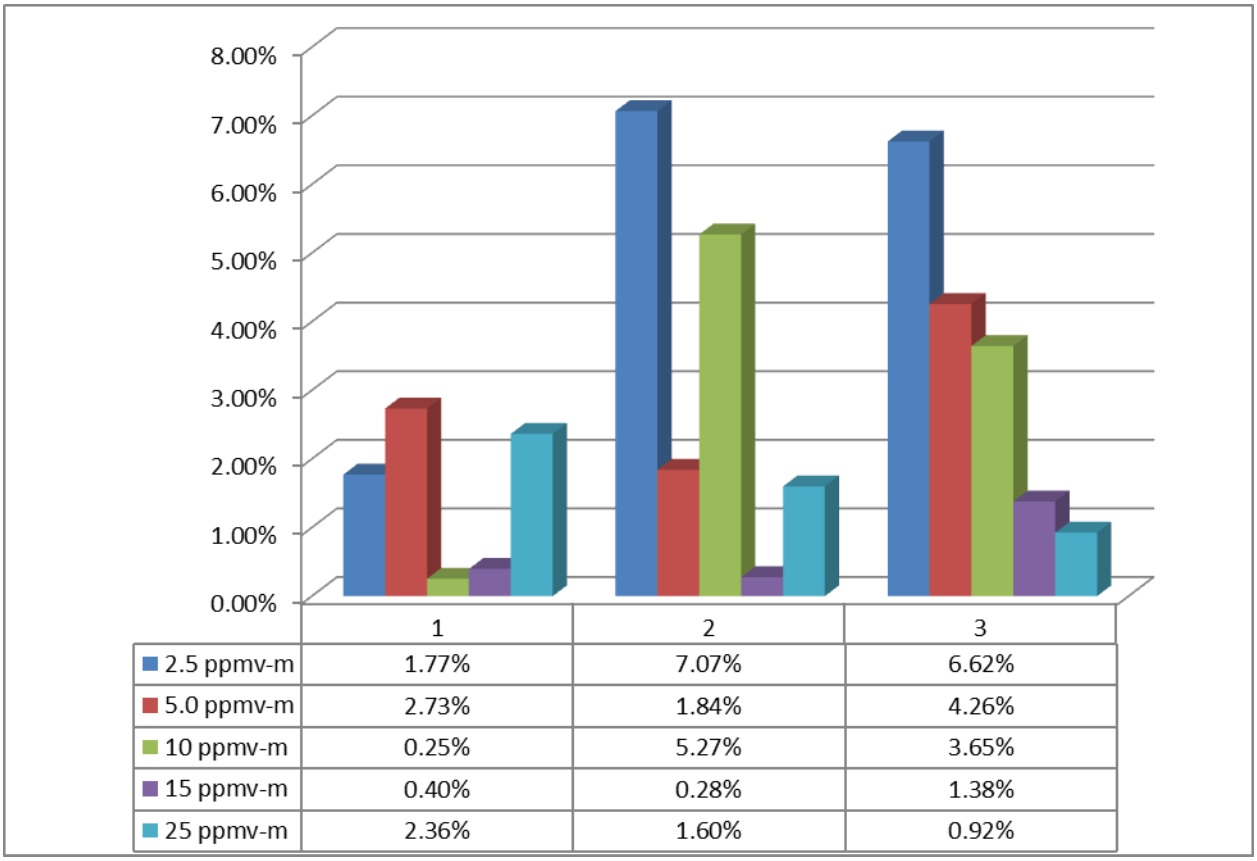
1. Group 1: 1.0 meter sampling cell 100 ºC.
2. Group 2: 1.0 meter sampling cell 200 ºC.
3. Group 3: 1.0 meter sampling cell 200 ºC interference testing

Table 4-5
Lists the Average Percent Difference of the Measured Results Obtained with Respect to the Standard Gas Values Obtained with the Following Grouping: Group 1: 100 ºC, Group 2: 200 ºC, Group 3: 200 ºC Interference Testing

HCl ppmV-m (25 C)	HCl ppmV-m (100 C)	Average % Difference
0.0	0.06	
2.5	2.54	1.77%
5.0	5.14	2.73%
10.0	10.03	0.25%
15.0	15.06	0.40%
25.0	25.59	2.36%

