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Mr. Steve Zappe
New Mexico Environment Department
Hazardous & Radioactive Materials Bureau
2044 A Galisteo Street
Santa Fe, NM 87505

Subject: WIPP Volatile Organic Compound Monitoring Using Extractive Fourier Transform Infrared Spectroscopy

Dear Mr. Zappe:

I am pleased to submit, for your review, the Department of Energy's Fourier Transform Infrared (FTIR) Technology Report for the monitoring of volatile organic compounds (VOCs) in ambient air at the Waste Isolation Pilot Plant (WIPP). This report is a presentation of the testing performed at the WIPP facility to determine improved ways of monitoring for VOCs in air. A potential method available today to replace the canister sampling method , which was described in the Confirmatory VOC Monitoring Plan (Appendix D20) of the Resource Conservation and Recovery Act (RCRA) Part B Permit Application, is extractive FTIR.

The canister sampling method of VOC monitoring, which is based on the concepts in the EPA Compendium Method TO-14, has been used at the WIPP facility for six years. In order to obtain VOC data using this method, we must use samplers to take canister samples underground near waste panels, ship the canisters to an analytical laboratory, and days later, receive valid data to report. New technology, such as the use of FTIR in the field to analyze for VOCs, offers potentially better and more efficient ways for operating a VOC monitoring system. With an extractive FTIR method, the entire process would occur underground, operate automatically with a computer, and be able to record data continuously. We will also be able to monitor near real-time data and review data remotely (i.e., on the surface away from waste operations), which will reduce potential occupational exposures and increase our ability to take administrative actions in areas such as waste handling operations, if necessary.

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At this time, we are not proposing to replace the monitoring plan submitted in the permit application, but rather to submit a permit modification with a new plan (using extractive FTIR) after the permit has been issued. We would like to begin discussions with you as soon as possible regarding the use of this method of VOC monitoring at the WIPP facility during the disposal phase. We also plan on beginning discussions regarding the FTIR monitoring technology with the EPA. Our goal is to obtain approval and incorporate this new method prior to the receipt of waste at the WIPP facility.

We are also providing this report to Messrs. Reid Rosnick and Barry Lesnick of the EPA.

If you have questions or require further information, please contact me at (505) 234-7452 or sniderc@wipp.carlsbad.nm.us. I will be contacting you in a few weeks to continue this communication.

Sincerely,

Craig A. Snider
Compliance Engineer

Enclosure

cc w/o enclosure:
K. Day, WID
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C&C File

WIPP Library

FOURIER TRANSFORM INFRARED (FTIR) TECHNOLOGY REPORT

DOE/WIPP-96-2197

Processing and final preparation of this report was performed by the Waste Isolation Pilot Plant Management and Operating Contractor for the U.S. Department of Energy under Contract No. DE-AC04-86AL31950

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EXECUTIVE SUMMARY

The Waste Isolation Pilot Plant (WIPP) has been designed and constructed for the long-term disposal of transuranic (TRU) and TRU mixed waste (TRU waste mixed with hazardous constituents) generated by DOE defense programs. In 1997, the WIPP will receive a RCRA Part B Permit to dispose of TRU mixed waste in the repository. As a condition of the RCRA Permit, the WIPP will be required to monitor the air pathway for volatile organic compounds (VOCs) as specified in the Confirmatory Monitoring Plan.

The WIPP is currently conducting air monitoring utilizing pressurized sampling systems which draw air samples into SUMMA™ passivated canisters. The air samples are then analyzed with a gas chromatograph in an analytical laboratory.

In order to keep up with emerging state-of-the-art sampling technologies, several monitoring methods were investigated. Process on-line gas chromatography, on-line mass spectrometry, open-path Fourier Transform Infrared (OP-FTIR) spectrometry, and extractive FTIR spectrometry were evaluated for applicability and use. The FTIR technology was chosen as the most promising because of the extent of Environmental Protection Agency (EPA) research, which is currently being conducted. A dual-cell extractive FTIR system was selected for use at the WIPP site.

The WIPP conducted prototype testing of an extractive FTIR system for analysis of VOCs in the ambient mine air. This report includes a detailed description of the FTIR monitoring system and focuses on the operational aspects, the facility support requirements, and the system's ability to measure the levels of VOCs in ambient air to detect potential migration or releases above acceptable levels.

WIPP specific tests were conducted on the surface and in the WIPP underground. The tests included generation of background spectra used as a baseline for the analysis of samples. The instrument detector linearity, spectral resolution, and system alignment were assessed. Instrument path calibrations and signal-to-noise test were conducted and minimum detectable concentrations (MDC) for the target compounds calculated. Tests were also performed to evaluate the effects of salt loading on the inlet line filters, as well as any target compound losses that may be attributed to the inlet lines or the system sample cells. Tracer gases were released to evaluate the detection capability of the instrument. Gas standards were introduced into the system to evaluate precision and accuracy. Quality assurance and quality control (QA/QC) issues associated with implementation of an FTIR program are QA/QC procedures, routine maintenance, data review and interpretation, and records management.

The FTIR prototype testing discussed in this report offers promising results which warrant further examination. The extractive FTIR system can function in the WIPP mine, provide on-line information that can be viewed remotely, and operate unattended for weeks at a time, thereby providing efficient measurements with a high degree confidence.

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ATTACHMENT

1 OPERATING PROCEDURE CHECKLISTS DEVELOPED FOR WIPP EXTRACTIVE FTIR PROTOTYPE SYSTEM

1.0 Introduction and Objectives

The Waste Isolation Pilot Plant (WIPP) is an underground repository constructed in a massive salt bed formation. The WIPP has been designed and constructed for the long-term disposal of transuranic (TRU) and TRU mixed wastes (TRU waste mixed with hazardous constituents) generated by Department of Energy (DOE) defense programs. The repository is located 2,150 feet below the surface and consists of waste panels, each of which contains seven rooms and two access drifts. Each room is approximately 300 feet long, 33 feet wide, and 13 feet high. Access drifts are 13 feet high and 14 feet wide downstream from the waste panel and 20 feet wide upstream.

In 1997, the WIPP will receive a Resource Conservation and Recovery Act (RCRA) Part B Permit to dispose of TRU mixed waste in the repository. As a conditions of the RCRA Permit, the WIPP will be required to monitor the air pathway for Volatile Organic Compounds (VOCs) in accordance with the Confirmatory Monitoring Plan (Appendix CMP, DOE 1996a and Appendix D20, DOE 1996b). This will involve monitoring upstream and downstream of Panel 1 during disposal of waste in the panel, and for at least six months after the panel is certified closed. The purpose of the monitoring program will be to confirm that estimated hazardous constituent concentrations do not exceed acceptable levels. This report focuses on confirmatory VOC monitoring and the technologies available for producing the data necessary for making the confirmation.

Currently, a baseline monitoring program utilizing SUMMA™ passivated canister sampling with gas chromatography analysis is in operation at the WIPP site. This report compares FTIR monitoring with current monitoring technologies in order to determine the best and most efficient system for producing accurate and reproducible data. One of the drivers for evaluating more current technologies is found in 40 CFR §268.6 (b) (1) which states, "All waste and environmental sampling, test, and analysis data must be accurate and reproducible to the extent that state-of-the-art techniques allow."

This report presents the prototype testing results of a Fourier Transform Infrared (FTIR) Spectroscopy system and focuses on the operational aspects, the facility support requirements, and the system's ability to measure the levels of hazardous constituents in ambient air to detect potential migration.

2.0 Definitions and Acronyms

2.1 Definitions

Absorbance Units - Units used to measure the amount of infrared radiation absorbed by a sample; absorbance is linearly proportional to VOC concentration.

Apodization - Multiplication of an interferogram by a mathematical function to reduce the truncation effect by the detector response.

Background Spectrum - A spectrum collected in the absence of compounds in the sample to be used as a baseline reference.

Below Detection Limit (BDL) - The minimum concentration of an analyte that can be measured by the instrument.

Bias - Interference which can affect the quantitation of a certain compound due to the presence of another compound. In FTIR spectroscopy, the major biases are due to carbon dioxide and water.

