## JOHN COLLINS

Evaluation of an Optical Remote Sensing Device for Laboratory Validation of Optical Remote Sensing/Computed Tomography Theory

Under the direction of Lori A. Todd, Ph.D.

## ABSTRACT

Optical remote sensing/computed tomography technology has been demonstrated in theoretical studies to be a feasible methodology for measuring gases and vapors in workplace air. This non-invasive, near real-time sampling system scans a room and reconstructs concentration maps with good spatial and temporal resolution. This system would require an optical remote sensor capable of providing accurate measurements over the beam pathlength.

This research evaluated the accuracy of a commercially-available, optical remote sensing (ORS) device to determine its feasibility for use in the laboratory validation of optical remote sensing/computed tomography theory. Experiments were performed using direct-reading validation methods to assess accuracy in both uniform and non-uniform gas concentrations of SF<sub>6</sub> using both a single and a reflected beam. The effect of pathlength on accuracy was determined, and the effect of inputting incorrect values of pathlength and detector signal levels into the control system was also determined. The efficiency of the mirrors used to reflect the beam was also determined.

Results indicate that the device is a promising tool for this application.

# ACKNOWLEDGMENT

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I dedicate this thesis to my wife, Maria, my parents, and my grandmother, Ruth Collins. They must know that without their presence, love and encouragement, this accomplishment would be meaningless.

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# LIST OF ABBREVIATIONS

cc/min	cubic centimeters per minute
СТ	Computed Tomography
d.c.	direct electrical current
DIAL	Differential Absorption Laser
DOAS	Differential Optical Absorption Spectrometer
ECD	electron capture detector
FTIR	Fourier Transform Infrared
GC	gas chromatograph
I.D.	inner diameter
IR	Infrared
LDL	lowest detectable level, (ppm-m)
LIDAR	Light Detection and Ranging
lpm	milliliters per minute, flowrate
MDL	maximum detectable level, (ppm-m)
mV	millivolts
ORS	Optical Remote Sensing
ORS/CT	Optical Remote Sensing and Computed Tomography
ppm	concentration in parts per million, volume basis
ppm-m	concentration density in parts per million meters, volume basis
SF <sub>6</sub>	sulfur hexafluoride
STEL	short-term exposure limit, (ppm)
TLV	threshold limit value, (ppm)
UV	Ultraviolet
v	walte

# LIST OF SYMBOLS

I	intensity of transmitted beam
Io	intensity of incident beam
A	absorption coefficient of a gas or vapor
С	concentration of a gas or vapor, (ppm volume)
L	pathlength, distance traversed by beam
<sup>n</sup> ref	reflectivity of mirror at reference wavelength
<sup>n</sup> abs	reflectivity of mirror at absorbed wavelength
R <sub>ref</sub>	reference signal level in reflected-beam configuration, (millivolts)
Sref	reference signal level in single-beam configuration, (millivolts)
Rabs	absorbed signal level in reflected-beam configuration, (millivolts)
Sabs	absorbed signal level in single-beam configuration, (millivolts)
<sup>n</sup> mult,ref	resultant reflectivity at reference wavelength upon multiple reflections
<sup>n</sup> mult,abs	resultant reflectivity at absorbed wavelength upon multiple reflections
nref	single-mirror reflectivity at reference wavelength
<sup>n</sup> abs	single-mirror reflectivity at absorbed wavelength
N	number of mirrors used
Y	path-averaged concentration displayed by device, (ppm)
х	actual path-averaged concentration, (ppm)
М	slope of regression line
в	y-intercept of regression line
La	pathlength of cell a, (meters)
Ca	actual concentration in cell a, (ppm)
Li	pathlength between receiver and transmitter, (meters)
Lcell	pathlength of single-compartment calibration cell, (meters)
Ccell	actual concentration in single-compartment calibration cell, (ppm)

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# INTRODUCTION

## Traditional Methods of Workplace Exposure Assessment

In assessing worker exposure to airborne gases and vapors, industrial hygienists conduct sampling using both time-integrating and direct-reading methods.(1) Typically, two types of sampling are performed, personal and area sampling.

Time-integrating methods involve passing a known volume of air through media that collects contaminants from the sampled air over a specified time period. This results in one number representing the time-weighted average exposure. Typically, the collected samples require laboratory analysis. The direct-reading method involves the collection of a small point-sample of air which is measured in real-time; laboratory analysis is not necessary. Portable direct-reading instruments that can provide real-time monitoring of changing contaminant levels are invaluable to the industrial hygienist for locating sources of emission of hazardous gases, checking the performance of control equipment, and determining whether or not or not peak exposure limits are being exceeded in certain areas.

Personal sampling involves attaching the sampling device directly to a worker for a specified period of time to collect air from the worker's personal breathing zone. A measurement is obtained of the worker's time-weighted average exposure during the workshift. Area sampling involves placing one or more sampling devices at strategic locations in the workplace. Depending upon the equipment used, either time-integrated samples or direct-reading measurements can be obtained from isolated locations in the workplace.

# Deficiencies of Traditional Assessment Methods

Time-integrated methods smooth out the inherent fluctuations in concentrations that occur throughout the day. Monitoring these fluctuations is very important for evaluating exposures to acute chemical hazards and highly toxic materials. Monitoring this peak exposure information including the concentration, time, and place of occurrence is important to the industrial hygienist in assessing and controlling these hazards.

The loss of time and concentration information in integrated sampling results in poor temporal resolution of chemical concentrations. The individual numbers obtained for isolated workers or isolated locations in a room results in poor spatial resolution.

In direct-reading sampling, the availability of time and concentration information results in good temporal resolution. Direct-reading instruments used in area sampling have the advantage of real-time measurement of a contaminant and can determine the concentration of a peak exposure if the exact location is known; if the exact location is not known, direct-reading instruments may entirely "miss" peaks. Because a finite number of small, point samples are usually collected, the spatial resolution is typically poor. A large number of simultaneous measurements collected throughout the workplace would be required to gain spatial resolution; this is generally not feasible due to the high cost of direct-reading instruments.

The lack of good temporal and spatial information is a distinct limitation to gaining a better understanding of exposures, contaminant generation, and contaminant flow in the workplace. This research begins to investigate an alternative method that would ultimately result in both good temporal and spatial resolution of airborne contaminants in the workplace. This method involves the use of optical remote sensing equipment for measuring airborne chemicals in real-time over a large space and the use of the mathematical techniques of computed tomography to produce two-dimensional maps of the concentrations over the entire work room.(2)

# An Alternative to Conventional Assessment Methods

Optical Remote Sensing (ORS) equipment uses a collimated beam of electromagnetic energy projected by a transmitter over some path into a receiver which directs the energy into one or more detectors. The molecules of a gas or vapor interact with the beam of electromagnetic energy allowing for their detection and measurement. This detection technique is referred to as open-path monitoring; the optical beam is open to the atmosphere allowing gases and vapors to drift through it. No actual sample collection or laboratory analysis is required. Optical remote sensing equipment uses either a single beam or a reflected beam that uses mirrors to extend the path. The distance travelled by the beam from transmitter to receiver is referred to as the pathlength. To date, the application of ORS equipment to the detection of gases and vapors has focussed primarily on the outdoor environment where pathlengths of up to one kilometer or more are used; the indoor application of this equipment has received far less examination.

With ORS equipment, a gas or vapor entering any part of the beam path is detected and measured in real-time; this results in good temporal resolution. When either a single or a reflected beam is used, greater spatial coverage is obtained than with the finite number of point samples taken in traditional area sampling. Although a larger area of the workplace is sampled in real-time, each single beam provides one number representing the integrated concentration over the pathlength; good spatial resolution is not provided. If multiple beams are used in the workplace, and the mathematical techniques of computed tomography are applied to these remotely-sensed data, two-dimensional maps of the gas concentrations in a room are created and good spatial and temporal resolution can be obtained.(2)

# Optical Remote Sensing and Computed Tomography

In theory, two-dimensional maps of the gas concentrations in a room can be generated from near real-time measurements taken using the ORS equipment and strategically placed mirrors to allow the workplace to be scanned with an intersecting network of reflected beams.(2) Figure 1 illustrates this network of beams in a room. The maps created would provide spatial and temporal information concerning fluctuations in exposures. An example of a concentration map that might be generated is presented in Figure 2.

Before this new technique can be applied in the workplace, it must first undergo theoretical and experimental validation. Theoretical validation of this method using computer simulations has been the subject of research by Todd.(2) Experimental validation is the subject of this research.

## Statement of Problem

The ultimate goal of this research was to evaluate an ORS device for the eventual laboratory validation of the ORS/CT theory. It needed to be determined whether or not a commercially-available ORS device possesses the accuracy to measure open-path concentrations of a gas or vapor in the indoor environment. As stated before, most ORS devices have been designed for outdoor use.

Before proceeding with a network of reflected beams, an ORS device had to be selected and then calibrated using an independent validation method to verify that a single beam accurately measured gas concentrations. A single test gas was used to serve as a model for other gases and vapors in the workplace. This research initially required a review of the types and applications of optical remote sensors as well as a review of the methods used to calibrate them.



\* Shaded ellipses represent different gas or vapor concentrations



Map of Workplace Gas Concentrations

# BACKGROUND

## Methods of Detection in Optical Remote Sensing (ORS)

The methods used by ORS devices for detecting gases or vapors include Raman scattering, fluorescence, and absorption.(3,4,5) These methods were reviewed to determine which was the most feasible for this indoor research.

In the Raman scattering method, light energy strikes the gas molecules and is scattered at wavelengths unique for each pollutant. The intensity of scattering at each wavelength gives an indication of the respective pollutant concentrations. The disadvantage of this method is the isotropic nature of Raman scattering which necessitates the use of very large optics in these instruments.(4) This limits its use to high concentration applications where a very large space is available to locate the instrument. This method is not particularly useful for monitoring in the workplace where low concentrations of contaminants may need to be measured.

Fluorescence results when certain types of molecules release excess energy in the ultraviolet or visible regions after becoming excited by absorption of energy at a different wavelength. This method is not favored in the indoor environment because high concentrations of gases may be present causing the molecules to collide with one another before emission; this results in quenching, the reduction of fluorescent output.(5)

For optical remote sensing of the workplace, the most useful method of detection is absorption because many gases and vapors of interest in the workplace possess good absorption characteristics that allow for their detection and measurement.(3) In absorption, gaseous constituents in the beam path absorb energy at wavelengths unique to each molecule.(9) The absorption of energy by a gas or vapor is governed by Beer's Law, Equation (1).

$$I/Io = e^{-ACL}$$

where,

I is the intensity of the transmitted beam,

Io is the intensity of the incident beam,

A is the absorption coefficient of the gas or vapor,

C is the concentration of the gas or vapor, and

L is the pathlength, or distance traversed by the beam.

When ORS equipment is used, all variables of the equation are known except for the gas or vapor concentration, C. ORS devices using absorption measure the pathintegrated concentration, the product of average gas concentration along the path and the pathlength. When the device indicates a path-integrated concentration of 100 ppmmeters, no information concerning the distribution of gas within the beam is available; the same reading results from a uniform concentration of 10 ppm over a pathlength of 10 meters as that from a plume of 100 ppm contained within just 1 meter of the path. Dividing the path-integrated quantity by the pathlength yields the average gas concentration over the path. This is referred to as the path-averaged concentration. Software available with some ORS devices enables the direct measurement of pathaveraged concentrations.

ORS devices using absorption can use light energy in the visible, infrared (IR), or ultraviolet (UV) spectral regions.(6,7,8) Absorption of visible light (380 to 800 nanometers) by a molecule results in energy changes involving the valence electrons. Most gases do not absorb visible light energy. IR energy (0.8 to 50 micrometers), the range associated with the generation of heat, causes molecular vibrations and

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(1)

rotations.(9) Many of the gases and vapors of importance in the workplace have good absorption characteristics in the infrared spectral region. UV light (185 to 380 nanometers) absorption causes energy changes that involve the ionization of atoms and molecules. UV can be used to detect certain gases that cannot be detected with IR such as chlorine gas and hydrogen sulfide.

## Types and Applications of ORS Devices

Several different types of ORS devices have been developed over the past 25 years which use absorption to determine the concentrations of gases and vapors over an open-path.(7) These instruments are generally classified according to the type of electromagnetic energy used for detection: monochromatic or spectrally broad-band. Monochromatic devices emit light energy of a narrow spectral range while spectrally broad-band devices emit energy of a much wider range. A review of these instruments was required to determine the most suitable, commercially-available device for use in this research.