HCl ppmV-m (25 C)	HCl ppmV-m (200 C)	Average % Difference
0.0	0.09	
2.5	2.32	7.07%
5.0	5.09	1.84%
10.0	10.53	5.27%
15.0	14.96	0.28%
25.0	25.40	1.60%

HCl ppmV-m (25 C)	HCl ppmV-m (200 C) Int	Average % Difference
0.0	0.16	
2.5	2.33	6.62%
5.0	5.21	4.26%
10.0	10.36	3.65%
15.0	15.21	1.38%
25.0	25.23	0.92%



	1	2	3
2.5 ppmv-m	1.77%	7.07%	6.62%
5.0 ppmv-m	2.73%	1.84%	4.26%
10 ppmv-m	0.25%	5.27%	3.65%
15 ppmv-m	0.40%	0.28%	1.38%
25 ppmv-m	2.36%	1.60%	0.92%

Figure 4-21
Graphical Representation of the Percent Difference over the Three Groupings at Each of the Sampling Levels, Group 1: 100 ºC, Group 2: 200 ºC, Group 3: 200 ºC Interference Tests

Linearity

Linearity was assessed by a linear regression analysis of the 15-minute averaged values for all 10 tests that were done at the same concentration over the range of moisture and temperature and interference variables.

Linearity is expressed in terms of slope, intercept, and coefficient of determination (R^2) and is shown below in Figure 4-22.

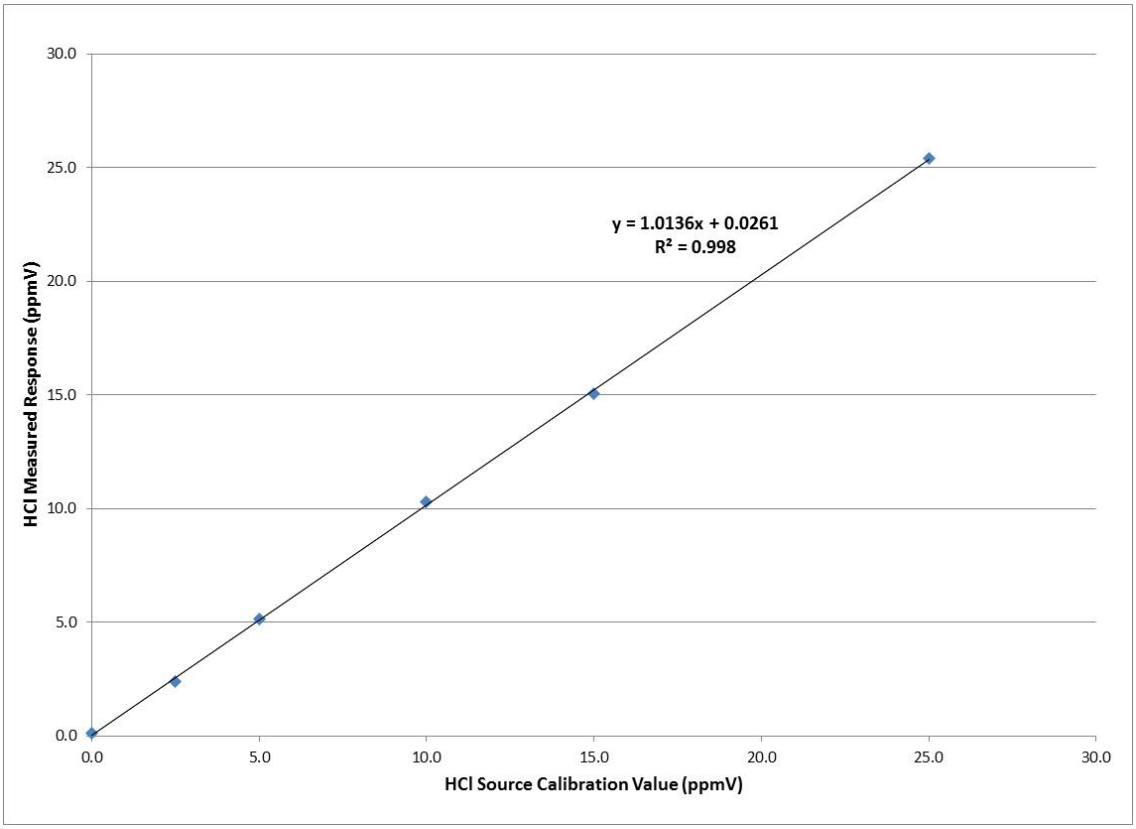


Figure 4-22
Linear Regression of the measured response from the Unisearch S Series LasIR SM410 as compared tp the source calibration value. The measured responses are averaged from all 10 tests at each source calibration value that encompassed the range of moistures and temperatures used in this evaluation.