Classical Least Squares (CLS) Fit - Mathematical technique for quantitation of samples that contain multiple components of gases. Other variants of this mathematical technique are Partial Least Squares (PLS) and Iterative Least Squares (ILS), each technique having their strengths and weaknesses in quantitation of specific compounds.

Co-adding - Addition of individual interferograms to obtain a better signal-to-noise ratio, thereby improving the quantitation and lowering the method detection limits.

FTIR (Fourier Transform Infrared) - Most chemical compounds absorb infrared energy. In FTIR monitoring, infrared energy passes through a sample area and obtains "fingerprint" characteristics due to analytes present in the sample. This sample is converted to a spectrum using a personal computer and specialized spectroscopic software which is also capable of interpreting the data. Multi-component analysis of the spectral data is conducted to immediately determine which constituents are present and how much of each have been detected.

Interferogram - Plot of the detector response versus optical path difference. An interferogram is the raw data produced by an FTIR instrument and saved to a data acquisition computer. Interferograms may be Fourier transformed to give infrared transmittance spectra.

Interferometer - An optical instrument that splits a beam of light such that the two beams created travel two different optical paths. The controlled change of the optical paths creates an interferogram.

Noise Equivalent Absorbance (NEA) - A measure of signal-to-noise ratio for the prototype extractive FTIR system.

Signal-to-Noise Ratio - A ratio of the intensity of a sample to noise present in the FTIR system. The higher the signal-to-noise ratio, the higher the quality of the sample. The prototype extractive FTIR system uses the term Noise Equivalent Absorbance.

Spectroscopy - The study of spectra. In the context of this document, the study of infrared spectra generated by performing Fourier transforms on interference patterns generated by an FTIR spectrometer.

TO Method - Compendium Method of potential sampling and analysis techniques established by the Environmental Protection Agency.

Torr - Unit of measurement of pressure. 760 torr is equivalent to one atmosphere.

Zero Path Difference (ZPD) - The displacement of the mirror at which point the optical path difference of the split beams in the interferometer is zero.

2.2 Abbreviations and Acronyms

111TA	1,1,1 - Trichloroethane
1122T	1,1,2,2 - Tetrachloroethane
11DCE	1,1 - Dichloroethylene
12DCA	1,2 - Dichloroethane
AWMA	Air and Waste Management Association
BDL	Below Detection Limit
CD	Compact Disc
CD-ROM	Compact Disc-Read Only Memory
CH4	Methane
CCL4	Carbon Tetrachloride
CHFRM	Chloroform
CHBNZ	Chlorobenzene
CLS	Classical Least Squares
CMP	Confirmatory Monitoring Plan
CO	Carbon Monoxide
CO_2	Carbon Dioxide
C7H8	Toluene
DCM	Dichloromethane (Methylene Chloride)
DAC	Digital to Analog Converter
DOE	Department of Energy
DVD	Digital Video Disc
E-300	East 300 Drift
EMI	Electromagnetic Interference
EPA	Environmental Protection Agency
Exp Val	Expected Values
FTIR	Fourier Transform Infrared
GC/MS	Gas Chromatography / Mass Spectrometry
HDO	Deuterated water (heavy water)
H_20	Water
ILS	Iterative Least Squares
KBr	Potassium Bromide
LN2	Liquid Nitrogen

INEL	Idaho National Engineering Laboratory
MCT	Mercury Cadmium Telluride
MDC	Minimum Detectable Concentration
N_2O	Nitrous Oxide
NEA	Noise Equivalent Absorbance
NMD	No Migration Determination
NMVP	No Migration Variance Petition
OP-FTIRS	Open Path Fourier Transform Infrared Spectroscopy
PLS	Partial Least Squares
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per thousand by volume
psi	Pounds per Square Inch
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
rms	root-mean-square
S-1600	South 1600 Drift (measurement location in the downstream airflow)
S-1950	South 1950 Drift (measurement location in the upstream airflow)
SF_6	Sulfur Hexafluoride
TMF	TRUPACT-II Maintenance Facility
TO	Toxic Organic
TRU	Transuranic
UPS	Uninterruptible Power Supply
VOC	Volatile Organic Compound
WIPP	Waste Isolation Pilot Plant
ZPD	Zero Path Difference

3.0 Monitoring Criteria

3.1 Media

Since the WIPP repository is located 2,150 feet below the ground, and no substantial sources of ground water or surface water are in the vicinity, the only credible pathway for the release of hazardous constituents during disposal operations is via the repository ventilation air stream (Appendix CMP, DOE 1996a). Air is drawn from the ground level, directed through the repository, and exhausted back to the surface. This ventilation is required to keep air supplied to personnel in the repository. Upon facility closure, the ventilation system will no longer be required and will be decommissioned.

3.2 Migration Source

3.2.1 Disposal Operations

Disposal of waste will include emplacing containers of waste in a panel while directing fresh air through the panel. The containers will contain vents to prevent the buildup of gases. After the panel is full, a panel closure system will be installed, thereby isolating the waste from the remaining repository.

The monitoring systems described in this report can be used to quantify concentrations of VOCs in the air. At the generator sites, the headspace of waste containers is sampled and analyzed for 30 compounds. Based on the data currently available from the headspace gas analyses and chemical toxicity data, nine of those compounds, which are VOCs, contribute to more than 99% of the human health risk and will be evaluated as the target constituents in the monitoring program (DOE 1996a).

The nine compounds are as follows:

- 1,1 - Dichloroethylene
- Carbon Tetrachloride
- Methylene Chloride
- Chloroform
- 1,1,2,2 - Tetrachloroethane
- Chlorobenzene
- Toluene
- 1,1,1 - Trichloroethane
- 1,2 - Dichloroethane

Table 1 shows the concentration level at which each VOC must be detected just downstream of the waste panel East 300 drift [E-300] to accurately report releases at regulatory levels of concern (Appendix CMP, DOE 1996a).

Table 1. Target Analytes and Reporting Levels at E-300 and S-1600 Drifts in the WIPP Underground

Target Analyte	Chemical Formula	Molecular Weight (g/mole)	Average Annual Reporting levels (ppbv)
1,1-Dichloroethylene	$C_2H_2Cl_2$	96.95	27
Carbon Tetrachloride	CCl_4	153.80	6
Methylene Chloride	CH_2Cl_2	84.94	326
Chloroform	$CHCl_3$	119.40	5
1,1,2,2 -Tetrachloroethane	$C_2H_2Cl_4$	167.90	13
Chlorobenzene	C_6H_5Cl	112.60	2,300
Toluene	C_7H_8	92.13	57,000
1,1,1 - Trichloroethane	$C_2H_3Cl_3$	133.42	600
1,2 - Dichloroethane	$C_2H_4Cl_2$	98.96	10

3.2.2 Concentration Range

The range of concentrations of these VOCs in the headspace of the containers may vary from parts-per-billion by volume (ppbv) to parts-per-thousand by volume (pptv). The rate at which these VOCs diffuse from the waste container will vary according to headspace VOC concentration within the container. The concentration range for monitoring will depend on the rate at which these VOCs are released as well as the air flow rate of the ventilation system where monitoring will occur and the VOC concentrations in the air entering the repository.

3.2.3 Background Concentrations

The WIPP facility has been monitoring background concentrations of five VOCs since 1991. The five VOCs are as follows:

- Carbon Tetrachloride
- Methylene Chloride
- 1,1,1 - Trichloroethane
- Trichloroethylene
- 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)

These compounds were determined to be target analytes in the test-phase No-Migration Determination (NMD) for WIPP (EPA 1990). Currently, the baseline monitoring program includes eleven target compounds (the original five targets, plus the six new ones) and will continue monitoring until a disposal phase NMD or a RCRA Permit has been issued.