Monochromatic devices typically operate by differential absorption: absorption at a wavelength of maximum absorption is compared to absorption at a second wavelength that is not absorbed by the gas of interest. The difference in absorption is directly related to gas concentration. Typically, these devices are dedicated to detection of a single gaseous contaminant at a time. The monochromatic class of ORS devices includes Long-Path Differential Absorption Laser (DIAL) and Differential Absorption Light Detection and Ranging (DIAL or Differential Absorption LIDAR) instruments.

Spectrally broad-band devices can detect concentrations of many different gases by scanning over a spectral region and comparing the generated scan to a reference scan; a spectrally broad-band device can also be dedicated to single gas detection by differential absorption with the use of filters that permit only a narrow range of

wavelengths to reach the detectors. Spectrally broad-band instruments consist of differential optical absorption spectrometers, the correlation spectrometers, and other spectrometers including the Fourier-transform infrared (FTIR) spectrometer.(6,7,8)

## Long-Path Differential Absorption Laser

The long-path Differential Absorption Laser (DIAL) remote sensor uses a pair of continuous-wave (cw) lasers to create a collimated beam of electromagnetic radiation that can often be tuned to a particular wavelength for the molecular species of interest.(7,8,10) This technique may also use pulsed lasers. The instrument uses differential absorption to detect a gas by operating one laser at the wavelength of maximum absorption for the pollutant of interest and a second laser operating at a nonabsorbing wavelength. The long-path monitoring technique employs a topographical target or retroreflector to define a path over which the average gas concentration is determined.(10) Types of lasers used include carbon dioxide lasers, tunable diode lasers, and neutral gas lasers.(6,7,12) The selection of the laser depends on the pollutant being monitored. Presently, the use of this technique is limited to research and these devices are not commercially-available.(6)

# Differential Absorption Light Detection and Ranging

Differential Absorption Light Detection and Ranging (LIDAR) is a second type of monochromatic optical remote sensor; it also uses differential absorption to measure gas concentration. The main distinctions between it and Long-Path Differential Absorption Laser monitoring are the use of a pair of pulsed lasers and the absence of targets or retroreflectors.(7,8) LIDAR depends on atmospheric backscatter for the return signals to determine both concentration and distance to a pollutant cloud. This added capability of ranging makes LIDAR a more popular technique than the Differential Absorption Laser technique. The common laser systems employed include: 1) dye lasers for sulfur dioxide, ozone, and nitrogen dioxide; 2) carbon dioxide lasers for ozone and ethylene; 3) helium neon lasers for methane; and 4) tunable diode lasers for a wide variety of gases.(8)

Since the mid 1960's, LIDAR has been used to measure trace gases in the atmosphere.(11-19) More recently, a LIDAR system has been used to perform rangeresolved monitoring of atmospheric atomic mercury pollution.(20,21) Using the LIDAR technique, researchers were able to construct a three-dimensional map of the pollutant cloud. LIDAR has also been used to make long-term measurements of stratospheric ozone concentration profiles from 20 to 50 km altitudes.(22) For the remote sensing of sulfur dioxide, LIDAR offered a sensitivity of a few parts per billion at ranges in excess of one kilometer.(23)

Currently, the use of LIDAR is limited to research applications, and no LIDAR systems are commercially-available.(7)

#### Differential Optical Absorption Spectrometers

The Differential Optical Absorption Spectrometer (DOAS) is a type of spectrally broad-band optical remote sensor. This device uses a scanning spectrometer operating in the near UV and visible spectra and is well suited to the monitoring of compounds having weak IR spectra. Absorption spectra over a long path are generated and compared to a library spectra of known gases.(6) This instrument typically uses either a remotely located UV-visible light source or a collocated light source with a retroreflector to create a long path.

Researchers at the Lund Institute of Technology have used a DOAS system for atmospheric mercury monitoring.(24) Mercury levels in the parts per trillion range were assessed. The U.S EPA has operated a DOAS system at pathlengths up to 1824 meters to measure urban air pollution levels.(25,26) A DOAS system was also used in the 1987 Southern California Air Quality Study to measure atmospheric levels of trace

gases over a total optical pathlength of 800 meters.(27) These devices are commercially-available.(7)

#### Gas Cell Correlation Spectrometers

The Gas Cell Correlation Spectrometer is a second type of spectrally broad-band optical remote sensing device. This instrument uses a rotating gas filter consisting of a sample cell and a reference cell.(6,7,28,29,30) The difference in energy transmission between the two cells relates the concentration of the gas in the sample cell to that in the reference cell.

Gas Cell Correlation Spectrometers have been used for atmospheric monitoring.(31-32) A correlation spectrometer that uses the sun as a light source, COSPEC, was developed in the 1970's and has been used to make remote SO<sub>2</sub> mass flux measurements.(29) A second type of correlation spectrometer, GASPEC, was also developed.(28) In the early 1980's, another system was used by NASA to perform carbon monoxide measurements in the troposphere.(30) Some of these devices are commercially-available.(7)

#### Other Spectrometers

Broad-band spectrometers have been commercially-available since the 1970's. These systems typically consist of a separate transmitter and receiver and use differential absorption in the IR or UV to detect the presence of a gas. These spectrometers are normally dedicated to the detection of a single contaminant by using filters; however, some instruments may scan a spectral region for the detection and measurement of a number of gases.

One commercially-available IR spectrometer consists of an explosion-proof monitor which uses an infrared beam to detect hydrocarbon leaks at levels as low as 20

parts per million over a 100 meter pathlength.(34) MDA Scientific has developed a similar instrument dedicated to single gas monitoring.(33)

Spectrometers operating in the UV are also available and have been used outdoors to detect nitrous and sulfurous emissions from coal and oil fired industrial plants.(34)

#### Fourier Transform Infrared Spectrometers

The Fourier Transform Infrared (FTIR) Spectrometer is another type of spectrally broad-band optical remote sensing device that has been extensively used since the late 1970's. This device operates in the IR spectral region and uses a pair of mirrors, one stationary and one movable, and an interferometer to "transform" the spectral distribution of wavelengths into a form that can be mathematically converted to a conventional infrared intensity spectrum.(6,7,35) The main advantage of using this instrument is that the entire spectral region is scanned very quickly. The generated interferograms obtained in the field are then compared to laboratory spectra for known compounds.

FTIR spectroscopy has been extensively used over the past 10 years in openpath, outdoor air monitoring. It has been used to measure California smog and has been applied to the remote measurement of emissions from industrial operations where pathlengths of up to a kilometer or more were used.(37-43)

Recently, a transportable, FTIR instrument was built that is able to detect and quantitate individual gases and vapors at or below their respective TLV's.(44) This instrument was designed to operate indoors at pathlengths of up to 40 meters. Most recently, the same researchers tested an FTIR optical remote sensor in a controlled ventilation chamber using acetone vapor as a test gas and found the device to be quite accurate in both homogeneous and heterogeneous environments.(45)

## History of ORS Calibration Methods

Calibrating an ORS device presents a unique set of problems as compared to the calibration of other monitoring instruments due to the open-path monitoring technique. Other monitoring instruments typically have a sample cell into which a sample of air is extracted and becomes stable in its isolation from the environment. ORS devices, however, measure gases and vapors over a path that is entirely open to the atmosphere and, therefore, unstable. The atmosphere causes fluctuations in the concentrations over the beam path making it nearly impossible to achieve a stable concentration for calibrating the device.

The calibration of ORS devices has been performed by other investigators by using stationary or moving point monitors placed along the path (43,46,47), or by using calibration cells placed in the beam path.(40,48-51)

Typically, in the outdoor application, ORS devices calibrated over a long path have used several, stationary point samplers such as gas canisters placed along the beam path.(46) Each sampler simultaneously collected a time-integrated sample during a specified sampling period. The integrated measurements were then averaged to obtain a path-averaged concentration.(43) A second method was proposed that used a single, moving point sampler to traverse the open path.(46) The moving sampler performed a time-integrated measurement as it traversed the beam path during a specified period of time. Recently, this technique was used to compare FTIR spectrometer measurements of volatile organic compounds in an outdoor, industrial setting.(47) Point samplers were mounted on the back of a bicycle and moved along the path at a constant speed.

In calibration, accurate measurement of actual gas concentration within the beam path is necessary to effectively validate the ORS device. The methods typically used for calibrating ORS devices outdoors over a long path using integrated pointsampling devices are less than ideal. In the outdoor environment, gas concentration variability within the beam can be significant; the concentrations are almost never uniform, or homogeneous. The concentration can vary as a function of position along the beam path and as a function of time. The collection of a finite number of time-integrated samples along the path may result in entirely "missing" plumes of gas that cross the path. Although the ORS device can detect a plume crossing its path, the plume may drift between two point monitors and be entirely undetected. This may cause the point-sampling validation equipment to underestimate the actual gas concentration along the path. Even if the plume is not missed, the use of time-integrating validation methods results in a loss of information concerning the fluctuating concentration of this plume because gas concentrations are averaged over time. In addition, time integrating methods may have sampling and analysis errors that are different from direct-reading methods that could bias the results. For these reasons, calibrating the ORS device which operates in realtime with the use of a finite number of time-integrated, point samples is not ideal.

The disadvantages of using a moving point-monitor to calibrate ORS devices over a long path are similar to those of using stationary point monitors. Again, a timeintegrated sample is collected resulting in a loss of plume concentration information. Also, the possibility of missing gas plumes is significant because the point monitor cannot cover the entire beam simultaneously. As with the previous method, this also involves calibrating the ORS device which operates in real-time with a time-integrating method.

Another method used to calibrate ORS devices involves the use of calibration cells placed in the beam path.(40,48-51) This has been conducted both in the field and in the laboratory. Calibration cells are commercially-available and are equipped with transmissive windows to allow the beam to pass through the cell which is filled with a known concentration of calibration gas. In the calibration of a FTIR spectrometer, measured amounts of gas were introduced into a cell of known volume using a gas-tight

syringe.(47) Interference-free air was then flowed into the cell until a specified pressure was attained. Reference spectra were then recorded as the beam was passed through the cell containing a uniform, known concentration. Actual gas concentration is usually not verified with other equipment but is calculated based on the volume of gas injected and the volume of the cell.

Gas flow cells have also been used to calibrate ORS devices. These are a type of calibration cell where a constant flow of calibration gas is passed through the cell which is placed in the beam path. An IR spectrometer was recently calibrated using mixtures of pure carbon dioxide and carbon monoxide mixed with nitrogen which were passed through the flow cell using mass-flow controllers.(49) The ratio of flowrates was used to calculate the concentration of each species within the cell.

The use of calibration cells in calibrating ORS devices does not suffer from the concentration variability problems associated with the long-path, point sampling methods because the concentration within the cell is uniform, or homogeneous. As stated before, calculated concentrations are generally not verified with a validation method but are assumed to be correct. (49) The disadvantage of this method is that the accuracy of the ORS device in a non-uniform, or heterogeneous environment, is not measured.

## EXPERIMENTAL

The objective of this work was to evaluate the accuracy of a selected optical remote sensing device for the laboratory validation of Optical Remote Sensing/Computed Tomography theory. The accuracy of a selected optical remote sensing device was examined by performing calibrations in the indoor environment at relatively short pathlengths using two, direct-reading validation methods.

For this research, several decisions had to be made before work could begin. The test gas, ORS device, calibration methods, and validation equipment had to be selected. Before the experiments could be conducted, a calibration cell and a mirror stand had to be designed and built.

## Selection of the Test Gas

Several factors were involved in the selection of the test gas for use in the experiments: 1) The gas must have good absorption characteristics in the infrared allowing for its detection and measurement, 2) It should not be routinely present in indoor air, and 3) The selected gas should have low human toxicity.

Sulfur hexafluoride (SF<sub>6</sub>) was selected for use in this research. It has excellent absorption characteristics in the infrared region and is generally absent from the indoor environment. The gas has a low toxicity; it has a high threshold limit value (TLV) of 1000 parts per million and no short-term exposure limit (STEL).(52) A compressedgas cylinder containing a 30.0% mixture of SF<sub>6</sub> in air was obtained for this research.