Precision

Precision was calculated in terms of the average % RSD at each concentration of the Unisearch S Series LasIR SM410 readings over the duration of each of the 10 sets included in the overall test matrix. This included 10 zero samples during each individual test. For each fifteen-minute period

4-22

during each test , all 1-minute readings from the SM410 were recorded, and the mean and standard deviation of those readings were calculated.

The average precision $<P>$ was then determined as:

$$< P > = < S/(X) > x\ 100 \qquad \textbf{Equation 4-3}$$

where S is the standard deviation of the Unisearch S Series LasIR SM410 readings and X is the mean of the SM410 readings for each individual period each period, and $<S/(X)>$ is an average over all 10 samples at each concentration. The average precision is reported for each of the ppmV-m source calibration values and overall for all values.

HCl Source (ppmV)	Average Precision
2.5	6.50%
5.0	2.77%
10.0	2.95%
15.0	0.87%
25.0	2.49%

Average precision over the entire range for all 10 tests is 3.12%

Zero Drift and Minimum Detection Limit

Zero drift is reported in terms of the RSD of the stable readings obtained from the Unisearch S Series LasIR SM410 in daily sampling of the same HCl standard gas and zero gas supplied to the sample cell. A total of 10 zero samples each containing fifteen 1-minute samples were taken during the evaluation.

Zero drift was found to be 1.78% over the 10 tests.

Minimum detection limit is reported at three times the average standard deviation of all the one-minute zero measurements made at each of the temperatures used in the evaluation when the instrument was evaluated over the entire range of tests.

The three temperatures, were 25 ºC (1 set of measurements, 15 points), 100 ºC (3 sets of measurements, 45 points) and 200 ºC (6 sets of measurements, 90 points).

The numbers are reported in ppmV per meter, and are also shown with a 5 meter path, typical to power plant installations as detection limits improve with longer path lengths.

Temperature degrees °C	Minimum Detection Limit ppmV/m	Minimum Detectiom Limit 5-meters ppmV
25	0.35	0.07
100	0.66	0.13
200	1.10	0.22

5
SUMMARY

Table 5-1 summarizes the results for the evaluation of the Unisearch S Series LasIR SM410 for HCl response.

Parameter	Results	Notes
Percent difference with respect to moisture	3.33 %	Overall 4 tests in the matrix
Percent difference with respect to temperature	2.69 %	Overall 9 tests in the matrix
Maximum percent difference	8.80%	@ 100 C 0% moisture 2.5 ppmV-m test 1
Minimum percent difference	0.20%	@100 C 0% moisture 15.0 ppmV-m test 2
Linearity	Regression slope y = 1.014x-0.026 R^2=0.998	Calculated over entire range for all 10 tests
Precision	3.12%	Average precision for all 10 tests.
Zero drift	1.78%	Average zero drift for all 10 tests
Minimum detection limit	@25 ºC 0.35 ppmV/m @100 ºC 0.66 ppmV/m @200 ºC 1.10 ppmV/m	For 1 test For 3 tests For 6 tests