3.3 Environment

The environment in which the disposal-phase monitoring system will be placed is summarized below:

Temperature range:	60 - 90 °F
Atmospheric pressure:	13 psi (670 torr)
Relative Humidity:	10 - 60%
Air contaminants:	salt dust, diesel exhaust, etc.
Air flow range:	65,000 to 100,000 cubic feet per minute (ft^3/min)
Elevation:	1,100 feet above sea level (2,150 feet below the surface)
Background Concentrations:	above and below health-based levels for target compounds

3.4 Monitoring Frequency

Currently, the Confirmatory Monitoring Plan (Appendix CMP, DOE 1996b) specifies that monitoring samples be obtained twice weekly (two 24-hour periods per week). This sampling interval can be accomplished using the existing canister program which collect samples over a 24- hour period. There are numerous advantages, however, to implementing a continuous VOC monitoring program at the WIPP facility. There is uncertainty in the estimation of releases of VOCs from the emplaced waste. A continuous monitor can denote increases/decreases in observed concentrations of VOCs over time. This can facilitate data trending and provide more complete annual reports to environmental regulators. Continuous monitoring can better distinguish the types of releases from the waste as being either a spike, a slow continuous type of release, or somewhere in between. Lastly, because the Confirmatory Monitoring Plan has not yet been approved, requirements for continuous monitoring may still be invoked by the regulators.

4.0 Evaluation of Monitoring Technologies

To assess the most feasible monitoring technology for use at the WIPP facility, alternative sampling and analytical technologies are described in the following sections.

4.1 SUMMA™ Canister Pressurized Sampling with GC/MS Analysis

Currently, the WIPP VOC Monitoring program utilizes samplers and 6-liter stainless steel canisters with SUMMA™ passivated interior surfaces to collect samples. These systems undergo rigorous cleaning and certification processes to assure cleanliness. The analytical laboratory procedures are documented and apply the concepts described in Environmental Protection Agency (EPA) Compendium Method TO-14 (EPA 1986). All gas sampling units are automated ambient air VOC canister samplers which use a diaphragm pump, a stainless-steel flow controller, a vacuum/pressure gauge, a programmable electronic timer, and have two ports for connecting the sample canisters. The sampler also has an expansion port for attachment of a secondary sampling module for 4-canister sampling.

4.2 Process/On-Line Gas Chromatography

The first alternative technology evaluated to monitor VOCs at the WIPP facility was Process/On-Line Gas Chromatography. In addition to use in laboratory analysis, gas chromatography has on-line applications. Gas chromatography is an analytical method that isolates a mixture of components present in a sample. A chromatograph column separates a sample into its individual constituents. A detector is located at the end of the chromatograph column to ascertain the concentration of each compound in the sample. On-line gas chromatographs can detect compounds in the parts-per-million level. The addition of a trap concentrator would extend the lower detection limits of the process gas chromatograph and shorten analysis times for some VOCs by separating and concentrating the specific compounds in a matrix.

For on-line applications, the gas chromatograph instrument is controlled by a personal computer that logs the data for reports. In addition, automatic calibration software is generally included in the control software to minimize the maintenance of the analyzer and maintain an accurate analysis. One limitation to this technology, according to vendor documentation, is that the number of target compounds is limited to three in an off-the-shelf model. Additional target compounds require special configuration. There does not appear to be any published guidance from the EPA on this technology for ambient air monitoring applications.

4.3 Process/On-line Mass Spectrometry

Mass spectrometers operate by ionizing molecules and then resolving the positively charged ions using electric or magnetic fields. Identification of components is achieved by measuring the masses of positively charged ions striking a detector. Ions can be identified in this manner because their trajectories in electric or magnetic fields are dependent on their masses. When positively charged ions strike a detector, an electronic signal is generated that is directly proportional to the number of ions striking the detector. This enables quantification of the sample by comparison with calibration gases. Calibration is normally carried out using standard calibration gases. When a gas molecule is ionized, it breaks into smaller fragments. This fragmentation is unique for each particular component and enables identification and

quantification of multi-component mixtures. These mass spectrometer data systems provide the capability of on-line monitoring, digital storage of data, outputting to alarm relays, and automatically creating daily, weekly, and monthly statistical reports. Remote sampling can occur over several hundred meters by heated extraction lines. Some mass spectrometers may even have the capability to collect samples from multiple inlet locations. One vendor has showcased a model that can monitor up to 60 sample points.

While traditionally viewed as an expensive laboratory analytical instrument, on-line mass spectrometry is now being used in rugged environments. Specifically, the petro-chemical industry has adopted on-line mass spectrometry to quickly detect accidental releases in their process-control systems, ensure lower worker exposure to these same accidental releases, and keep a more accurate statistical database of their process information. There does not appear to be any published EPA guidance on this technology for ambient air monitoring applications. One operating limitation is the need for a temperature-controlled, very clean environment to house the unit. Another potential limitation is that the instrument has to be specifically configured for target analytes. The instrument does not have the flexibility to detect other target compounds without a hardware modification.

4.4 Fourier-Transform Infrared Technology

Fourier-Transform Infrared (FTIR) technology operates on the premise that most compounds absorb infrared energy. FTIR monitoring systems can operate in an open path or an extractive mode. In either mode, the fundamental process is:

1) Propagate an infrared light beam through the gas to be monitored,
2) Capture the beam after it traverses the monitored path,
3) Spread the light out into a spectrum of its constituent colors, and
4) Analyze the spectrum to identify the compounds present and their concentrations.

Identification of individual compounds and their concentrations using FTIR is possible because molecules in space are vibrating and rotating. The energies associated with these vibrations and rotations turn out to be equal to those of infrared radiation. As a result, a molecule can absorb some of the infrared light that impinges on it and in the process, increase its vibrational or rotational speed. Because the molecular vibrations and rotations are determined by the structure of that molecule, each molecule or compound has its own unique vibrational and rotational energies. Therefore, each molecule will absorb its own unique combination of infrared energies. Given this, when the infrared beam that has passed through a sampling volume is spread out into a very highly resolved spectrum, a series of weakened or totally absorbed patterns in the spectrum is observed. Each of these patterns is the "fingerprint" of the molecule that produced it. In addition, the actual amount of light that is missing or absorbed is directly proportional to the number of molecules of each substance that is present in the monitored volume. This, in effect, allows all compounds present to be identified via their "fingerprints" in the spectrum and their concentrations to be quantified by measuring the amount of light that has been absorbed by the "fingerprint". This is essentially the process used in all FTIR systems to detect and quantify gases in a sample.

4.4.1 Open Path FTIR

Open Path FTIR (OP-FTIR) monitoring uses an FTIR instrument that emits an infrared beam in the open atmosphere to a retro reflector array (tuned mirrors that decrease the adjustment of the device by duplicating and concentrating the reflected infrared ray). The effective path length (the sum of the incident and reflected ray) can be up to 1,000 meters. One advantage to OP-FTIR is that the unit can be mounted on skids or an apparatus with wheels for changing monitoring requirements and configurations. OP-FTIR also provides path-averaged measurement data, which is particularly useful for continuous perimeter monitoring and locating accidental releases. When monitoring in an open environment, other factors besides path length can affect the detection capability of the instrument. The EPA is currently developing a Toxic Organic (TO) Method (Russworm and Childers 1996) specifically for OP-FTIR monitoring. Section 4.6 of this report contains a brief description of some open-path testing conducted at the WIPP facility in conjunction with personnel from Idaho National Engineering Laboratory (INEL).

4.4.2 Extractive FTIR

An extractive closed path FTIR system extracts a sample from a gas or ambient air stream into a leak-tight cell. The sample contained in the cell is then analyzed using FTIR spectroscopy. The optical path of an extractive cell can be lengthened by having a tuned set of reflecting mirrors that reproduce the reflection path several times. In some cases, several hundred-meter path lengths can be achieved. A variable length closed-path cell for FTIR has been termed a "white cell." The INEL facility has developed an extractive FTIR system for waste characterization. This extractive FTIR instrument is being used in parallel with canister sampling and analysis. FTIR will take the place of canister sampling because it is faster, more efficient, and more reliable. The EPA Office of Solid Waste has recently approved the extractive FTIR system for headspace gas analysis and is writing a new (Solid Waste) SW-846 method (draft method 8450) based on the system.