#### Selection of the ORS Device

The selection of SF<sub>6</sub> dictated that the chosen ORS device must be sensitive to this gas. Because this work involved using a single gas to model other gases and vapors, an instrument capable of detecting and measuring multiple gases simultaneously was not needed. This narrowed the selection to an instrument dedicated to the detection of a single gas in the infrared spectral region. Of great concern was the eye safety of the light energy used by the ORS device. Laser-based devices were eliminated from consideration because this high-intensity light source poses a significant risk of eye damage.

The INFRASAFE Single-Gas Open-Path Spectrometer (Six-inch optics model) manufactured by MDA Scientific, Inc. of Lincolnshire, Illinois was chosen for this research. The INFRASAFE is sensitive to  $SF_6$  over a wide range of concentrations and can be dedicated to its detection.(33) It operates in the infrared spectral region and has a low-intensity source of electromagnetic energy, a glowbar. The components of this device are sufficiently small for use in the laboratory.

#### Theory of Operation

The INFRASAFE uses differential absorption in detecting the presence of a specific gas. For this research, the INFRASAFE was equipped with filters designed for SF<sub>6</sub> detection. Other filters are available from the manufacturer to enable detection of different gases.

The INFRASAFE is composed of three major components: the transmitter which provides and collimates the infrared energy, the receiver which focuses the beam to the reference and absorbed detectors, and the control system which converts the voltage signal levels obtained at the detectors to a path-averaged gas concentration.

The optical components housed within the transmitter are illustrated in Figure 3 and include the source, the chopper wheel, and the mirror. The glowbar source



# Figure 3 Schematic of Transmitter

operates at 20 volts d.c. and reaches temperatures up to 1300 degrees Celsius. The light produced by the source is spectrally broad-band and includes the visible and infrared regions. The chopper wheel rotates, alternately blocking and passing energy to the mirror. The transmitter mirror collimates the modulated light energy from the source into a six-inch diameter circular beam of light; the beam is dispersive, increasing in diameter as a function of distance from the transmitter. A temperature controller maintains the interior at a constant temperature to minimize the effects of fluctuating ambient temperatures on optical alignment and to prevent moisture condensation on mirror surfaces.

The components within the receiver are illustrated in Figure 4 and include the primary and secondary mirrors, the beam splitter, and the reference and absorbed detectors. The beam first strikes the primary mirror and then converges onto a smaller secondary mirror. It then passes through a transmissive beam splitter where it is divided and sent to each detector. Narrow band-pass filters mounted on front of the detectors pass energy at a wavelength of 10.6 micrometers to the absorbed detectors are mounted on X-Y-Z translation stages which allow for precision adjustments. Likewise, optics within the receiver are adjustable for tilt (up and down) and pan (left and right) to facilitate the process of optical alignment. A temperature controller maintains the interior at a constant temperature.

The Control system consists of an 80286 computer which uses software to convert detector signal levels into path-averaged gas concentrations in parts per million (ppm) over a known pathlength which is input into the program.

#### Optical Alignment of the INFRASAFE

Prior to operation of the INFRASAFE, the device must be optically aligned; the optical components in the receiver must be adjusted to obtain the maximum signal level





# Figure 4 Schematic of Receiver

in millivolts (mV) at both detectors without SF<sub>6</sub> in the beam path. These maximum signal levels are referred to as the baseline signal levels and are input into the control system.

After alignment, the distance between the receiver and transmitter apertures, the pathlength, is measured, and its value is input into the control system.

The INFRASAFE control system is capable of operating with a single pair of baseline signal levels and a pathlength value. Because the dispersive nature of the infrared beam results in a lower intensity of light reaching the receiver as pathlength is increased, baseline signal levels tend to decrease as pathlength is increased. If the device is moved to a new position providing a different pathlength, the system must be re-aligned and these new levels and pathlength value should be input into the control system.

## Usable Range of the INFRASAFE

The INFRASAFE has both a maximum detectable level (MDL) and a lowest detectable level (LDL) which define a usable range for each chemical over which the device can reliably operate. For SF<sub>6</sub> detection, the manufacturer claims a LDL of one ppm-meter. The claimed MDL is 100 ppm-meters.(33) Beyond the MDL, the reference signal begins to be absorbed to a significant degree resulting in a loss of accuracy.

The LDL and MDL are specified in terms of path-integrated concentrations. Because the INFRASAFE displays path-averaged gas concentration, the LDL and MDL need to be converted to the path-averaged quantity by dividing each level by the pathlength. For example, the upper path-averaged concentration limit using a pathlength of 10 meters is the MDL, 100 ppm-meters, divided by 10 meters, or 10 parts per million.

## Modifications to INFRASAFE Required for Indoor Use

Initial work with the INFRASAFE immersed in a room-size chamber filled with SF6 revealed that the lid seals of both components were not sufficiently air-tight to prevent intrusion of the gas. This gas intrusion resulted in unintended absorption and prevented the INFRASAFE from returning to a reading of zero ppm when all gas was evacuated from the chamber. Figure 5 illustrates this problem. The ascending set of data was taken as concentration in the chamber was increasing, and the descending set of data was taken as the chamber concentration was decreasing. These two sets of data should lie on the same line, but gas that had leaked into the housings while the chamber concentration was increasing prevented the INFRASAFE from returning to a reading of zero ppm.

To solve this problem, the receiver and transmitter housing lid seals were removed, and a continuous bead of silicone rubber was applied in place to create a nearly air-tight seal.

The receiver has a longer internal pathlength, the distance light travels between the internal optics, than does the transmitter; therefore, gas intrusion into this component caused more unintended absorption than in the transmitter.

To further prevent gas intrusion, a nitrogen purge system was installed in the receiver housing to create a slight, internal, positive pressure. The receiver housing was fitted with inlet and outlet fittings, and nitrogen from a compressed gas cylinder purged the housing via a two-stage regulator at an optimum flowrate of one liter per minute. This flowrate did not affect the signal levels and created an internal pressure of one-half inch of water. A flowrate in excess of 1.5 lpm resulted in cooling of the optical components and caused the baseline signal levels to drift.



Figure 5

Actual versus Indicated Concentrations prior to modification of INFRASAFE
# Validation of the ORS Device

# Calibration

Before the ultimate goal of using the INFRASAFE in the laboratory validation of ORS/CT theory could be realized, the device required calibration to verify that the measured gas concentrations displayed by the instrument were correct. For this research, two methods of calibrating the device were devised which were improvements over typical ORS calibration methods.

# Calibration of the INFRASAFE

After review of the calibration methods described in the optical remote sensing literature, two improved methods were developed. In experiments using a homogeneous environment where the concentrations were uniform, several point samples were taken along the beam path and analyzed by a direct-reading instrument. Each sample was collected individually, and sampling was completed very quickly. The path averaged concentration was calculated by averaging the point-samples.

In experiments using a heterogeneous environment, where concentrations vary in space along the beam path, calibration was performed using a calibration cell with five separate compartments. This was used to create a stable, heterogeneous environment. The contents of each cell were analyzed with a direct-reading instrument.

Compared with the time-integrated, point-sampling methods used by other researchers to calibrate open-path instruments, for this research, in the calibrations using a homogeneous environment, direct-reading, point samples were collected along the beam path. Stable, homogeneous environments were created in a 850 cubic foot chamber. Because this environment was homogeneous, gas concentration variability over the path was eliminated; no plumes of gas were present that could have been missed by the point samples. In experiments using heterogeneous environment, a different, homogeneous gas concentration was present in each compartment of the calibration cell. This simulated a heterogeneous environment when the beam passed through all the cells. The stability afforded by the individual compartments eliminated the problem of concentration variability along the path. The concentration in each cell was validated by a direct-reading instrument.

### Validation Instruments

The two instruments chosen for calibrating the INFRASAFE, a MIRAN 1A infrared gas analyzer and an electron capture detector (ECD) device with a gas chromatograph (GC) column, were both sensitive to sulfur hexafluoride and were direct-reading. The MIRAN was used only in the experiments using a single beam in a homogeneous test environment. The ECD device was used in all of the experiments.

The MIRAN 1A is a miniature, infrared, gas spectrophotometer with a 5.6 liter sample cell.(53) The unit is supplied with a fan to draw air through the sample cell. Sample analysis with the MIRAN was limited by its comparatively large cell volume; only two points along the beam path were sampled with the MIRAN because of the length of time required to purge the cell contents and acquire the next sample. Another limitation of the MIRAN's large cell volume was that it prevented the attainment of a small, point sample; the MIRAN actually draws air from a much larger space. These limitations and a desire to validate the INFRASAFE with a non-infrared method of analysis led to the construction and use of the ECD device.

An ECD device with a chromatographic column was constructed of materials from Valco Instrument Co. of Houston, Texas, Radio Shack, Inc., and ITI, Inc. (see Appendix A). Figure 6 is a schematic of this device.

An electron capture detector is a gas ionization chamber in which conduction electrodes are created at a known rate and captured by the electro-negative species



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within the gas sample.(54) The concentration of the gas sample is related to electrical measurements made at the chamber's electrodes.

With the ECD device, sample volume was small and was determined by the size of the syringe selected for use. The design of the instrument permitted the use of syringes that were thirty-milliliter or smaller. With this device, multiple syringe samples could be collected quickly and then injected into the instrument.

After selection of the validation instruments, a procedure was designed for their routine calibration.

### Calibration of the Validation Instruments

Both validation instruments were calibrated for each experiment during this research. A calibration gas was made by injecting measured volumes of 30% SF<sub>6</sub> by syringe into a closed-loop calibration loop of known volume. Three complete calibrations were performed before and after an experiment. The average reading at each test concentration was plotted over the calibrated range. Checks of stability were made during the experiments by testing a few points on the calibration curve.

The MIRAN was calibrated using the closed-loop calibration circuit recommended by the manufacturer. This loop consists of a diaphragm pump, tubing, a septum, and the MIRAN's 5.6 liter sample cell. The pump circulated the air through the loop which had a total volume of 5.65 liters. This same 5.65 liter, closed-loop was used to calibrate the ECD device. Routine calibration of this instrument was particularly important during the first few weeks of operation after building the device because its sensitivity tended to increase the more it was used.

### **Calibration Cell**

The multi-compartment calibration cell required transparent windows to separate the contents of adjacent compartments; the beam ultimately passes through several layers of window material. As the beam passes through the cells, each layer of window material absorbs a percentage of the incident infrared energy resulting in a less intense beam. It was necessary to minimize this energy loss to retain a good signal to noise ratio.

For the window material, layers of 0.5 mil thick clear polyethylene film were selected; a single layer of this film absorbs about 10% of the incident infrared energy. Saran film was considered, but the use of this film resulted in absorption of approximately 30% of the incident energy per layer.

A calibration cell was constructed that had five, separate compartments; this required the use of six layers of polyethylene film for windows. Five compartments would allow the simulation of a heterogeneous environment without unacceptable reductions in signal levels. A compromise had to be reached between the number of compartments and signal level reduction by the polyethylene film.

The cell housing consisted of a sectional, rectangular wooden frame. Each of the five compartments comprising the unit had an internal volume of 5.85 liters and provided a pathlength of 14 centimeters. The individual compartments of the cell were designated as cells A, B, C, D, and E. The entire cell provided a pathlength of 70 centimeters.

The interior surfaces of each cell were coated with two coats of polyurethane to prevent absorption of sulfur hexafluoride. A fan (10,800 RPM, 6V DC electric motor fitted with a plastic mixing blade) was mounted inside the top of each compartment to rapidly mix the injected gas. Electrical wires were routed through 1/16" diameter holes drilled in the bottom of the side wall. Silicone gasket material formed the mating surface between each cell. All interior joints in each compartment were covered with a bead of silicone material to prevent gas leakage. On each side of the cell, a three foot long, 1/4"-20, threaded steel rod was inserted through holes drilled horizontally through the length of the vertical wall; steel fender washers and 1/4"-20 hex nuts were

used to draw the components together as a unit. A septum was installed in the center of one side wall of each of the five compartments for injection and withdrawal of gas with a syringe. In the top wall of each compartment, two 5/16" diameter holes were drilled for the purpose of purging with vacuum equipment; these holes were plugged during the course of each experiment.

Before this cell could be used in the experiments, it had to be tested to ensure that injected concentrations did not change during the time required to complete one trial of an experiment. It was determined that thirty minutes were sufficient to complete one trial. To test gas stability over this time period, each compartment was injected with one ml of 30% SF<sub>6</sub>. Ten-ml syringe samples were taken every ten minutes and analyzed with a direct-reading instrument. No detectable change in concentration occurred in any compartment over a thirty minute period.