6
REFERENCES

1. **Ahlberg H**., S. Lundqvist, R. Tell, and T. Andersson, "*Industrialized high sensitivity fiber-optic near-IR diode laser based gas analysis system*," in Tunable Diode Laser Spectroscopy, Lidar, and DIAL Techniques for Environmental and Industrial Measurements, H. I. Schiff, A. Fried, and D. K. Killinger, eds., Proc. SPIE 2112, 118–129 (1994).
2. **Cooper,**David E. and Russell E. Warren, "Frequency modulation spectroscopy with lead-salt diode lasers: a comparison of single-tone and two-tone techniques," Appl. Opt. **26**, 3726-3732 (1987)
3. **Cooper,**David E. and Clinton B. Carlisle, "*Two-tone frequency-modulation spectroscopy with a CO_2 laser*," J. Opt. Soc. Am. B **7**, 164-171 (1990)
4. **Fried Alan**, Bruce Henry, David D. Parrish, James R. Carpenter, Martin P. Buhr "*Intercomparison of tunable diode laser and gas filter correlation measurements of ambient carbon monoxide"* Atmospheric Environment. Part A. General Topics Volume 25, Issue 10, 1991, Pages 2277-2284
5. **Goldman, R.** R. Gamache, A. Perrin, J.-M. Flaud, C. P. Rinsland, and L. S. Rothman, "*HITRAN partition functions and weighted transition-moments squared*," J. Quant. Spectrosc. Radiat. Transfer 66, 455–486 (2000).
6. **Himes R**., J.Pisano and T. Durbin, "*Ammonia Lab Test Verification – Unisearch LasIR SM410"* (EPRI 1014664, 2006).
7. **Mackay G**., Chanda A., and Mackay K., *Unisearch Associates Inc. LasIR System Manual*, (2010)
8. **Schiff, H.I**., Mackay, G.I., Bechara. J.: "The use of tuneable diode laser absorption
9. Spectroscopy for atmospheric measurements", in Chemical Analysis Series, Vol. 17 (Wiley, New York 1994).
10. **Silver, Joel A**., "Frequency-modulation spectroscopy for trace species detection: theory and comparison among experimental methods," Appl. Opt. 31, 707-717 (1992)

Ammonia Monitor Evaluations / Reports

- Survey of Ammonia Monitor Applications and Experience (1017560, 2009)
- Ammonia Monitor Lab Test Verification – LTG Lightwise TDL Monitor (1019372, 2009)
- Field Demonstration of Tunable Diode Laser Ammonia Monitors – TVA Allen Unit 3 (1016368, 2008)

- Ammonia Monitor Lab Test Verification – Siemens LDS 6
  (1014745, 2007)
- Ammonia Monitor Lab Test Verification – Norsk Electo Optik's (NEO) LaserGas II
  (1015315, 2007)
- Ammonia Monitor Lab Test Verification – Opsis LD500
  (1016116, 2007)
- Ammonia Monitor Lab Test Verification – Unisearch LasIR SM410
  (1014664, 2006)

A
APPENDIX

Figure A-1 shows three different versions of the analyzer, portable, 20 channel and 8 channel respectively.

The beam is not beamsplit but optically multiplexed which permits most of the individual laser emission to be directed along each optical path.

Front-panel keypad allows relevant operational parameters to be entered by the user. No field calibration is required as they use the fast scan technique for signal analysis. Fast, real-time in-situ measurements of gas concentrations can be made under various industrial environments.

These analyzers are suitable for ambient air monitoring and for industrial process control.

The Unisearch S-Series LasIR™ consists of a control unit containing the laser, central power supply, and signal processing electronics, plus multiple sets of remote optics depending on application. The SM410 model accommodates up to four sets of optics, while the SM810 accommodates up to eight sets. In the “SM series, the light is optically multiplexed so that it can supply 100% of the available power sequentially to each location.

The analyzer is typically housed in a control or instrument room and coupled to the remote optics by means of fibre optical cables for transmitting the laser light and co-axial cables for signal return. A typical layout for a fibre coupled LasIR® system is shown in Figure A-2. All signal processing, data reporting, and data storage functionality is incorporated in the analyzer, although an optional external computer may be connected for set-up and supplementary external data logging.

According to Unisearch the physical and optical layout is similar to that used in the previous LasIR®, but the analyzer and signal processing technologies in the SM and related series LasIR’s now incorporate fast scan techniques instead of modulation techniques.

The lasers now routinely used have high output powers (up to 20 mW), are stable, and have excellent tuning characteristics.

The previous LasIR® instruments used two tone frequency modulation for low level signal processing yielding a quasi second derivative signal of the absorption spectrum. Quantification in 2f frequency modulation is based on the second derivative of the absorption signal. This gives enhanced sensitivity, but the required frequency modulation makes the measurement sensitive to external factors such as the length of the signal return cable or other electronic effects.