4.5 Summary of Research

The technologies described in this report do not encompass the entire range of technologies and instruments available to perform ambient monitoring of VOCs. Rather, these technologies are the options available for detecting the target compounds in the ranges required to demonstrate no-migration at the WIPP facility. Table 2 summarizes the comparison of different technologies on a wide range of concerns.

Of the most recent monitoring technologies, the FTIR technology was chosen as the most promising because of the extent of EPA research, which is currently being conducted. In addition, FTIR is being implemented at other DOE facilities, most notably at the INEL. The INEL has recently proposed and gained EPA acceptance of extractive FTIR as a cost effective alternative to canister sampling for conducting drum headspace gas analyses for waste characterization. INEL deploys an OP-FTIR system for ambient air monitoring applications. A new EPA method for measuring VOCs in ambient air using on OP-FTIR is currently in development.

Table 2. Comparison of Monitoring Technologies

CONCERN	CANISTER SAMPLING WITH GAS CHROMATOGRAPHY ANALYSIS	ON-LINE GAS CHROMATOGRAPHY	ON-LINE MASS SPECTROMETRY	OPEN-PATH FOURIER TRANSFORM INFRARED	EXTRACTIVE FOURIER TRANSFORM INFRARED
1) Will it detect target compounds simultaneously?	Yes	Yes	Yes	Yes	Yes
2) Lowest detection level	0.2 ppbv	10-100 ppbv	10-100 ppbv	2 ppbv	1 ppbv
3) Special shelter required to operate in the mine?	Yes	Yes	Yes	No, except for computer	Yes
4) Will it run continuously?	Yes - samples, No - Analysis	Yes	Yes	Yes	Yes
5) Is the operation based on an EPA recommended method?	Yes (modified TO-14)	No	No	TO-16 (draft)	No (Method 301 Validation)
6) Engineering support to implement? (High, Med, Low)	Medium	Medium	Medium	Low	Medium
7) Operations support? (High, Medium, Low)	Medium	Medium	Medium	Low	Low
8) Construction support? (High, Medium, Low)	Medium	Medium	Low	Low	Low
9) Does it require full time Analytical Chemist in the field?	No	No	No	No	No
10) Estimated capital cost?	$150K including flow controller modification	$75K - $80K	$80K - $300K	$80-150K	$100-200K
11) Estimated operating cost per year? (Vendor estimates)	Note: Cost for off-site lab Weekly sample: >$180K 2 samples / week:>$215K Daily sample: >$395K	NA	<$15K	<$50K	<$50K
12) Is it portable and easy to transport in a mine?	Yes	No	No	Yes	No
13) What is the fastest reporting time?	(After sampling for 24 hours) 2 hrs for onsite analysis; 2 days for offsite analysis	30 minutes	1 minute	5 minutes	5-10 minutes
14) Power requirements	115 VAC for pumps	115 VAC	115 VAC or 240 VAC	115 VAC	115 VAC
15) Level of operator training? (High, Medium, Low)	Medium	High	High	Medium	High
16) Reliable? (Run continuously without intervention?)	NA	No	No	Yes	Yes

Table 2. Comparison of Monitoring Technologies (continued)

CONCERN	CANISTER SAMPLING WITH GAS CHROMATOGRAPHY ANALYSIS	ON-LINE GAS CHROMATOGRAPHY	ON-LINE MASS SPECTROMETRY	OPEN-PATH FOURIER TRANSFORM INFRARED	EXTRACTIVE FOURIER TRANSFORM INFRARED
17) Years instrument may operate without replacement?	5-10 years	NA	5-10 years	5 years	Not enough info (Supplying vendor systems have been in operation 3 years)
18) Acceptance level from EPA for measuring toxics in air?	High (EPA 1986)	NA	Low	Medium (AWMA 1996)	Medium
19) Remote Monitoring Capability?	No	No	Yes	No	Yes
20) Will it meet Data Quality Objectives?	Yes	NA	Yes	Yes	Yes
21) Any part of system cleaned/certified free of VOCs.	Yes	Yes	Yes	No	Yes

4.6 Open Path FTIR Testing at WIPP

Because the INEL was deploying an OP-FTIR configuration for ambient air monitoring applications, the INEL personnel were contacted and a request to provide a demonstration of this system at the WIPP facility was made.

In 1995, INEL's OP-FTIR unit was deployed at the South 1600 (S-1600) and E-300 drift in the WIPP mine for approximately one week (INEL 1995). Limiting factors noted by WIPP facility personnel during this test were the following:

- Obtaining a good background spectrum (I_o) is relatively difficult because of the uncontrollable environmental parameters that are factors in FTIR quantitation such as pressure, existence of background compounds, humidity, and temperature.
- Over time, the retro reflector mirror array may tend to accumulate salt particulate that could inhibit the detection capability of the instrument. After a week of testing, salt particulate was visibly apparent on the retro reflector array. This, however, did not appear to decrease the amount of infrared signal being transmitted and reflected.
- The specific data processing algorithms that were used required a significant amount of manipulation. Since that time, INEL has indicated that their data processing method has improved dramatically.

The OP-FTIR system passed the following tests during FY1995:

- Rapid detection of the harmless tracer gas, Sulfur Hexafluoride (SF_6), within five minutes of the expected dispersion from a controlled source.
- Acceptable detection accuracy of the five standard audit gases representing the original target compounds.
- Unattended monitoring over a weekend.

The results of the INEL OP-FTIR demonstration at the WIPP warranted further research of this technology. It was still not clear whether an open path or an extractive configuration would be the system to satisfy the detection criteria as well as be best suited to operate in the WIPP underground environment. The support of an FTIR vendor that had extensive experience in both open path and extractive FTIR technologies was solicited.

5.0 Expert Recommendation of System Configuration

5.1 Recommended WIPP Prototype FTIR System

After the FTIR vendor was solicited and chosen, the vendor provided descriptions of their open path and extractive FTIR systems in response to the WIPP operational and functional criteria.

The main difference between open path and extractive FTIR systems lies in their configuration and operation. In open path monitoring, shown schematically in Figure 1, the infrared light is transmitted from one telescope, propagated through the open air, and received by a second telescope. Once the infrared beam is received, it is relayed to an appropriate infrared detector, digitized, and then analyzed. The transmitted light is modulated by the FTIR in such a way that the signal produced by the detector can be mathematically manipulated producing the infrared spectrum. The spectrum can then be directly analyzed. In extractive monitoring, shown in Figure 2, the gas sample is "extracted" from the source and placed into a cell within the instrument. The infrared light is then passed through the cell and focused onto the infrared detector. This is similar to open path monitoring except that the sample is now in an enclosed chamber, rather than in the open air.

To improve sensitivity, an infrared beam can be made to traverse the monitoring path more than once. The sensitivity of an infrared detection system is proportional to the total path length traversed by the beam in the gases to be detected (within the sample cell or in the defined volume of the open path). If the infrared beam traverses ten meters in the gas, the detection is ten times more sensitive than if it traverses only one meter. Consequently, with the OP-FTIR, a retro mirror is used to reflect the beam from the transmitter back to the receiver, therefore doubling the path length and doubling the system sensitivity. The extractive FTIR system uses internal mirrors that allow the beam to traverse the cell numerous times before entering the detector. This provides for path lengths comparable to open path FTIR systems. The extractive FTIR utilizes a small space and can provide as good or even better detection limits than open path systems.

5.2 Advantages and Disadvantages of Open Path and Extractive FTIR Systems

Open path and extractive systems each have unique strengths and weaknesses that make them appropriate for specific measurement scenarios. Table 3 outlines some of the issues and contrasts of the two systems with regard to these issues.

One of the major differences between the two approaches is spatial coverage. The open path system can monitor path lengths ranging hundreds of meters to kilometers, while the extractive system is strictly a point sampler. If spatial coverage is necessary, such as for fence-line monitoring at an industrial complex, then the open path system is preferred. For applications similar to that of the WIPP site, a single sample from one or more locations is sufficient, and the extractive system is appropriate.