To create a single-compartment calibration cell, the layers of polyethylene film could be removed leaving only a film window at each end. This resulted in a singlecompartment cell that provided a pathlength of 70 cm with an internal volume of 29.25 liters.

After the calibration cell had been designed, it was necessary to design and construct a stand to hold a pair of mirrors to reflect the transmitted beam in the reflected-beam experiments.

### Mirror Stand for the Reflected Beam Experiments

An adjustable mirror stand was designed and constructed to reflect the transmitted beam into the receiver. This device consisted of a wide metal base, an aluminum pole, two sliding pole brackets, two mirror mounts, and two first-surface mirrors.

A wide, weighted metal base 15 inches wide and 20 inches long was fitted with a 7 foot long, 2 1/4-inch diameter, aluminum pole mounted vertically. Two aluminum pole brackets were constructed which could be clamped at any position on the pole. A reverse-angle mirror mount (Cat. no. B37,922; Edmund Scientific Co., Inc., Barrington, NJ) was attached to each bracket; a 169 by 194 millimeter first-surface mirror (Cat. no. B41,405; Edmund Scientific Co., Inc., Barrington, NJ) was fastened to the face of each mount. The mirror mounts provided precise adjustment of the mirrors for both tilt and pan. The mirrors were mounted orthogonally to deflect the transmitted beam 180 degrees into the receiver.

## **Overview of Experiments**

Throughout this work, the INFRASAFE was calibrated by comparing the openpath measurements to point-sample measurements taken along the beam path with the direct-reading validation equipment. The following experiments were performed:

- Calibration of the INFRASAFE using a single beam in an environment containing a uniform, or homogeneous, gas concentration.
- Calibration of the INFRASAFE using a single beam in an environment containing a non-uniform, or heterogeneous, gas concentration.
- Calibration of the INFRASAFE using a reflected beam in an environment containing a homogeneous gas concentration.
- Calibration of the INFRASAFE using a reflected beam in an environment containing a heterogeneous gas concentration.
- Calibration of the INFRASAFE using a single beam and a calibration cell at various pathlengths to determine the effect of pathlength on accuracy.

- Calibration of the INFRASAFE using a reflected beam and the input of incorrect pathlength values
- Calibration of the INFRASAFE using a reflected beam and the input of incorrect baseline signal levels.
- Experiments to determine the reflectivity of the mirrors used in this research.

# Experimental Design

Experiment one was performed to verify that the INFRASAFE accurately measured path-averaged concentrations in the simple case of the homogeneous environment using a single beam. This was an important first step in examining the accuracy of the INFRASAFE indoors. If the device failed to accurately measure gas concentrations in this simple environment, it could not be expected to work well in the more complex and realistic case of a heterogeneous environment.

Experiment two was performed to verify that the INFRASAFE accurately measured path-averaged concentrations using a single beam in the heterogeneous environment, an environment typical of workplace air. The five-compartment calibration cell was used to create a stable, heterogeneous environment.

Experiments three and four were performed to verify that the device performed accurately in the reflected-beam configuration. In practice, mirrors will probably be used to reflect the beam in the workplace. Experiment three was conducted to verify that the INFRASAFE accurately measured path-averaged gas concentrations in the homogeneous environment, and experiment four was conducted to verify accuracy of the INFRASAFE in the heterogeneous environment. Experiment four used the fivecompartment cell to simulate a stable, heterogeneous environment.

In the validation of ORS/CT theory in a chamber, a scanning device will probably be used to project the beam over several different paths to create a network of reflected beams. In this network, the pathlengths of the beams will not be equal; therefore, it was important to determine that the INFRASAFE accurately measured path-averaged concentration over different pathlengths. Experiment five was performed to determine whether or not the accuracy of the INFRASAFE was affected by using different pathlengths. This experiment determined whether or not the algorithm used by the control system software accurately corrected for the different input pathlengths and involved calibrations at four different pathlengths, 1.50, 3.00, 4.50, and 6.00 meters. Prior to each calibration, the correct baseline signal levels and the correct pathlength value were input into the control system.

In the creation of a network of beams, several different pathlengths will probably be encountered. However, the configuration of the INFRASAFE's control system software permits the input of a single pathlength value. This limitation of the software requires that the displayed concentration information be mathematically corrected when the actual pathlength used is different from the input pathlength. Experiment six was conducted to determine whether or not path-averaged concentrations displayed by the INFRASAFE could be mathematically corrected by multiplying displayed concentrations by the input pathlength and dividing by the actual pathlength. This experiment involved calibrations at the same four pathlengths as used in experiment five. In this experiment, prior to each calibration, the correct baseline signal levels were input in the control system for each pathlength, but the pathlength value was held constant at 6.00 meters. As a result, incorrect pathlength values were input for calibrations at 1.50, 3.00, and 4.50 meters.

In the creation of a network of beams, the unequal pathlengths will each result in a different pair of baseline signal levels due to the dispersive nature of the INFRASAFE's beam. The software used by the INFRASAFE is also limited to the input of a single pair of baseline signal levels. Therefore it was important to determine whether or not the input of baseline signal levels obtained at one pathlength could be used to accurately measure concentrations when another pathlength is encountered even though the levels are incorrect for that pathlength? The purpose of experiment seven was to determine whether or not the INFRASAFE could accurately measure pathaveraged concentrations if it is supplied with incorrect baseline signal levels.

In experiment seven, baseline signal levels corresponding to one pathlength were entered into the control system and calibrations were performed at two other pathlengths using the single-compartment calibration cell. This cell was used because a homogeneous test environment using pathlengths longer than those attainable in the exposure chamber was desired.

Several assumptions were made in designing experiment seven. To determine the different pathlengths to be used, it was first assumed that the INFRASAFE will be used in a square workroom. The components were assumed to be located adjacent to one another in one corner of the room. It was further assumed that three different pathlengths would be encountered in the room, Paths 1, 2, and 3 as illustrated in Figure 7. In this scan, an angle of 22.5 degrees would be formed by two adjacent paths, and Path 3 would be the longest pathlength created. The longest pathlength attainable in the lab using the reflected-beam configuration was 16.8 meters; for the purpose of the experiment, this maximum pathlength was assumed to be the length of Path 3. The geometry of the scan then dictated the lengths of Paths 1 and 2 to be 11.9 and 12.9 meters, respectively.

The creation of a network of beams will probably involve mirrors to project the beam around the room; therefore, it is important that the mirrors be efficient in



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reflecting the beam so that signal strength is not seriously deteriorated resulting in a poor signal to noise ratio. Experiment eight was performed to quantify the reflectivity of the mirrors used in this research so that energy loss due to multiple reflections might be estimated.

In experiment eight, the INFRASAFE was used in the determination of mirror reflectivity. The INFRASAFE was aligned in the single-beam configuration at a specified pathlength, and the baseline signal levels were recorded. The device was then aligned at the same pathlength but in the reflected-beam configuration using the mirrors to reflect the beam. The baseline signal levels at this position were recorded. By comparing the signal levels obtained at these two configurations, the mirror reflectivity was calculated; any decrease in signal levels in the reflected-beam configuration were attributed to mirror losses, and the extent of these losses in the absorbed and reference wavelengths were calculated using the relationship in Equations (2) and (3).

$$n_{ref} = (R_{ref}/S_{ref})^{1/2}$$
(2)

 $n_{abs} = (R_{abs}/S_{abs})^{1/2}$ (3)

#### where,

 $n_{ref}$  is the reflectivity of the mirror at the reference signal wavelength (10.17  $\mu$ m),

 $n_{abs}$  is the reflectivity of the mirror at the absorbed signal wavelength (10.6  $\mu$ m), R<sub>ref</sub> is the reference signal level in volts in the reflected-beam configuration, S<sub>ref</sub> is the reference signal level in millivolts in the single-beam configuration, R<sub>abs</sub> is the absorbed signal level in volts in the reflected-beam configuration, and S<sub>abs</sub> is the absorbed signal level in volts in the single-beam configuration. It was not known to what extent signal levels obtained at a specified pathlength could vary from one alignment to another. Therefore, in experiment eight, five consecutive alignments were performed in each configuration. The smaller the variation in baseline signal levels among the consecutive alignments, the more accurately mirror reflectivity could be determined.

# **Gas** Administration

An 850 cubic foot exposure chamber in the School of Public Health was used in experiments conducted in a homogeneous environment. Gas was released into the chamber from a compressed-gas cylinder using a 2-stage regulator. A radial-blade, mixing fan was placed inside the chamber near the gas inlet to ensure adequate mixing and the creation of a homogeneous environment.

The experiments using a heterogeneous environment were conducted in the laboratory using the five-compartment calibration cell placed in the beam path. Gas flowed through a line equipped with a septum into a flexible exhaust trunk using a twostage regulator and was extracted through this septum with thirty-milliliter polypropylene syringes (Model 9662, Beckton Dickenson, Rutherford, NJ) fitted with 1"-18 gauge stainless steel needles.

# Equipment Configuration

Experiments conducted in the single-beam configuration were performed with the INFRASAFE receiver and transmitter located at opposite ends of the chamber or laboratory as illustrated in Figure 8. Experiments conducted in the reflected-beam configuration were performed with the receiver and transmitter located in a rack; the transmitter was positioned directly beneath the larger, heavier receiver as illustrated in Figure 9. The vertical distance between beam centers of the transmitter and receiver was 35 cm.

# Sample Collection

In experiments using a homogeneous environment, Tygon sample lines (1/32" I.D.) twelve feet in length were suspended so that the inlets were located just at the edge of the optical beam at equally-spaced increments along the path. All sample lines were routed through a porthole in the exposure chamber. Four lines were used in the single-beam configuration experiments; eight lines were used in the reflected-beam configuration experiments. These single-beam and reflected-beam sampling configurations are illustrated in Figures 8 and 9, respectively.

Thirty-milliliter polypropylene syringes were fitted to needles cut to a length of one-half inch thereby eliminating the sharp point capable of puncturing the sample line. Stability of SF<sub>6</sub> within a polypropylene syringe has been shown to be quite good. Laboratory trials by another investigator revealed that sample deterioration due to leaks or absorption by the syringe material did not exceed 2% over a two-week period.(55)

Before the samples were taken, the syringes were fully filled and emptied three times to condition the interior walls. This practice has been shown to reduce adsorption on the syringe wall. (56) During sampling, the syringes were individually drawn and then capped to await analysis.

In the experiments using a heterogeneous environment, polypropylene syringes were used to draw gas from each compartment of the calibration cell. The same practice of syringe conditioning was followed. Each of the five compartments was sampled individually, and syringes were capped for analysis.

## Experimental Procedure

Single and Reflected-Beam Experiments Using a Homogeneous Environment





The INFRASAFE components were aligned in the single-beam configuration in the exposure chamber at a pathlength of 1.90 meters; this was the maximum pathlength attainable in the exposure chamber using the single-beam configuration. The upper concentration limit at this pathlength was about 55 ppm.

After entering baseline signal levels, SF<sub>6</sub> was slowly released into the chamber. The INFRASAFE display was monitored visually until the gas concentration had increased by about 5 ppm. The flow was then stopped, and three minutes were allowed for the gas to evenly mix throughout the chamber. Point samples were then collected along the length of the beam, and the INFRASAFE display was noted concurrently. Both the MIRAN 1A and the ECD device were used for analysis of collected path samples. The process of adding gas, waiting for chamber mixing, and sampling and recording the monitor display was repeated until the upper concentration limit was approached. This experiment was repeated three times.

In the reflected-beam experiments conducted in the homogeneous environment, the same procedure was followed. A maximum pathlength of 5.35 meters was provided by using this configuration, and the upper concentration limit at this pathlength was approximately 20 ppm. Gas was added in steps of about 3 to 4 ppm. Again, three trials were performed. The ECD device was used to analyze the collected samples.

# Single and Reflected-Beam Experiments Using a Heterogeneous Environment

The size of the exposure chamber used in the homogeneous experiments limited the experiments to very short pathlengths. In the heterogeneous experiments, the use of a five-compartment calibration cell to simulate a stable, heterogeneous environment allowed longer pathlengths to be used. The INFRASAFE components were moved into a larger laboratory for these experiments. The nitrogen purge was disconnected and fittings were capped because the components would not be immersed in the SF6 environment.