Figure A-1
Different Configurations of UnisearchLasIRTM S-Series Controller

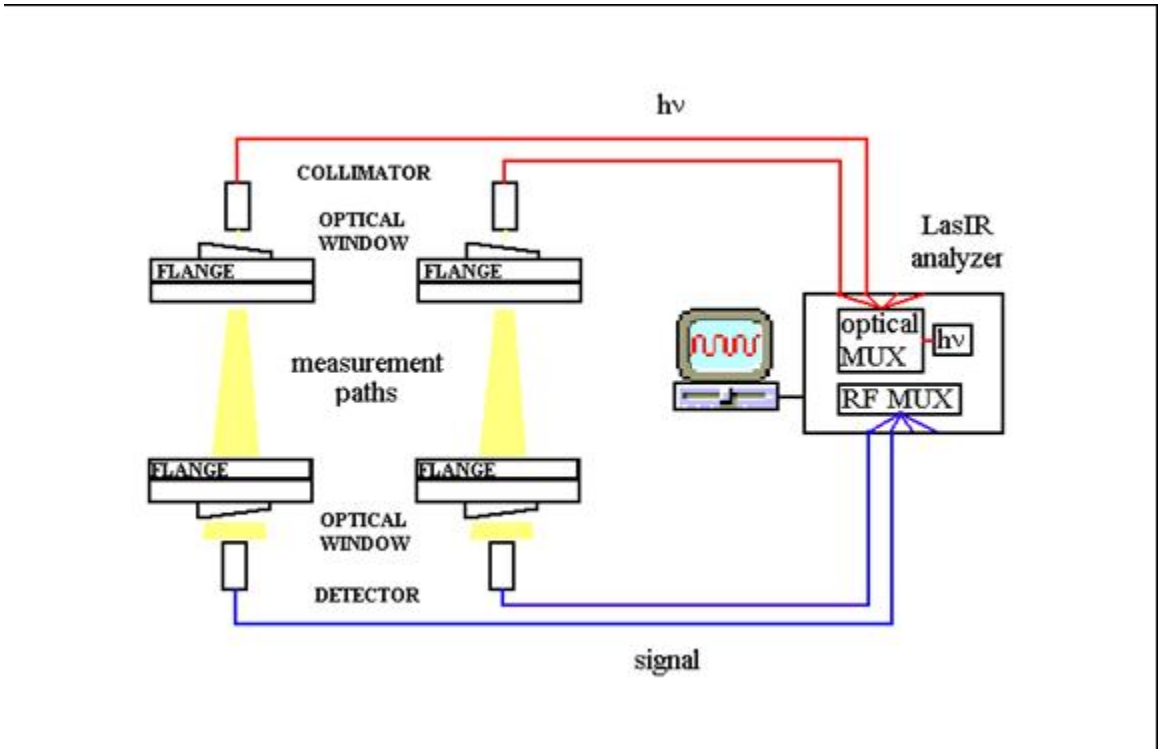


Figure A-2
Schematic of Fiber Coupled LasIR System

Direct absorption signal processing, where quantification is based on Beer's law, as in the current analyzers, is a direct measurement of the absorption feature. According to Unisearch, recent advances in fast electronics have made it possible to achieve similar sensitivities using the new fast scan direct absorption signal processing technology when compared to 2f measurements.

Unisearch has also developed a computer controlled gain adjust feature. This feature is necessary to compensate for changes in power specifically in environments where dust loadings can change rapidly and over a large range. The gain adjust feature increases the dynamic range of the instrument and reduces noise by keeping the amplified signal within the optimum range.

In certain circumstances, it is desirable to measure ammonia concentrations at temperatures above ambient. From Beer's law, the strength of the absorbance depends on the number of absorbing species. The LasIR is normally calibrated assuming T_{cal} = 298 K (25 °C) and P_{cal} = 1013 mbar (1 atm). Mixing ratios reported in ppm, ppb, or % by volume are independent of temperature and pressure, as they are simply a ratio and do not change as the gas expands or contracts. The absolute absorbance responds to the actual number density of absorbing molecules, which does change with T or P. Thus to obtain an accurate mixing ratio at temperatures or pressures other than T_{cal}, P_{cal} , it is necessary to apply a correction factor based on the ideal gas law (PV = nRT). These corrections are calculated automatically by the LasIR analyzer if the process temperature and pressure are known. This may be achieved either by

entering fixed values for process temperature and pressure upon initial set-up, or by connecting an external sensor which communicates with the LasIR via a 0-10 V analog input.