The two systems have comparable measurement speed, which is usually limited by the averaging time required to produce a sufficient signal-to-noise ratio for low-level detection. If signal-to-noise is not an issue, as could be the case in detecting very high-level emissions from accidents, then the open path system is capable of performing measurements faster than the extractive

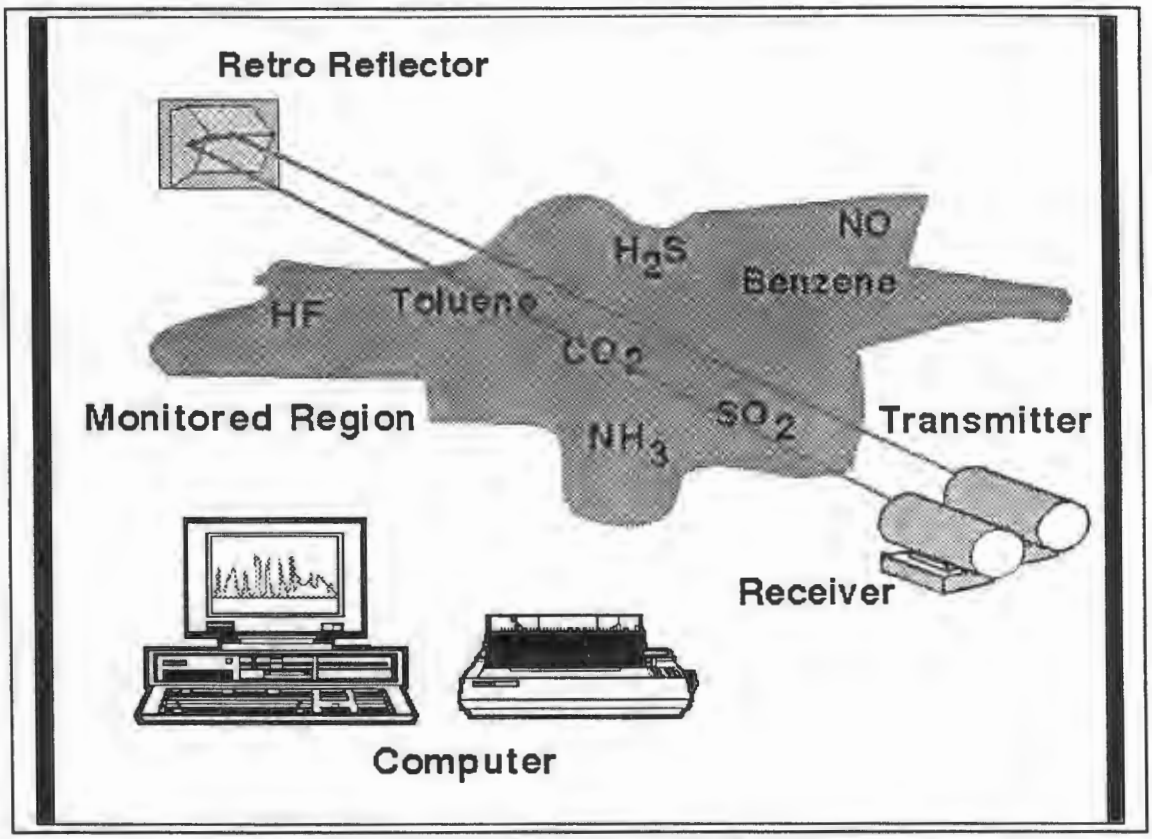

Figure 1. Vendor Open Path FTIR Monitoring System

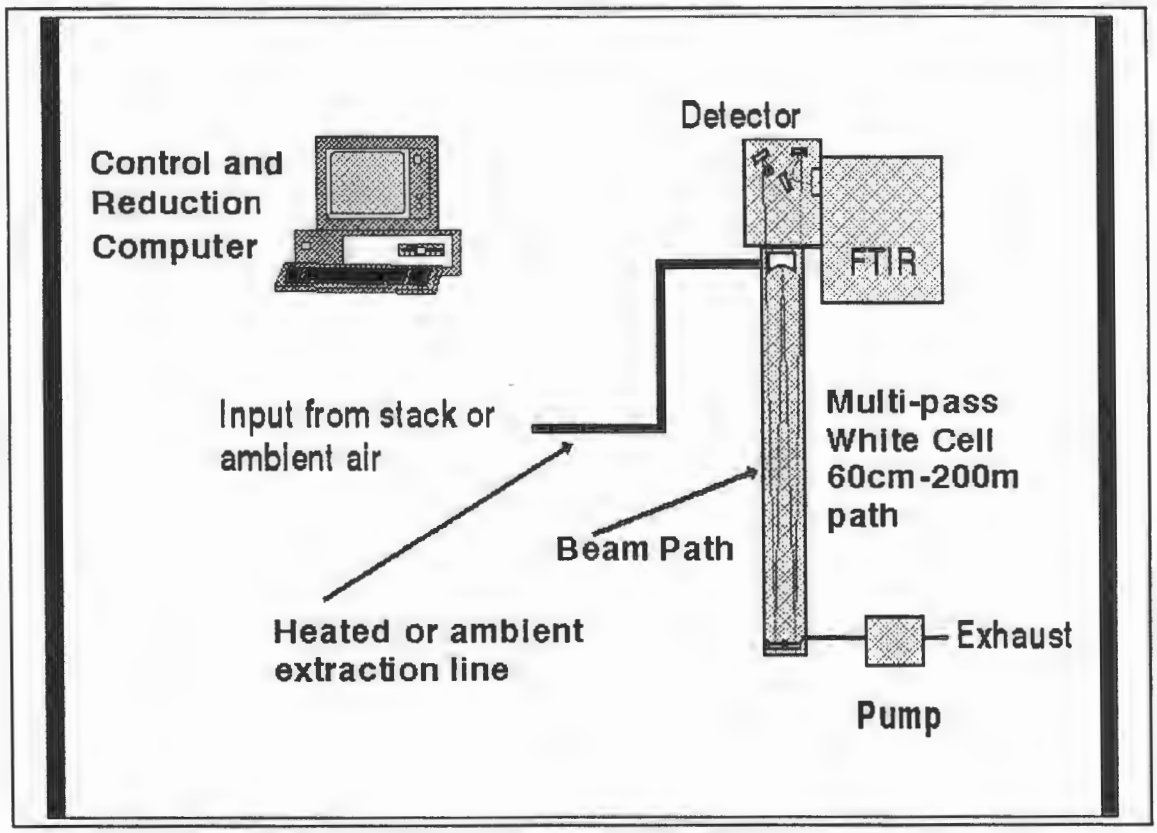

Figure 2. Vendor Extractive FTIR Monitoring System

system. The limiting factor with the extractive system is the time it takes to get a sample into the cell and to flush the cell completely with the new gas sample. If gas is flowing through the cell, a flow of three cell volumes is necessary to assure a "fresh" cell sample. If the cell is large (i.e., 50 liters) and the pump rate modest (10 liters/minute), this can take five minutes or more. To speed this process, extractive system cells can be flushed/filled more quickly by pumping out the cell and then backfilling by opening the cell to the ambient air. If required, the fill times can be reduced to less than one minute, even in large cells.

A significant issue with these systems is the defendability of the data, which is related to the system's ability to be calibrated or calibration checked. Open path systems are limited in this area because they are monitoring a volume of atmosphere (path) over which one has no control. One of the fundamental pieces of data required to generate reliable infrared spectra is a background (I_o) spectrum. This is the spectrum of the system response which must be representative of the system in the absence of any molecular absorption. This is very hard to produce in the open air where there is no way of removing all the infrared-absorbing gases. Techniques have been developed to handle this situation (i.e., generation of a so-called synthetic I_o spectra), but I_o cannot be measured directly. In the extractive system this is not a problem. The cells can be pumped out to remove all the air and the I_o spectrum can be measured.