The INFRASAFE was first aligned in the single-beam configuration which provided a pathlength of 7.28 meters, the maximum pathlength attainable in the laboratory using the single-beam configuration. The upper concentration limit at this pathlength was approximately 14 ppm.

The five-compartment calibration cell was placed in the beam path without SF6 present in any cell. Baseline signal levels were entered in the control system with the empty calibration cell placed in the optical beam path.

The simulation of a stable, heterogeneous environment was performed in a systematic way. The entire experiment used a total of fifteen injections of SF<sub>6</sub> into different compartments to create a stable, heterogeneous environment of fifteen, distinct path-averaged concentrations over the usable range of the INFRASAFE. Based on the volume and pathlength of the calibration cell, it was determined that fifteen, nine-hundred microliter injections of 30% SF<sub>6</sub> were required to cover the usable range. Each injection increased the concentration of a compartment by about 45 parts per million volume.

The procedure used in creating the heterogeneous environment is illustrated in Figure 10. Nine-hundred microliters of SF<sub>6</sub> was first added to cell A, and two minutes were allowed for mixing of the gas. A sample was then drawn from cell A for concentration validation with the ECD device, and the INFRASAFE display concentration was noted. The same quantity of gas was then injected in cell B. Again, two minutes were allowed for mixing before a sample was drawn from cell B. Because of the demonstrated stability of gas within each cell, a sample was drawn only from the cell that last received an injection of gas. Using the same procedure, cells C, D, and E then received individual, 900 microliter injections of SF<sub>6</sub>. After each individual injection, two minutes were allowed for mixing prior to drawing a sample. After all



# Figure 10 Illustrati

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five cells had been injected with 900 microliters of SF<sub>6</sub>, cells B, C, D, and E then received individual injections of SF<sub>6</sub> while cell A received no additional gas. Continuing, cells C, D, and E received additional gas while cells A and B received none. Continuing the pattern, cells D and E then received additional SF<sub>6</sub> while cells A, B, and C received none. Lastly, cell E received a final injection of SF<sub>6</sub> while all other cells received none.

### Experiments to Determine the Effect of Pathlength

Experiment five was conducted in the single-beam configuration in the main laboratory area. The single-compartment calibration cell was used, and all five, mixing fans were run during the experiment to provide rapid mixing of injected gas. To cover the usable range of path-integrated concentration, it was determined that a total of seven, two ml injections were required. Each injection resulted in increasing concentration in the cell by about 20 parts per million volume.

The INFRASAFE was first aligned at 1.50 meters. After entering baseline signal levels into the control system, two milliliters of  $SF_6$  was then added to the cell. Two minutes were allowed for mixing, and a sample was then drawn from the cell and the INFRASAFE display concentration was noted. Three complete calibrations were performed using the ECD device to analyze collected samples. This procedure was repeated at pathlengths of 3.00, 4.50, and 6.00 meters; at each pathlength, actual baseline signal levels were entered in the control system, and three calibrations were performed.

Experiments Using Incorrect Input Pathlength Values

Experiment six followed the same procedure described in experiment five. Three complete calibrations were performed at pathlengths of 1.50, 3.00, 4.50, and 6.00 meters. At each pathlength, correct baseline signal levels were entered in the control system, but the input pathlength value was held constant at 6.00 meters.

## Experiments Using Incorrect Baseline Signal Levels

In experiment seven, the single-compartment calibration cell was used. To cover the usable range, a total of seven, two ml injections were performed for each calibration as in the previous experiment. The INFRASAFE was first aligned at a pathlength of 11.90 meters, a pathlength corresponding to Path 1 (see Figure 7). The baseline signal levels were recorded, and three complete calibrations were performed using the ECD device to analyze collected samples. Alignments at pathlengths of 12.90 and 16.80 meters, pathlengths corresponding to Paths 2 and 3, were also performed, baseline signal levels were recorded, and three complete calibrations were performed.

To determine the effect of using incorrect baseline signal levels, the INFRASAFE was aligned at Path 3 and the baseline signal levels obtained previously at Path 2 were input in the control system. Three calibrations were performed using the ECD device to analyze collected samples. Baseline signal levels from Path 1 were then input in the control system, and three calibrations were again performed. The INFRASAFE was then aligned at Path 2, and baseline signal levels from Path 1, and then Path 3, were input and calibrations performed. Finally, the INFRASAFE was aligned at Path 1, and baseline signal levels from Path 3, were input and calibrations performed.

### Experiment to Determine Mirror Reflectivity

In experiment eight, the INFRASAFE was aligned in the single-beam configuration at a pathlength of 5.00 meters. The transmitter was then dislocated several inches to one side effectively "destroying" the state of optical alignment. The

transmitter was then brought back in line with the receiver and the optical alignment was restored. The baseline signal levels obtained during this alignment were then recorded. This procedure was performed five consecutive times.

In the reflected-beam configuration, the INFRASAFE was aligned at the same 5.00 meter pathlength. Baseline signal levels obtained at this initial alignment were recorded. The optical alignment was then "destroyed" by moving the mirror stand several inches to one side. To restore optical alignment, the mirror stand was returned to its original position, and the optical alignment process was repeated. Baseline signal levels obtained during this second alignment were then recorded. This process was repeated a total of five times.

# RESULTS

# Calculation of Actual Path-Averaged Concentrations

The actual path-averaged concentrations were calculated in one of two different ways depending upon the test environment used.

In the experiments using a homogeneous environment, actual path-averaged gas concentrations were calculated by averaging the point samples taken along the beam path. In the heterogeneous experiments, the actual path-averaged gas concentrations were calculated using the actual cell concentrations as determined by the ECD device, the pathlength of absorption provided by the calibration cell, and the actual pathlength, the distance between the transmitter and receiver. Equation (7) was used to determine the actual path-averaged concentration when the five-compartment calibration cell was used.

 $X = [\Sigma((C_a \times L_a) + (C_b \times L_b) + (C_c \times L_c) + (C_d \times L_d) + (C_e \times L_e))]/L_i$ (7) where,

- X is the actual path-averaged concentration in parts per million volume,
- Ca thru Ce are actual cell concentrations of cells A through E in parts per million volume,
- La thru Le are the pathlengths of cells A through E in meters, and
- Li is the actual pathlength between the INFRASAFE receiver and transmitter.

Equation (8) was used to determine actual path-averaged gas concentration when the single-compartment calibration cell was used.  $X = [\Sigma(C_{cell} \times L_{cell})]/L_i$ 

where,

X is the actual path-averaged concentration in parts per million volume,

Ccell is the actual cell concentration in parts per million volume,

Lcell is the pathlength of the single-compartment cell in meters, and

Li is the actual pathlength between the INFRASAFE receiver and transmitter.

# Analysis of Calibration Data

Two types of linear regressions were performed on the calibration data using the SYSTAT MGLH package. The data were first fitted to a line of "best" fit in the form of equation (9).

Y = B + MX

where,

Y is the path-averaged concentration indicated by the INFRASAFE,

B is the y intercept,

M is the slope of the regression line, and

X is the actual path-averaged concentration.

Confidence intervals were determined for values of y-intercept and slope using a t-test with a 95% level of confidence. If the interval for the y-intercept term, B, included the value of zero, it was reasonable to fit the data to a best-fit line forced through the origin in the form of equation (10). If the interval did not include zero, the equation of the regression line is herein presented in the form of Equation (9).

(10)

(8)

(9)



where,

- Y is the path-averaged concentration indicated by the INFRASAFE,
- M is the slope of the regression line, and
- X is the actual path-averaged concentration.

Fitting the calibration data to a line in the form of Equation 10 allowed the accuracy of the INFRASAFE to be described and compared using a single term, the slope of the regression line. Confidence intervals for the slope, M, were determined for each calibration using a t-test with a 95% level of confidence. Values of  $\mathbb{R}^2$  were also calculated as a measure of fit of the regression line to the data.

# Experiments Conducted in the Single-Beam Configuration

In experiment one, calibrations were conducted using a single-beam in a homogeneous environment. Figure 11 shows actual concentration determined with the MIRAN versus concentrations indicated by the INFRASAFE. Equation (11) is the equation of the regression line. Figure 12 shows actual versus indicated concentrations using the ECD device as the validation method. The equation of the regression line is given in equation (12). Table 1 lists calculated values of standard deviation and coefficient of variation for collected path samples analyzed with the ECD device.

In experiment two, calibrations were performed using the single-beam configuration in a heterogeneous environment. Figure 13 shows actual concentration as determined by the ECD device versus indicated gas concentrations. The equation of the regression line is given in equation (13).

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = 1.120X	$1.104 \le M \le 1.136$	0.99	(11)

Y = 1.098X	$1.082 \le M \le 1.114$	0.99	(12)
Y = 1.106X	$1.098 \leq M \leq 1.114$	0.99	(13)

## Experiments Conducted in the Reflected Beam Configuration

In experiment three, calibrations were performed using the reflected-beam configuration in a homogeneous environment. Figure 14 shows actual versus indicated concentration, and Equation (14) is the equation of the regression line. Table 2 lists calculated values of standard deviation and coefficient of variation for collected path samples analyzed with the ECD device. In experiment four, calibrations were conducted using the reflected-beam configuration in a stable, heterogeneous environment. Figure 15 shows actual versus indicated concentrations, and Equation (15) is the equation of the regression line.

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = 1.105X	$1.089 \le M \le 1.121$	0.99	(14)
Y = 1.119X	$1.109 \le M \le 1.129$	0.99	(15)

# Experiments to Determine the Effect of Pathlength

In experiment five, calibrations were conducted to examine the effect of pathlength. Actual versus indicated concentrations are plotted in Figures 16, 17, 18 and 19 for pathlengths of 1.50, 3.00, 4.50, and 6.00 meters, respectively. Equations (16-19) are the respective regression line equations.

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = 1.115X	$1.101 \leq M \leq 1.129$	0.99	(16)
Y = 1.123X	$1.107 \le M \le 1.139$	0.99	(17)
Y = 1.125X	$1.111 \leq M \leq 1.139$	0.99	(18)
Y = 1.123X	$1.113 \le M \le 1.133$	0.99	(19)

# Experiments Using Incorrect Pathlength Values

Experiment six was conducted to examine the effect of inputting incorrect pathlength values into the control system. For calibrations performed in experiment six, actual versus corrected, indicated concentrations are plotted in Figures 20, 21, and 22 for pathlengths of 1.50, 3.00, and 4.50 meters, respectively. Corrected, indicated concentrations were calculated by multiplying the displayed concentrations by the input pathlength value (6.00 meters) and dividing by the actual pathlength value. Equations (20-22) are the respective regression line equations. Actual versus indicated concentrations for calibrations at a pathlength of 6.00 meters using an input pathlength value of 6.00 meters are plotted in Figure 23. Equation 23 is the respective regression line equation.

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = 1.101X	$1.089 \le M \le 1.113$	0.99	(20)
Y = 1.104X	$1.090 \le M \le 1.118$	0.99	(21)
Y = 1.118X	$1.102 \leq M \leq 1.134$	0.99	(22)
Y = 1.102X	$1.090 \le M \le 1.114$	0.99	(23)

# Experiments Using Incorrect Baseline Signal Levels

Experiment seven was conducted to determine the effect on accuracy of inputting incorrect baseline signal levels. The baseline signal levels obtained at each pathlength were as follows:

Path	Absorbed (mV)	Reference (mV)	Ratio (Abs/Ref)
1 (11.9 m)	58.4	53.2	1.098
2 (12.9 m)	51.2	46.5	1.101
3 (16.8 m)	40.0	36.2	1.105

For calibrations performed in experiment seven, Figures 24, 25, and 26 show actual versus indicated concentrations for calibrations at Paths 1, 2, and 3, respectively. Equations (24-26) are the regression lines for these calibrations.

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = 1.109X	$1.097 \le M \le 1.121$	0.99	(24)
Y = 1.103X	$1.089 \le M \le 1.117$	0.99	(25)
Y = 1.118X	$1.102 \leq M \leq 1.134$	0.99	(26)

Figures 27 and 28 show actual versus indicated concentrations for calibrations performed in experiment seven using the baseline signal levels obtained at Path 1. Figure 27 corresponds to calibration at Path 2, and Figure 28 corresponds to calibration at Path 3. Equations 27 and 28 are the regression line equations for calibrations at Path 2 and Path 3, respectively.