The strength of a given absorption feature can vary with temperature. This can be corrected for if the relationship is known. The peak height at calibration temperature (usually 298 K) is defined to be one. Unisearch has measured the appropriate correction factors at different temperatures. Automatic correction for this effect is included in the system software.

The laser contained in this analyzer is tuned thermally across the spectral feature selected to monitor the gas. It is mounted on a thermoelectric cooler (Laser Head Assembly) that monitors and controls the coarse temperature of the laser. Fine-tuning is achieved by a cyclic current ramp that facilitates repetitive scanning of a given laser frequency range. Multi-scan averaging improves the sensitivity of the system. .

The laser diode is mounted on a thermoelectric cooler to maintain a stable temperature environment. The laser is coupled to a fiber-optic cable, which is in turn coupled to a fiber-optic beam splitter where the beam is divided into equal outputs in the ‘Multiplexer’ mode of operation.

The number of channels of the multiplexer depend on the lines of site that the application requires. Typically muliplex systems are from 4 to 16 channels, where as a beam split system would be used for up to 2- channels. Refer to Figures A-3 and A-4 which show the front and back panel of a Unisearch S-Series 2 channel LasIR. Refer to Figure A-5 which shows the front panel of a rack mounted eight channel multiplexed S-Series LasIR and a two channel table top beamsplit S-Series LasIR.

Figure A-3
Front Panel of Unisearch S-Series Two Channel LasIR

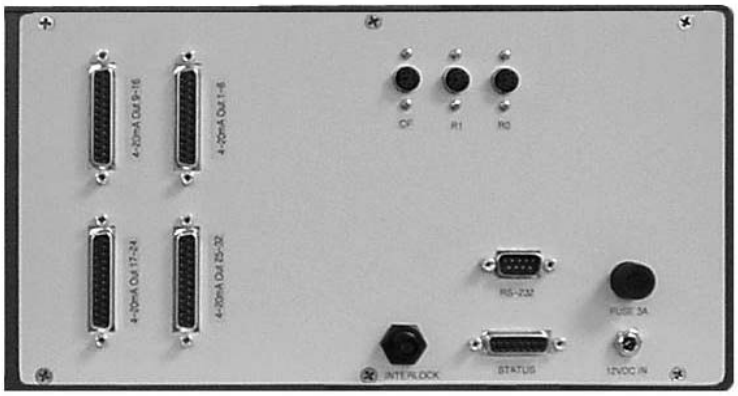


Figure A-4
Back Panel of Unisearch S-Series Two Channel LasIR

Unisearch RoHS-compliant Rack-mount and mini-series TDL Gas Analyzers

19”x6”x11”
(4, 8, 12 &16 channels)

11”x6”x11”
(1 and 2 channels)

Figure A-5
The Front Panel of an Eight Channel Multiplexed Rack Mounted S-Series LasIR and Two Channel Table mount Beamsplit S-Series LasIR with Dimensions and Channel Availability

The outputs using an optical multiplexer from the fiber-optic beam splitter are sent to the fiber outputs of the analyzer where they provide the laser emission for the signal measurements for each of the measurement targets.

One output from the beam splitter provides the laser emission for the reference channel. The laser emission on the reference channel passes through a small cell (Reference Cell) containing a high concentration of the target gas that is used to lock the laser wavelength onto the absorption feature and also serves as a secondary calibration standard.

Unisearch has multiple optical configurations depending on the application. They have systems that can go single path with an emitter on one side and a detector on the other side (refer to Figure A-6). They also have a dual pass system, (refer to Figure A-7) with a transmitter/receiving assembly on one side and a retroreflector on the other side. This monostatic

setup effectively doubles the optical path length and yields double the sensitivity of the measurements undertaken.