A related issue is how to determine precision and accuracy of the instrument. Again, in the open path, these measurements are complicated because the path cannot be filled with a calibration gas. To calibrate the open path system, a small cell in the instrument is filled with very high concentrations of calibration gases. The short path of this cell makes the concentrations appear much lower to the instrument when viewed against the total open air path (the concentration will actually look to the instrument like a concentration decreased by the ratio of the cell length to the total open air path length). The differences in the spectra with the short cell in and out of the beam path can then be used to deduce precision and accuracy. While the short cell approach is adequate, it is better to have total control over the measurement conditions, as one has in the extractive system. In the extractive system, the cell is evacuated and then backfilled with calibration standards. The accuracy and precision are then measured in the same manner as the data is taken. Data from the extractive systems are more defendable.

Table 3. Issues, Strengths, and Weaknesses Of Open Path and Extractive FTIR Systems

Issue	Open Path Systems	Extractive Systems
Spatial Coverage	Can cover hundreds of meters to kilometers in the open air.	Monitors at a point; sample is extracted with a probe at a fixed location or locations.
Speed of Measurements	Can perform measurements at a few seconds per sample, although to achieve low detection limits, several minute averaging is usually required.	Can perform measurements rapidly as with open path systems, but the exchange rate for the air sample in the cell can be the limiting factor. This is typically one minute.
Ease of Calibration	Calibration of the system is problematic because one has no control over the monitoring path. Generation of background (I_o) spectra is very difficult because the atmosphere cannot be removed from the path. Challenging the system with calibration gases can also be difficult, although short path in-situ cells can be used.	Calibration and generation of background (I_o) spectra is straightforward. The cell can be evacuated for I_o, and it can be filled with calibration gases to test precision and accuracy.
Detection Limits	Detection limits can be good to excellent if sufficient path exists in the gas to be monitored. However, detection limit is dependent on atmospheric conditions over which one has no control, so they vary with time.	Detection limits are typically as good and usually better in extractive systems than in open path systems. This is in part because of the better energy capture of the system, but also because the sample can be conditioned as needed to optimize detection. This also allows the system performance to be more independent of ambient conditions.
System Maintenance	Minimal maintenance required unless severe storms contaminate the telescope and mirror optics in which case regular cleaning is required.	Minimal maintenance. System can be totally enclosed to protect it from ambient conditions, and the air sample can be filtered as required to remove particulate.

The detection limits of the two instruments are comparable. The longer path of the open path systems and the higher energy throughput of the extractive systems tend to equalize their respective detection limits. However, the most important difference between these two approaches is the capability of the extractive systems to condition the sample. Water vapor and carbon dioxide are major interferents to infrared detection. If these vary, as water vapor typically does, the additional complication of variable interference and possibly some bias are introduced. In open path systems, additional limiting factors can be fog, smoke, or other atmospheric obscurants. These will limit the energy throughput of the system and, consequently, limit system performance. In the closed path system, these effects can be controlled by conditioning the sample. For example, the gas can be dried or carbon dioxide (CO_2)-scrubbed and filtered to remove particulate. For the WIPP site, this is critical because of the possible heavy salt loading in the air. By filtering, drying, or scrubbing the sample, the detection limits can be substantially improved compared to what is possible in open path systems.

A final issue differentiating open path and extractive systems is maintenance. In most cases, both systems are fairly maintenance free. However, when operating in a dirty or highly aerosol-laden environment, any system component that is exposed to the environment will need regular maintenance. In the open path systems, some components must be open to the air such as the transmitter, receiver telescopes, and the retro reflector. If these components are coated with aerosol or dirt, system performance will degrade. Regular cleaning is necessary in these cases. If the contaminant is also corrosive, eventual damage to the optics will require replacement. With the extractive systems, all system components are enclosed and protected from the ambient conditions. In addition, the sample being introduced into the cells can be pre-filtered to remove aerosols which could potentially coat the cell walls and mirrors. In a highly contaminated environment, the extractive system will have a longer lifetime and will require less maintenance.

5.3 FTIR System Selected for Prototype Testing at the WIPP Site

An extractive FTIR monitoring system was selected for use at the WIPP site. This decision was driven by three main issues:

1) The environment in the underground can be heavily laden with salt particulate, and the monitoring system must be capable of operating for extended periods in this environment without need of regular maintenance.

2) The monitoring will be primarily differential, looking at the difference between incoming and exiting air as it passes through the drift past Panel 1.

3) Low level concentrations must be monitored, so the system chosen should have the lowest possible detection limits.

The most significant issue is that an open path system, by its nature, must be exposed to the environment. It was believed that such a system at the WIPP facility would require heavy maintenance to keep it functioning, particularly if mining operations create heavy salt loadings. By contrast, an extractive system could be protected from this environment.

The second issue was also considered to be very significant because the observation of small changes in the intake and exhaust air streams, which will be necessary to detect emissions from Panel 1, would require two open path systems operating simultaneously or a scanning open path system capable of alternately monitoring the input and output paths. The most economic approach would be to use a scanning system, but scanning systems do not typically exhibit the degree of stability that would be required to observe small concentration differences in the two paths. The alternative would then be to operate two open path systems, but this was not financially feasible. The extractive system, because it can contain two monitoring cells, is capable measuring the input and output air streams simultaneously. In addition, the spatial coverage of the open path system is not required and, in fact, could be a limitation when trying to detect incremental emissions from an open or closed panel.

Because the extractive system also has comparable detection limits to the open path system for all compounds of concern, it was believed that an extractive system was the optimum choice for the WIPP prototype test system.

5.4 Details of the Hardware System

The extractive monitoring system proposed for use in the underground at the WIPP facility was a dual-cell ambient air monitor. This is shown schematically in Figure 3. The main components are the FTIR interferometer, optical transfer and detector system, multi-pass absorption cells, gas extraction system, and the control/reduction computer. The beam path starts in the FTIR where infrared light from a high temperature (1200 K) ceramic light source is modulated by the interferometer. This light is then directed to one of the two multi-pass cells by the optics in the transfer box. These optics are computer controlled so the beam can be alternately directed to one cell or the other during unmanned operation. The multi-pass cells are glass chambers approximately two meters in length. They contain internal mirrors which cause the infrared light to travel back and forth a predetermined number of times before entering the detector. Typically, these cells are set for paths of 100 to 125 meters which allows detection of low parts per billion by volume (ppbv)-level gas concentrations. Once the light leaves these cells it is directed to one of two infrared detectors. The detectors used are Mercury Cadmium Telluride (MCT) and are operated at 77 K. The detectors are cooled by liquid nitrogen.