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = -0.120 + 0.973X	$0.959 \le M \le 0.987$	0.99	(27)
Y = 1.132X	$1.112 \leq M \leq 1.152$	0.99	(28)

Figures 29 and 30 show actual versus indicated concentrations for calibrations in experiment seven at Paths 1 and 3 using baseline signal levels obtained at Path 2. Figure 29 corresponds to calibration at Path 1, and Figure 30 corresponds to calibrations at Path 3. Equations 29 and 30 are the regression line equations for calibrations at Path 1 and Path 3, respectively.

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = 1.293X	$1.271 \leq M \leq 1.315$	0.99	(29)
Y = 1.273X	$1.257 \le M \le 1.289$	0.99	(30)

Figures 31 and 32 show actual versus indicated concentrations for calibrations in experiment seven at Paths 1 and 2 using baseline signal levels obtained at Path 3. Figure 31 corresponds to calibration at Path 1, and Figure 32 corresponds to calibration at Path 2. Equations 31 and 32 are the regression line equations for calibrations at Path 1 and Path 2, respectively.

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = 1.216X	$1.202 \leq M \leq 1.230$	0.99	(31)
Y = 1.011X	$0.995 \le M \le 1.027$	0.99	(32)

## Experiments to Determine Mirror Reflectivity

In experiment eight, the five, consecutive alignments in the single-beam configuration demonstrated a mean reference signal level of 68.7 millivolts with a standard deviation of 0.43 millivolts. The absorbed signal level demonstrated a mean level of 108.2 millivolts with a standard deviation of 1.62 millivolts. The five, consecutive alignments in the reflected-beam configuration demonstrated mean signal levels of 54.1 and 83.8 millivolts with standard deviations of 0.47 and 1.23 millivolts for the reference and absorbed wavelengths, respectively. Because the variation in signal levels was small for the consecutive alignments, the mean signal levels were used in the calculation of mirror reflectivity.

Calculations revealed that the mirror has a reflectivity of 0.89 at the reference wavelength, and a reflectivity of 0.88 at the absorbed wavelength.



Figure 11

Actual versus Indicated Concentrations from calibrations using a single beam in a homogeneous test environment (MIRAN)



Figure 12

Actual versus Indicated Concentrations from calibrations using a single beam in a homogeneous test environment (ECD Device)

Mean Concentration (ppm)	<u>S.D.</u>	<u>c.v.</u>
5.6	0.06	0.010
10.0	0.14	0.014
11.4	0.14	0.012
14.8	0.06	0.004
19.3	0.14	0.007
20.2	0.12	0.006
26.9	0.08	0.003
28.1	0.17	0.006
29.4	0.06	0.002
35.9	0.23	0.006
40.0	0.20	0.005
41.2 .	0.44	0.011
48.6	0.49	0.010
51.0	0.71	0.014

1.10

1

Table 1

Calculated values of standard deviation (S.D.) and coefficient of variation (C.V.) for path samples collected in experiment one.

56

35.

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Figure 13

Actual versus Indicated Concentrations from calibrations using a single beam in a heterogeneous test environment (ECD Device)





Actual versus Indicated Concentrations from calibrations using a reflected beam in a homogeneous test environment (ECD Device)

Mean Concentration (ppm)	<u>S.D.</u>	<u>c.v.</u>
3.3	0.09	0.027
4.0	0.06	0.015
4.6	0.09	0.020
5.9	0.09	0.015
6.6	0.14	0.021
7.9	0.09	0.011
9.0	0.07	0.008
9.7	0.08	0.008
12.3	0.25	0.020
12.8	0.11	0.009
13.1	0.07	0.005
15.8	0.07	0.004
16.3	0.33	0.020
17.5	0.34	0.019

20

Table 2 Calculated values of standard deviation (S.D.) and coefficient of variation (C.V.) for path samples collected in experiment three. 59

10.00

. . 18

....

-065

2.1453



Figure 15

Actual versus Indicated Concentrations from calibrations using a reflected beam in a heterogeneous test environment (ECD Device)


Actual versus Indicated Concentrations from calibrations evaluating the effect of pathlength at a pathlength of 1.50 meters (ECD Device)



Actual versus Indicated Concentrations from calibrations evaluating the effect of pathlength at a pathlength of 3.00 meters (ECD Device)





Actual versus Indicated Concentrations from calibrations evaluating the effect of pathlength at a pathlength of 4.50 meters (ECD Device)



Figure 19

Actual versus Indicated Concentrations from calibrations evaluating the effect of pathlength at a pathlength of 6.00 meters (ECD Device)



Actual versus Corrected Indicated Concentrations from calibrations using incorrect pathlength value of 6.00 meters at a pathlength of 1.50 meters (ECD Device)





Actual versus Corrected Indicated Concentrations from calibrations using incorrect pathlength value of 6.00 meters at a pathlength of 3.00 meters (ECD Device)



Figure 22

Actual versus Corrected Indicated Concentrations from calibrations using incorrect pathlength value of 6.00 meters at a pathlength of 4.50 meters (ECD Device)



Figure 23

Actual versus Corrected Indicated Concentrations from calibrations using pathlength value of 6.00 meters at a pathlength of 6.00 meters (ECD Device)





Actual versus Indicated Concentrations from calibrations at Path 1 using actual baseline signal levels (ECD Device)



Actual versus Indicated Concentrations from calibrations at Path 2 using actual baseline signal levels (ECD Device)





Actual versus Indicated Concentrations from calibrations at Path 3 using actual baseline signal levels (ECD Device)



Actual versus Indicated Concentrations from calibrations at Path 2 using baseline signal levels of Path 1 (ECD Device)



Actual versus Indicated Concentrations from calibrations at Path 3 using baseline signal levels of Path 1 (ECD Device)

73



Actual versus Indicated Concentrations from calibrations at Path 1 using baseline signal levels of Path 2 (ECD Device)



Actual versus Indicated Concentrations from calibrations at Path 3 using baseline signal levels of Path 2 (ECD Device)

75



Actual versus Indicated Concentrations from calibrations at Path 1 using baseline signal levels of Path 3 (ECD Device)



Actual versus Indicated Concentrations from calibrations at Path 2 using baseline signal levels of Path 3 (ECD Device)

#### DISCUSSION

## Creation of Homogeneous Test Environments

In experiments one and three using a homogeneous test environment, several samples were collected along the beam path and analyzed with the ECD device. Table 1 contains calculated values of standard deviation and coefficient of variation for path samples collected during experiment one in which a single beam was used in a homogeneous environment. These values are very small and suggest that chamber concentrations were very nearly homogeneous in this experiment. Similarly, Table 2 contains calculated values of standard deviation and coefficient of variation for path samples collected in experiment three in which a reflected beam was used in the homogeneous environment. Again, these values were all small and suggest that the concentrations were very nearly homogeneous in the chamber during this experiment.

### Accuracy of the INFRASAFE in the Single-Beam Configuration

The calibration data obtained in experiments using the single-beam configuration in both a homogeneous and a heterogeneous environment indicate that the INFRASAFE is capable of accurate measurement of path-averaged concentrations in this configuration. The device tended to, on average, overestimate the actual pathaveraged concentrations by 10 to 12%. Values of R<sup>2</sup> were 0.99 indicating excellent correlation. Using a t-test with a 95% level of confidence, regressions resulting from calibrations using the MIRAN and the ECD device in the homogeneous test environment were not found to be significantly different from one another and were both different from unity ( a slope of 1.00). The regression lines resulting from calibrations in the homogeneous environment were not significantly different from the regression lines resulting from calibrations conducted in the heterogeneous environment. This suggests that the INFRASAFE performs equally well in either environment using the single-beam configuration. This is important because heterogeneous concentrations are typical of workplace environments.

#### Accuracy of the INFRASAFE in the Reflected-Beam Configuration

The calibrations conducted using a reflected-beam indicate that the INFRASAFE is capable of accurate measurement of path-averaged concentrations in both homogeneous and heterogeneous test environments. The device, on average, overestimated actual path-averaged concentrations by about 11%. Values of R<sup>2</sup> were 0.99 indicating excellent correlation. No significant difference was found between accuracy in the homogeneous and heterogeneous environments using a t-test with a 95% level of confidence. This suggests that the INFRASAFE performs equally well in both environments. Again, this is important because heterogeneous concentrations are typical of workplace environments.

#### Accuracy with Single Beam versus Accuracy with Reflected Beam

Using a t-test with a 95% level of confidence, the slope of the regression lines resulting from calibrations in the reflected-beam configuration was not found to differ significantly from the slopes of the lines resulting from calibrations in the single-beam configuration. This suggests that the accuracy of the INFRASAFE in either test environment is not affected by the use of a pair of mirrors to reflect the optical beam. This is important because the laboratory validation of ORS/CT theory and the ultimate field use of the INFRASAFE will probably involve mirrors or retroreflectors to reflect the beam.

## Effect of Pathlength

In experiment five, varying the pathlength had no significant effect on accuracy at the 95% confidence level when the correct pathlength value was input into the control system. This suggests that the algorithm used by the control system software accurately corrects for pathlength at the very short, indoor pathlengths used in this research.

## Use of Mathematical Correction for Incorrect Pathlength Values

In experiment six, concentrations displayed by the INFRASAFE were mathematically corrected by multiplying by the input pathlength (6 meters) and dividing by the actual pathlength. Regression lines resulting from calibrations at 1.50, 3.00, and 4.50 meters were compared to the lines obtained in experiment five. Using a t-test with a 95% level of confidence, no significant difference was found between slopes of the regression lines in the two experiments. This suggests that the mathematical correction used in experiment six is equivalent to that performed by the algorithm in correcting for pathlength. If the INFRASAFE is to be used at several different pathlengths, the displayed concentrations can be mathematically corrected as in this experiment.

## Use of Incorrect Baseline Signal Levels

In experiment seven, the input of incorrect baseline signal levels seriously affected the accuracy of the INFRASAFE; nearly all regression lines from calibrations that used incorrect signal levels were significantly different from the calibrations that used correct signal levels.

When baseline signal levels obtained at Path 1 were input for calibration at Path 2, the INFRASAFE, on average, underestimated actual concentrations by about 3% with an  $R^2$  of 0.99. The resulting regression line was significantly different from lines

from calibrations using the correct signal levels. Calibrations at Path 3 revealed that the INFRASAFE, on average, overestimated actual concentrations by about 13% with an  $R^2$  of 0.99. The regression line resulting from calibrations at Path 3 was not significantly different from those resulting from calibrations using correct baseline signal levels.

When baseline signal levels obtained at Path 2 were input for calibrations at Path 1, the INFRASAFE, on average, overestimated actual concentrations by about 29% with an  $R^2$  of 0.99. Calibrations at Path 3 revealed that the INFRASAFE overestimated actual concentrations by about 27%, on average, with an  $R^2$  of 0.99. Both of these regression lines were significantly different from those resulting from calibrations using correct baseline signal levels.

When baseline signal levels obtained at Path 3 were input for calibrations at Path 1, the INFRASAFE, on average, overestimated actual concentrations by about 22% with an R<sup>2</sup> of 0.99. Calibrations at Path 2 revealed that the INFRASAFE slightly overestimated actual concentrations by, on average, about 1% with an R<sup>2</sup> of 0.99. Again, both of the regression lines were significantly different from lines resulting from calibrations using correct baseline signal levels.

As the results of experiment seven have shown, there is a significant effect on accuracy by inputting incorrect baseline signal levels into the control system.

The INFRASAFE control system uses software which converts the detector signal levels into a path-averaged concentration at a specified pathlength. The software calculates path-averaged concentrations using a mathematical curve created by the manufacturer. This curve is a plot of path-integrated concentration versus the ratio of the baseline signal levels, "absorbed" to "reference". The ratio of the input baseline signal levels is considered to be the y-intercept on this curve; the input ratio establishes the zero point where the device will display a reading of zero ppm.(57)

The signal level ratios obtained in the initial alignments at Paths 1, 2, and 3

were all approximately 1.10; however, several alignments at the same path may have shown that the ratio varies slightly from one alignment to the next.(62) Due to this possible variation at Paths 1, 2, and 3, it is conceivable that the actual ratio of the baseline signal levels differed slightly from the input ratio. If the actual ratio obtained was less than the input ratio, the software would interpret this as absorption caused by gas within the optical beam because the input ratio is used as the zero point. As the INFRASAFE is calibrated in this situation, concentrations would be consistently overestimated relative to the INFRASAFE's previously demonstrated accuracy in calibrations using the correct baseline signal levels. The opposite is true in the case that the actual ratio is greater than the input ratio, and concentrations would be underestimated relative to the INFRASAFE's previously demonstrated accuracy.