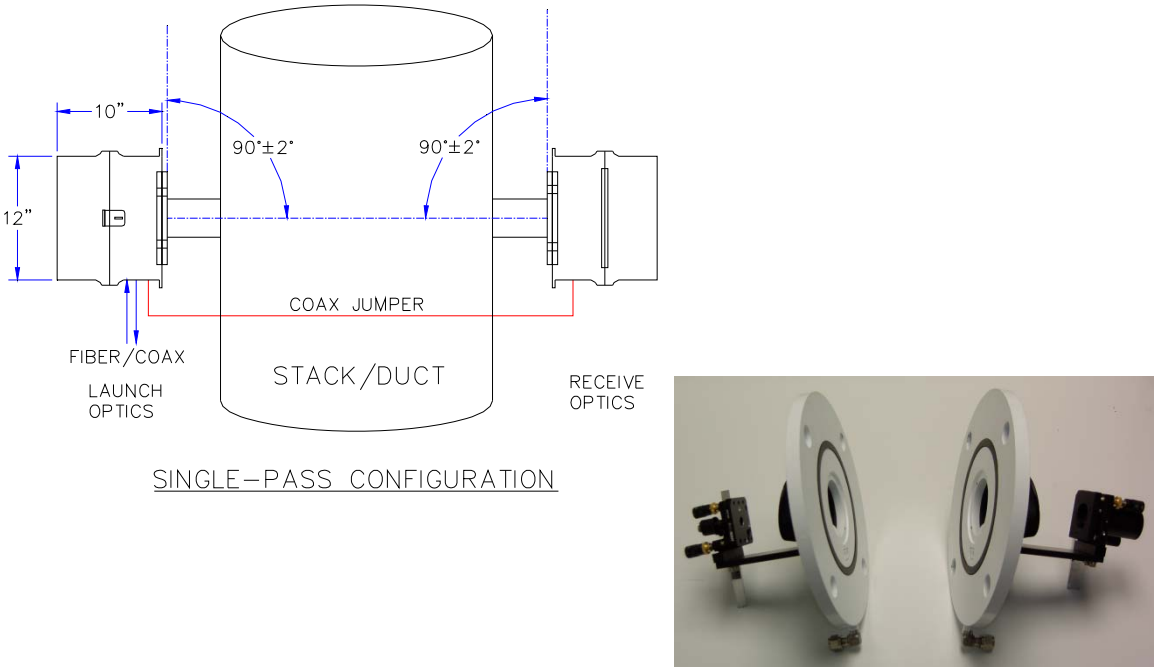


Figure A-6
Unisearch Optics that can go Single Path with an Emitter on One Side and a Detector

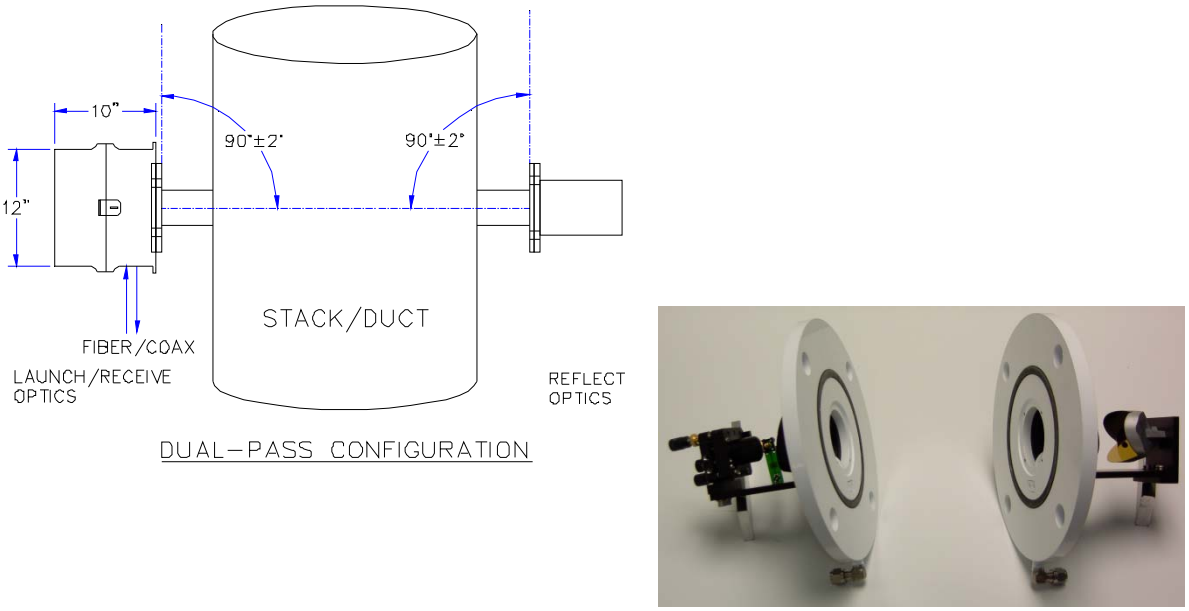


Figure A-7
Unisearch Optics with a Transmitter/Receiving Assembly on One Side and a Retroreflector on the Other Side

The optical heads are totally passive and only require the fiber optic and coaxial cable hookup.