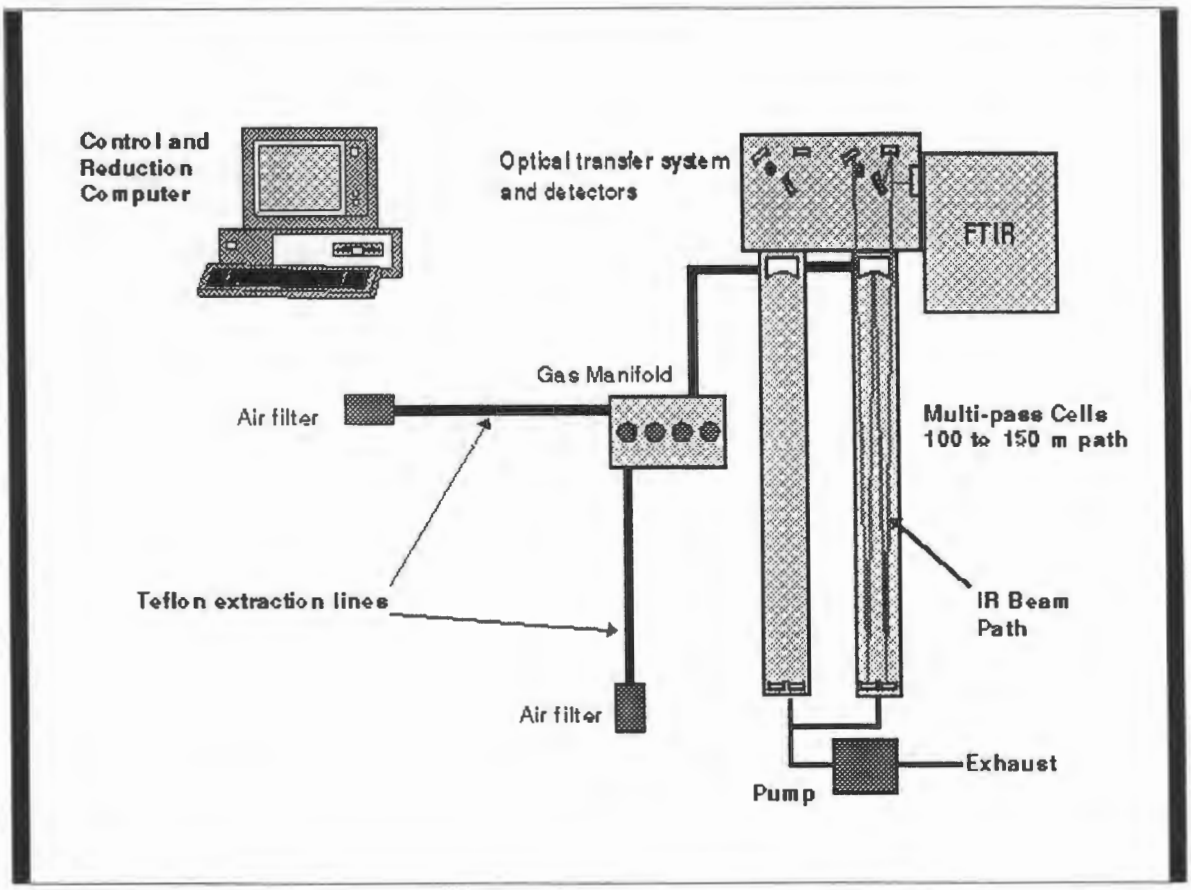

Figure 3. WIPP Dual-Cell Extractive FTIR Prototype System

Gas is admitted into the cells through a gas handling system. This system consists of a computer controlled gas manifold which controls the valves and pump. The computer can then pump the cells or fill them with sample as called for by the measurement sequence, which is programmed by the operator. The manifold receives the gas sample via one of two 100-ft Teflon® lines which connects to the manifold and route the sample from the inlet points into the cells. The extraction lines have particulate filters at the ends which extract salt and any other aerosols present in the air before allowing the sample to enter the FTIR system. The output of the cells is connected to a single vacuum pump which can evacuate the cells to less than 1.0 torr pressure (0.001 atmospheres).

6.0 Operational Aspects and Support

6.1 Basic Function of Major Components

The four major components of the prototype extractive FTIR system at the WIPP facility are as follows:

- Control and reduction computer
- FTIR spectrometer
- Optical transfer bench
- Multi-pass cells

These major components are housed in a 12-foot by 8-foot mobile trailer. In addition, there is also a zero-air generator to maintain the inside of the spectrometer free from carbon dioxide and water. A 180-liter dewar of liquid nitrogen is connected from the outside of the trailer to the detectors in the FTIR system. The detectors are automatically filled to maintain a predetermined temperature, usually every 12 hours.

6.1.1 Control and Reduction Computer

The control and data reduction computer is the center of the FTIR system. The computer initiates the control sequence for sampling which includes the following:

- Diagnostic checks of the system
- Automates dewar refill for cooling of the detectors
- Fills and evacuates the sampling cells
- Controls scan time of each sampling cell

In addition, a digital signal processing board within the computer receives the analog signal from the FTIR spectrometer and performs analog/digital conversions, Fourier transforms on the digitized signal, and a quantitation for multiple VOCs and stores the raw and processed data to a disk. The computer reboots the system to automatically restart after a power outage. Data can also be transferred, as well as viewed remotely via modem connection.

6.1.2 FTIR Spectrometer

The FTIR spectrometer originally generates the infrared beam. A potassium bromide (KBr) beamsplitter splits the infrared beam. A scanning mechanism creates the interference patterns used for analysis by the control and reduction computer.

6.1.3 Optical Transfer Bench

The optical transfer bench has circuitry to control which sample cell is being analyzed. This unit contains the cooled detectors used for generating the analog signal to the control and reduction computer.

6.1.4 Multi-Pass Cells

The multi-pass cells are constructed of glass and contain the air samples drawn from the sampling locations. One cell draws upstream samples from the South 1950 drift (S-1950). The other cell draws downstream samples from S-1600 drift. By subtracting the upstream measurement from the downstream measurement, the VOC emissions from Panel 1 can be

of the prototype extractive FTIR system is shown in Figure 4.

Figure 4. **Photo of WIPP Prototype Extractive FTIR System (infrared spectrometer in the foreground, optical transfer bench in the middle, and multi-pass cells in the background)**

6.2 Location and Configuration

For the purposes of this prototype demonstration, one sample inlet line (connected to Cell #1) is placed in the upstream air at S-1950 at the South end of Room 1, Panel 1. The air stream continues down the S-1950 drift, and once it passes through Room 7 (the last room in Panel 1), it returns through the S-1600 drift at the North end of Room 1. The second sample inlet line (connected to Cell #2) is placed in this location to receive air samples from this downstream air. This configuration allows subtraction of the VOCs detected in the upstream sample from those detected from the downstream sample to quantify for VOCs emitted from the emplaced waste. This extractive FTIR system measures upstream and downstream samples consecutively in 10-minute sampling intervals. The location and configuration of the prototype system is illustrated in Figure 5.