Calibrations at Path 1 using the baseline signal levels of Paths 2 and 3 reveal that the INFRASAFE overestimated concentrations more than its typical 10 to 12 percent. This suggests that the actual baseline signal level ratio obtained in this alignment at Path 1 may have been less than 1.10. Calibrations at Path 2 using the baseline signal levels of Paths 1 and 3 reveal that the INFRASAFE underestimated concentrations relative to the usual overestimation. This suggests that the actual baseline signal level ratio obtained in this alignment at Path 2 may have been greater than 1.10. Finally, calibrations at Path 3 using the baseline signal levels of Paths 1 and 2 reveal that the INFRASAFE overestimated concentrations relative to its usual performance. This suggests that the actual ratio obtained in this alignment at Path 3 may have been less than 1.10.

The results of experiment seven reveal that the correct baseline signal levels should be input into the control system for accurate performance at a certain pathlength. In the creation of a network of beams, this will probably not be feasible due to the time required to enter new signal levels. More specifically, the ultimate use of the INFRASAFE in the validation of ORS/CT theory will probably require rapid

movement from one pathlength to another. The several minutes needed to enter new signal levels at each different pathlength will not permit this rapid movement. For this reason, if the INFRASAFE is to be used at several, different pathlengths, the software should be modified to allow the input of several pairs of baseline signal levels.

#### Experiments to Determine Mirror Reflectivity

The standard deviation of the baseline signal levels obtained for the consecutive alignments at 5.00 meters

in both the single beam and the reflected-beam configurations was quite small. This suggests that the estimate of mirror reflectivity by this process should be an accurate one.

The reflectivities of the mirrors at the reference and absorbed wavelengths are essentially equivalent, 89 versus 88 percent, respectively. This high level of efficiency is important because the beam can be reflected multiple times without incurring excessive energy loss.

If multiple mirrors are used, the resulting reflectivity at each wavelength can be calculated using Equations (33) and (34).

$${}^{n}\text{mult,ref} = ({}^{n}\text{ref})^{X}$$
(33)

 ${}^{n}\text{mult,abs} = ({}^{n}\text{abs})^{X}$ (34)

where,

mult,ref is the resultant reflectivity obtained at the reference wavelength upon multiple reflections,

mult,abs is the resultant reflectivity obtained at the absorbed wavelength upon multiple reflections, <sup>n</sup>ref is the single mirror reflectivity at the reference wavelength,
 <sup>n</sup>abs is the single mirror reflectivity at the absorbed wavelength, and
 X is the number of mirrors.

#### Deviation From Linearity

The plots of actual versus indicated concentrations resulting from the calibrations performed in this research all exhibit a slight deviation from linearity. This is most apparent as the MDL of the INFRASAFE is approached; at a certain point, the curve begins to decrease in slope as concentration increases up to the maximum test concentration.

If the INFRASAFE is used at longer pathlengths, it is possible that a similar deviation from linearity would be observed as concentration is increased in small steps from a level of zero ppm. If this is the case, the calibration curve may take the form of an s-shaped curve that deviates from linearity at concentrations near the limits of detection.

## A Different Statistical Treatment of Calibration Data

The calibrations performed in this work consisted of three independent replicates for each calibration. The INFRASAFE displayed a reading of zero ppm at the start of each replicate. For this reason, each calibration actually consists of three sets of independent observations. Therefore, the data from each calibration can be manipulated in a different statistical fashion using than used in the Results section using a t-test with two degrees of freedom. This manipulation was performed on calibration data obtained in experiments one through four to determine whether or not the resulting confidence intervals would be reduced which might indicate the existence of a significant difference in accuracy between the two test environments and/or the two beam configurations. Refer to appendix D for the results of this work.

## CONCLUSIONS

In this research, experiments were conducted to determine the feasibility of using a commericially-available optical remote sensing device for use in laboratory validation of ORS/CT theory. The INFRASAFE Single-Gas Open-Path Monitor was selected for use in this research. This device was capable of measuring path-averaged concentrations of sulfur hexafluoride, the test gas used in this research to model other gases and vapors.

The INFRASAFE was calibrated in both homogeneous and heterogeneous test environments in both single and reflected-beam configurations using two direct-reading validation methods . Experiments were conducted to determine the effect of varying the pathlength. Additional experiments were conducted to determine the effect of inputting incorrect pathlength values and incorrect baseline signal levels into the INFRASAFE's control system. A mathematical correction was performed on the data and proved to be equivalent to the correction performed by the algorithm used by the INFRASAFE. The efficiency of the mirrors used in this research was also determined.

Results indicate that the INFRASAFE is a suitable ORS device for the accurate measurement of path-averaged concentrations using a network of reflected beams in the upcoming laboratory validation experiments.

The INFRASAFE accurately measured gas concentrations in both test environments using the single and the reflected-beam configuration. On average, the INFRASAFE overestimated actual concentrations by about 10 to 12% with an R<sup>2</sup> of 0.99. As expected, pathlength did not significantly affect the accuracy of the device when the correct value was input into the control system. When the INFRASAFE was provided with an incorrect pathlength value, results indicate that the displayed concentrations can be mathematically corrected to yield actual path-averaged concentrations. This mathematical correction was shown to be equivalent to the correction performed by the INFRASAFE software. When incorrect baseline signal levels were input, the accuracy of the INFRASAFE was greatly affected. Results indicate that the correct baseline signal levels should be input for accurate performance or the software should be modified to allow operation with several different pairs of baseline signal levels. The mirrors used in this research were found to have high reflectivities of approximately 90%.

Results from the experiments indicate that the INFRASAFE is a promising tool for evaluating optical remote sensing/computed tomography theory. Future work should focus on further evaluation of the INFRASAFE in a chamber using a scanning device to project the beam over several different pathlengths to create a beam network. The possibility of modifying the software to permit operation with several different pathlengths should be pursued.

## RECOMMENDATIONS FOR FUTURE WORK

Work conducted thus far has shown that the INFRASAFE is a promising tool for use in evaluating ORS/CT theory. Several additional experiments should be performed to ultimately confirm the feasibility of using the ORS device for this purpose. These experiments include calibrating the INFRASAFE in a multiplereflection condition, evaluating the effect of temperature and humidity on accuracy, designing, building, and testing a scanning device, and calibrating the INFRASAFE when the scanning device is used to create a network of reflected beams in a chamber. Also, a standard method of calibrating open-path devices should be developed for use in the field. The possibility of modifying the software used by the control system to calculate path-averaged concentrations should be pursued, and, ultimately, an FTIR spectrometer should be applied in this research.

## Multiple-Reflection Calibration

Previous reflected-beam experiments involved using two mirrors to reflect the beam from the transmitter into the receiver. Additional mirrors will probably be used by a scanning device to create a network of beams in a chamber. The efficiency of the mirrors has been determined; if other mirrors are used, their efficiency should be determined.

The INFRASAFE should now be validated using several additional mirrors to reflect the beam. This is important to ensure that the INFRASAFE accurately measures path-averaged concentrations when the beam is reflected multiple times. Multiple-reflection experiments should be conducted to validate the INFRASAFE in both the homogeneous and heterogeneous test environment using several additional mirrors. Point-samples should be collected along the beam path and analyzed with the direct-reading, ECD device.

### Temperature/Humidity Effect Experiments

Calibrations conducted in this research were performed at room temperatures between 60 and 70 degrees Fahrenheit and approximately 50% relative humidity. Calibrations should be conducted to evaluate the effect on accuracy of varying the room temperature and relative humidity. This is important because workplace conditions can differ significantly from those used in this work.

## Design, Construction, and Evaluation of a Scanning Device

A device capable of projecting the beam produced by the INFRASAFE around a chamber to create a beam network is essential to this research. Once this device is constructed, it should be tested with the INFRASAFE in a chamber; experiments should be performed to evaluate the performance of the INFRASAFE using the scanning device to project the beam from one path to another. Both homogeneous and heterogeneous test environments should be used in validating the accuracy of this system with point-samples analyzed by the direct-reading ECD device.

## Standard Method for Routine Calibration of the INFRASAFE

The need to routinely calibrate an open-path, optical remote sensing device in the field makes it important to develop a more efficient, standard method of calibration. As stated before, due to the open-path monitoring technique, the calibration of these devices is more complicated than most other air monitoring instruments. Although the calibration methods used in this research have proven effective, they might be cumbersome to apply in the field.

### Modifications to INFRASAFE Software

If the INFRASAFE is to be used in the validation of ORS/CT theory, it will be required to accurately measure path-averaged concentrations at several different pathlengths. Because accurate performance requires the input of correct baseline signal levels, the software should be modified to accept several different baseline signal levels obtained at the different pathlengths.

### Ultimate Use of FTIR System

As stated before, the INFRASAFE is currently limited to the detection of a single contaminant. However, the ultimate use of an optical remote sensing device in the workplace will rarely involve detection of a single gas. For this reason, an FTIR-based, optical remote sensing device should ultimately be used in this research so that several different gases and vapors can be monitored simultaneously. As discussed earlier, this type of optical remote sensor has shown promise in measuring workplace gas concentrations at short, indoor pathlengths.

#### Construction of an Exposure Chamber

An exposure chamber is currently being designed and constructed for the ultimate purpose of using the INFRASAFE in the laboratory to evaluate ORS/CT theory. This chamber will be located in the School of Public Health.

## **Construction of Additional Mirror Stands**

Experiments using multiple reflections and a network of reflected beams require several additional mirror stands to be constructed. These stands should be similar to the stand used in this research because the design has worked well. One necessary change from the design of the original mirror stand is the substitution of mirror mounts that are of heavier duty; the mounts used in this research did not provide sufficient mounting surface nor were the springs in the mount heavy enough to avoid being compressed by the weight of the mirror. Mounts having a larger, 4 1/2-inch mounting 'surface are available from Edmund Scientific, Inc.

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# APPENDIX A ECD DEVICE USER'S GUIDE

The Valco Electron Capture Detector (ECD) device was constructed for use in the validation of the INFRASAFE Single-Gas Open-Path Monitor. It serves this purpose well provided the user is familiar with the instrument's needs. This guide contains material relevant to operation and calibration, modification, troubleshooting, and materials of construction of this device.

### Initial Operation/Calibration Information

Carrier-Gas and Carrier-Gas Regulator Requirements

Prior to operating the ECD device, the user must assure that the carrier-gas and carrier-gas regulator are of sufficient purity to be used with this instrument. Regulator and carrier-gas purity requirements are very important; damage can result from the use of inferior materials that will be costly both in terms of money and in lost time.

The detector is extremely sensitive and susceptible to damage from accumulation of internal deposits; therefore, the gas flowing through the unit must be free of certain contaminants. Electrophilic materials such as oxygen, Freon, carbon tetrachloride, and chloroform may become deposited on the source foil resulting in a substantially reduced baseline current. All components in contact with the carrier-gas stream must be free of these contaminants.

The carrier-gas of choice is high-purity argon with 5% methane. This gas is available from National Welder's Supply, Raleigh, North Carolina. Pure nitrogen may also be used as a carrier. One-hundred percent pure argon has been demonstrated to be ineffective in this instrument; the 5% methane additive to argon is crucial to the performance of the detector.

The regulator used to control the flow of carrier-gas must be of the high-purity

specification and must not have been previously used in applications involving the above mentioned electrophilic materials.

### Factors Affecting Sensitivity of the ECD Device

The ECD device can operate at a range of carrier-gas flowrates, detector temperatures, baseline-adjust settings, and recorder output attenuation settings. All four factors individually affect the sensitivity of the detector and can be increased or decreased to afford the desired level of sensitivity.

The sensitivity of the detector is affected by flowrate; increasing the flowrate serves to decrease the sensitivity. Typical carrier-gas flowrates for the ECD device range from 80 to 100 cc per minute. Flowrates in excess of this range are needlessly wasteful of carrier gas.

The detector temperature also affects the sensitivity of the detector; increasing the detector temperature serves to decrease sensitivity.

The baseline-adjust setting also affects the sensitivity of the detector. This setting is adjusted by rotating the ten-turn control equipped with the turns-counting dial on the control system module. As the baseline-adjust setting is increased, the sensitivity of the detector increases.