For power plant applications, clean purge air is required at a pressure rating of 50 PSI.

Note that the optical assemblies are designed to mount on standard 4 inch flanges and can be covered with a NEMA4 enclosure as shown in Figures A-8 and A-9.

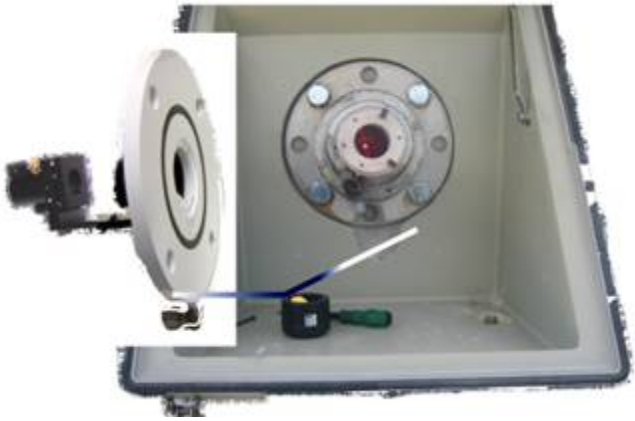


Figure A-8
Unisearch Optics Mounted in a NEMA4 Enclosure for Industrial Applications, Box Open

Figure A-9
Unisearch Optics Mounted in a NEMA4 Enclosure for Industrial Applications, Box Closed, Two Sizes are Available

Figure A-10
Unisearch Optics Mounted in a NEMA4 Enclosure Measuring HCl at an Incinerator

System Applications

Examples of system applications for power plants are NH_3 slip control in DeNOx installations. Currently Unisearch has over 20 installations in the US alone monitoring NH_3 slip.

Examples of HCl applications are for incinerators (numerous installations) as well as one continuous emission monitoring for coal fired power plants just installed.

Specifications

The following lists the specifications for a typical HCl system.

A typical HCl system has the following specifications:

One characterized near infrared DFB Diode Laser suitable for remote sensing measurements of the compound specified.

Fully integrated automatic operation with reboot on power down.

UNISEARCH Scan-and-fitTM software, which provides acquisition of one species (or two species forclosely lying lines with optional software) with a single laser with 1 sec resolution.

Real time fitting of ambient spectra to reference cell provides long-term stability and absorption line frequency locking.

Detectors: PIN InGaAs photodiode operating at room temperature

Detection Limits: ~ 0.5 ppm for a 1-m separation of emitter and retro reflector

Precision: + 1% of signal or detection limit, whichever is larger.

Sampling time: ~ 1 sec or longer

Accuracy: ~ ±5%.

Physical Specifications:

Dimensions: Electronics

Physical size 15 (W) x 30 (D) x 15 (H) cm

Weight<10 kg

Power <6 Amps at 12 VDC

AC adapter (supplied) 60 watts, 110/240 VAC

List of quoted sensitivity in ppmV for the Unisearch'sLasIR system for HCl at process temperatures of typically 200°C / 1 bar for 5 meters of optical pathlength normally expected in flue gas environments at coal-fired power plants is 0.2 ppmV, or approxiamately 1.0 ppmV-meters.

Company Information

For USA contact information Unisearch is represented by CEMTEK Systems Inc, which has two locations and can be contacted at the following:

Cemtek Systems, Inc.
2013 S. Wood Ave.
Linden, NJ07036

Tel. 908-474-9630
Fax 908-474-9413
Cell 609-577-0645

Cemtek Environmental, Inc.
3041 Orange Avenue
Santa Ana, CA 92707-4247

Tel. 714-437-7100
Fax 714-437-7177

Web address**:** www.cemteks.com

For direct contact with the Unisearch

Unisearch Associates Inc.
96 Bradwick Drive, Concord, Ontario, Canada
L4K 1K8

Phone 905 669 3547
Fax 905 669 8652

Email: info@unisearch-associates.com

Web address www.unisearch-associates.com