The recorder output attenuation control is another adjustment affecting sensitivity. This sixteen-position switch on the front panel of the system control module establishes the sensitivity of the recorder output relative to the concentration of the electron-capturing species present in the detector. The fully-clockwise position provides the greatest sensitivity. The fully-counterclockwise position is used to provide a zero-voltage output so that the recorder can be zeroed. The switch position labeling is in powers of two; each position corresponds to a factor of two change in system sensitivity.

### Initial Operation of the ECD Device

To operate the ECD device, first initiate the carrier-gas flow by adjusting the carrier-gas regulator for a flowrate of approximately 40 cc per minute, set the detector temperature to a setting between 330 and 370 degrees, turn the recorder output attenuation control to the position marked " $\infty$ ", and zero the recorder pen. Allow the device to warm-up for about four hours. After warm-up, adjust both the baseline adjust setting and the recorder output attenuation control so that the recorder pen is stabilized at zero. The device may now be calibrated.

### Calibration of the ECD Device

A useful calibration is one which covers the range of concentrations one expects to encounter during an experiment. The ECD device should be calibrated so that 125% of the maximum expected concentration encountered in an experiment will not run offscale on the chart recorder.

The ECD device must be calibrated against known challenge concentrations of sulfur hexafluoride in air. A closed-loop calibration circuit may be used for this purpose; it is imperative that the loop be free of gas leaks and that the volume of the loop be precisely known. The volume of the tubing and accompanying fittings must be included because they comprise a small portion of the loop volume.

To calibrate the device, increase the carrier-gas flowrate to approximately 100 cc/min. Create the 125% challenge concentration in the calibration loop, withdraw a sample with a 30cc syringe, fit the syringe into the female luer fitting in the side of the instrument enclosure, inject the sample, push the solenoid actuation switch on the side of the device housing, hold for approximately five seconds, and release. The ECD device will accept any syringe with a standard luer-lock tip. The syringe screws onto the female luer fitting on the side of the instrument enclosure; one-half turn clockwise is sufficient to seal the syringe against the luer fitting for a leak-free sample injection.

Once the sample is injected filling the internal sample loop, the momentary switch on the side of the instrument is depressed and held for about five seconds and then released. This actuates the solenoid which switches the two-position valve so that the injected sample is carried out of the sample loop, through the column and into the electron capture detector by the carrier-gas flow. A chart recorder connected to the attenuator console records the instrument response. The first peak recorded on the chart recorder is due to oxygen in the sample; at a flowrate of 100 cc/min, this peak is recorded within 20-30 seconds of solenoid actuation. The second peak recorded corresponds to sulfur hexafluoride in the sample; at the same 100 cc/min flowrate, this peak is recorded within 2 1/2 minutes of solenoid actuation. The height of the recorded peak is proportional to the concentration of sulfur hexafluoride in the injected sample.

If the sulfur hexafluoride peak is off-scale, the sensitivity of the device must be decreased. To accomplish this, either rotate the attenuator dial counter-clockwise one position or decrease the baseline adjust setting by about 10 units. A second sample is then injected and the adjustment process repeated until 125% of the maximum expected challenge concentration is recorded by a peak between 90 and 95 percent of full-scale.

Once these settings are obtained, proceed to calibrate the instrument over the range of concentrations expected. It is good practice to perform three injections at each calibration point and average these peak heights when creating a calibration curve. The ECD device should be calibrated before and after an experiment to verify that the instrument response has not drifted during the course of the experiment.

### Important Operational Details

Because carrier-gas flowrate, detector temperature, baseline-adjust, and recorder output attenuation settings all affect instrument response, changing any of these from the value at which the instrument was calibrated will render the calibration useless. A flow of carrier-gas must be supplied to the detector at all times when the device is being heated. It is very important that the carrier-gas flow be maintained after turning off the instrument until the detector has cooled for approximately two hours. To turn off the instrument, turn the detector temperature dial to the "off" position. Two hours later, return and shut off the carrier gas flow at the regulator. The detector may be damaged if this procedure is not followed.

#### Modifications: Changing of Sample Loop to Affect Sensitivity

The Valco ECD device is highly sensitive to sulfur hexafluoride. The range of adjustments provided in carrier-gas flowrate, detector temperature, recorder output attenuation, and baseline-adjust setting provide a wide range of sensitivity to this gas. To alter sensitivity, an additional adjustment that can be performed is the substitution of one internal, sample loop for another. The sample loop volume dictates the volume of injected sample that is actually retained for passage through the electron capture detector. This part is connected to the 6-port valve, at port #3 at one end and at port #6 at the other end. A small, 1/4" open-end wrench is required to disconnect the existing sample loop from the 6-port valve and install a smaller or larger sample loop. A smaller sample loop serves to decrease sensitivity of the instrument in that a smaller volume of sulfur hexafluoride is sent to the detector for analysis; conversely, a larger sample loop serves to increase sensitivity.

## Troubleshooting

One major source of possible problems with the ECD device was overlooked in the manufacturer's manual: Leakage around loose fittings and connections inside the instrument enclosure may result in erratic instrument response. Therefore, it is imperative that all fittings be tightened adequately when, for example, a sample loop is changed. A leak may cause sulfur hexafluoride in an injected sample to fill the

instrument enclosure and enter at another loose connection to flow through the detector. This situation will render the instrument ineffective at measuring the true concentration in an injected sample.

Other possible problems that are not addressed either here or in the instruction manual should be referred to the technical support department at Valco Instruments, Inc., phone 1 (800) 323 2000. Mr. Thomas Knapp, a technician for Valco, has been quite helpful in the past.

### Materials of Construction

The Valco ECD device is constructed of parts obtained primarily from Valco Instruments Company, Inc. of Houston, Texas. A list of these parts follows:

Electron Capture Detector-120V NI Source, #ECD140BN Attenuator O/P 1V for ECD, #I-21051-03 6 Port Valve, 1/16", A, 4SO, 175C, 400PSI, #A4C6UWP Heated Valve Enclosure, 8" x 8" x 6", 40W, #HVEC Oxygen Trap, OT3-2 (R&D Separations), #OT 1/16" Zero Dead-Volume Nuts, #ZN1 Ferrules, Zero Dead-Volume Fittings: 1/16", 303SS, #ZF1 Ferrules, Zero Dead-Volume Fittings: 1/8", 303SS, #ZF2 1/8" to 1/16" Zero Dead-Volume Reduction Unions, #ZRU21T 1/4" to 1/16" Zero Dead-Volume Reduction Unions, #ZRU42T Female Luer Adapter to 1/16" Fitting, #ZLA-1 Loop, Sample: 500 microliter for C6UW Valve, #SL500C6UW 1/8" Zero Dead-Volume Filter w/ Removable Frit, #ZUFR2F 1/16" Zero Dead Volume Bulkhead Straight-Thru Unions, #ZBU1T Loop, Sample: 100 microliter for C6UW Valve, #SL100C6UW

# 4-Way Air-Actuated Solenoid, 100PSI, 120V, #41E1

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Other parts include the chromatographic column which was obtained from ITI, Inc. The plastic "experimenter's box" located beneath the solenoid, the terminal strip, and the electrical switches and wire were obtained from Radio Shack, Inc.

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# APPENDEX B

VALIDATION INSTRUMENT CALIBRATION CURVES

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Figure 33 ECD Device calibration curve for experiment one





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Figure 36 ECD Device calibration curve for experiment three



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ECD Device calibration curve for experiments two and four



Figure 40 ECD Device calibration curve for experiments two and four



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Figure 44 ECD Device calibration curve for experiments two and four



Figure 45 ECD Device calibration curve for experiments five, six, and seven



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ECD Device calibration curve for experiments five, six, and seven





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Figure 49 MIRAN calibration curve for experiment one



# Figure 50 MIRAN calibration curve for experiment one

### APPENDIX C

### INFRASAFE ALIGNMENT PROCEDURE

The components of the INFRASAFE must be adjusted to maximize the baseline signal levels. A procedure for aligning the INFRASAFE is presented here. Coarse alignment of the receiver and transmitter is initially performed followed by fine adjustment of optical components within the receiver.

## Coarse Alignment

The initial coarse alignment is performed most easily in the dark; the visible component of the optical beam is more easily seen. The transmitter is first placed in the desired position. Open the lid of the transmitter and verify that the top of the glowbar source is located 6 17/32 inches from the bottom of the housing. This is most easily performed using a combination square.

Next, the receiver is placed in the desired position so that the transmitted beam enters the receiver aperture. Adjust the position of the receiver until the incoming beam falls directly on the primary mirror; the circular beam should be centered, entirely covering the mirror. An 8 1/2 by 11 inch sheet of white paper can be used to verify that the beam is centered on the mirror. Cut a six-inch diameter circle from the sheet and use it as a template by placing it over the primary mirror. The location of the incoming beam should be visible on the template.

#### Fine Adjustments

Next, adjust the primary mirror in the receiver using the two thumb screws on the rear of the mirror stand so that the reflected beam falls directly on the center of the secondary mirror. The top screw adjusts the left to right position (pan) of the mirror while the bottom screw adjusts the up and down (tilt) position. A smaller piece of white paper about the size of an index card can be used to view the location of the beam on the mirror.

After adjusting the primary mirror, the secondary mirror is adjusted so that the beam is reflected through the beam splitter. This device reflects a portion of the beam to the reference optical components and passes a portion of the beam to the absorbed optical components. The adjustment of the secondary mirror should direct the reflected beam through the center of the beam splitter mount. No portion of the beam should be obscured by the mount. A small, white piece of paper can be used to image the beam to the face of the mount. The thumb screws located at the rear of the secondary mirror mount perform the opposite pan and tilt movements described in the primary mirror adjustment.

For the next step in the alignment process, remove the filter holder from the absorbed detector housing. Adjust the translation stage of the absorbed detector so that the beam falls directly upon the detector element. Adjust the secondary mirror and absorbed detector alternately as required so that the beam splitter does not obscure the beam. The filter holder should then be reinstalled.

After adjustment of the secondary mirror and absorbed detector, the beam splitter is adjusted to place the reflected portion of the beam on the center of the reference detector element. This requires that the filter housing be removed from the reference detector. Alternately adjust the beam splitter and reference detector. Once the beam is centered on the element, reinstall the filter housing.

The final steps in the alignment process require the control system to be turned on and the operating program entered. The voltage levels of both the reference and absorbed detectors are easily read from the monitor screen. First, remove both filter holders from the detectors. Use the absorbed detector, translation stage adjustments to place the infrared beam directly on the center of the detector element. The required adjustment should not be greater than three of four turns in either direction. The

"ABS" signal level on the display in monitored while the x-axis micrometer handle is adjusted. The voltage level will increase or decrease depending on direction of travel. Adjust to maximum voltage level. Repeat this procedure with the y and z-axis micrometers. The reference detector is then adjusted in the same manner, and the signal level is monitored on the display while adjusting the x, y, and z-axis micrometers to obtain a maximum. Once the detectors have been adjusted, the optical alignment process is complete.

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# APPENDIX D STATISTICAL ANALYSIS SUPPLEMENT

Calibration data obtained in experiments one through four were analyzed in a different statistical manner using a t-test with a 95% level of confidence and two degrees of freedom. This was performed because the three replicate trials performed in each calibration are actually three independent sets of observations. Regression lines resulting from this statistical treatment are compared to regression lines contained in the body of this report which were calculated by treating the three replicates of each calibration as single sets of observations.

Listed below are the regression line equations obtained using this statistical treatment. Equations 35-38 correspond to experiments one through four, respectively. Confidence intervals for the slope and the values of R<sup>2</sup> are also provided.

EQUATION	95% C.I. FOR SLOPE	R <sup>2</sup>	
Y = 1.097X	$1.050 \le M \le 1.144$	0.99	(35)
Y = 1.106X	$1.066 \le M \le 1.146$	0.99	(36)
Y = 1.105X	$1.086 \le M \le 1.124$	0.99	(37)
Y = 1.121Y	1.101 < M < 1.141	0.99	(38)

In all four experiments, the slopes of the regression lines resulting from the two different statistical treatments are essentially equivalent, however, the confidence intervals for the slopes resulting from the new treatment are wider in all four experiments. This suggests that treating the three replicate calibrations in each experiment as three independent observations is a more conservative statistical treatment than treating the replicates as a single set of observations. Furthermore, if all calibrations performed in this research were treated in this more conservative fashion, it is reasonable to conclude that the findings of this research would not be affected.

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