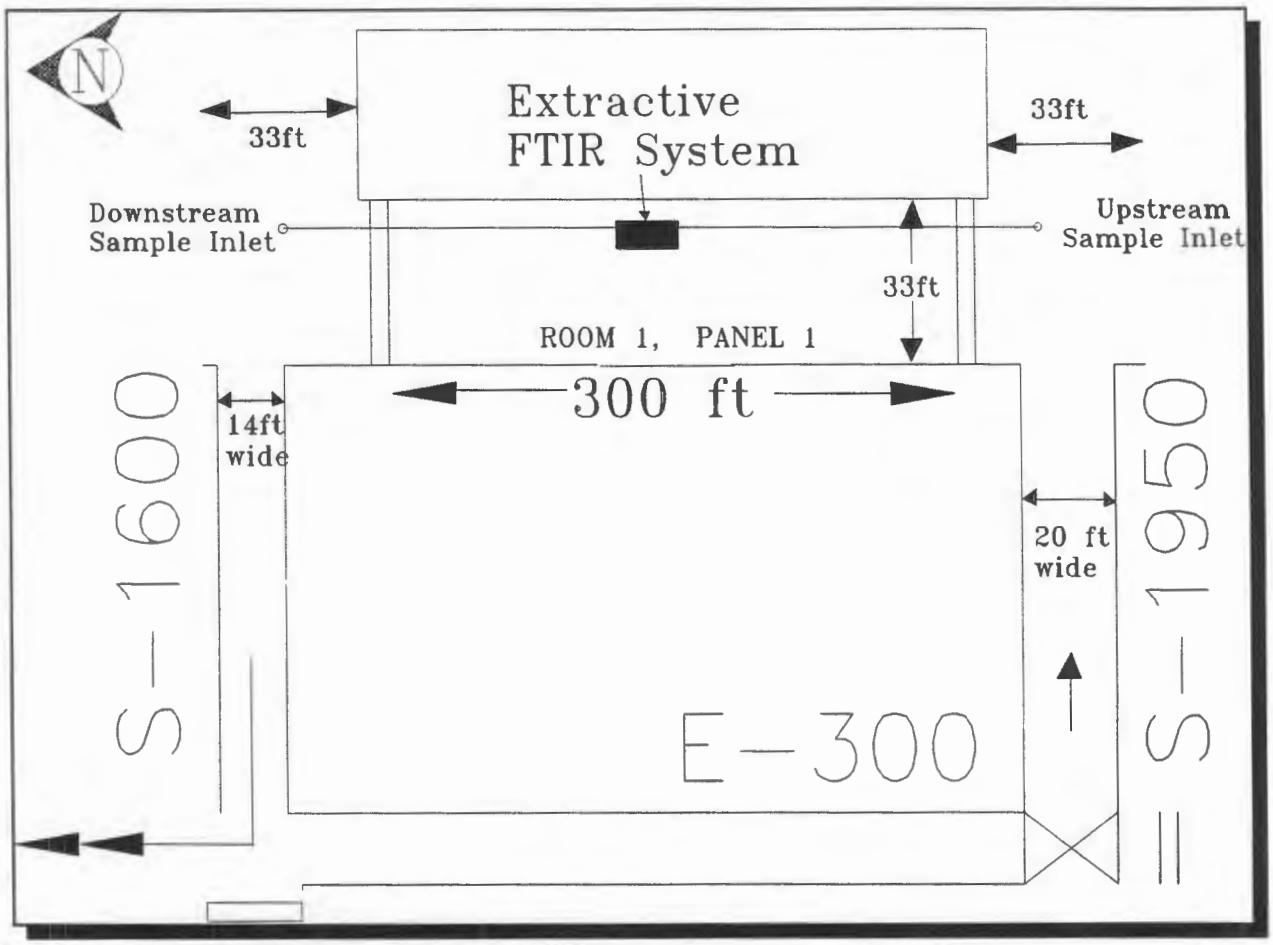

Figure 5. Present Location of WIPP Extractive FTIR Prototype System

6.3 Basic Operation

There is a set of operator actions that must be performed prior to automated operation of the instrument. They are the following:

- Liquid nitrogen dewar should be adequately filled and connected to the FTIR system
- Nitrogen auto-fill control system boxes must be turned on
- System control switches must be set for computer control
- The vacuum pump must be turned on
- The computer and modem must be turned on

Once the operator actions are completed and the computer is turned on, the system performs the following sequence of events, as illustrated in Figure 6:

1) Runs diagnostic system checks and then continuously checks its status via deadman timer circuitry.
2) Introduces an air sample into Cell #1 from the upstream air.
3) Analyzes the sample in Cell #1. While this analysis is taking place, an air sample is introduced into Cell #2 from the downstream air.
4) Analyzes the sample in Cell #2. While this analysis is taking place, a new air sample is introduced into Cell #1.
5) Stores the raw and processed data on the hard drive.
6) If there is no operator request to stop this automated process, go back to step 3.

6.4 Daily Checks of FTIR System

During the two-month period the prototype extractive FTIR system has been in place at the WIPP facility, a general understanding of the day-to-day instrument support requirements was determined. A daily check via modem is conducted to confirm the following:

- Detector voltage is operating between -5 to -3 volts and +3 to +5 volts (regulated DC voltage)
- Automated nitrogen dewar system is filling in an adequate time frame
- Fill pressure of the sampling cells is over 700 torr
- Concentrations of background compounds are within the defined ranges (i.e., Nitrous Oxide (N_2O) at 315 ppbv)

The FTIR vendor conducts a daily operability check of the instrument via modem. The vendor notifies WIPP facility personnel of any irregularities. The FTIR vendor has the capability of refining the quantitation method, adjusting the water vapor concentration reference, and changing the sampling and analysis times on each of the cells. To prevent unauthorized access to the FTIR computer, a password option may be invoked.

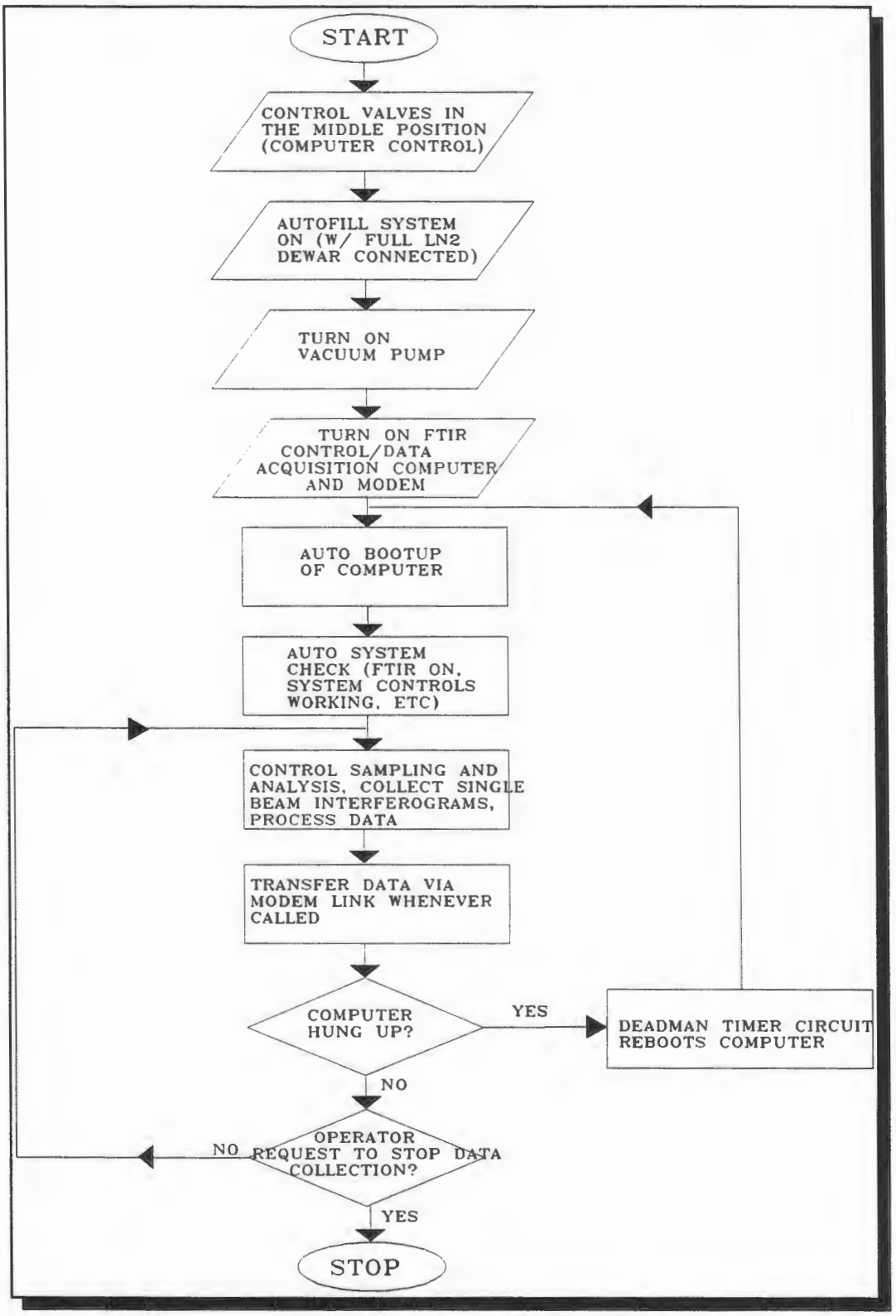

Figure 6. Basic Operation of Extractive FTIR Prototype System at the WIPP Facility

6.5 Examples of Operational Support Procedures

Included as Attachment 1 are operating procedure checklists for 1) change out of the nitrogen dewar, 2) movement of the FTIR trailer during roofbolt detensioning in Room 1, Panel 1, and 3) evaluation of the instrument signal-to-noise ratio or Noise Equivalent Absorbance (NEA).

6.6 Time Line of Events

Table 4 is a time line of the general FTIR prototype test activities conducted at the WIPP facility.

Table 4. Time Line of FTIR Prototype Test Activities

Week of:	Activities:
May 27, 1996	1) Verified underground configuration set up for supporting FTIR trailer (i.e., power, phone-lines, compressed air). 2) Verified TRUPACT-II Maintenance Facility (TMF) provided adequate space for FTIR trailer, as well as adequate power & compressed air. 3) Received one full liquid nitrogen dewar. 4) FTIR trailer delivered to WIPP site on Thursday.
June 03, 1996	1) FTIR vendors and supporting contractor arrived Monday for WIPP Underground Training. 2) Prototype testing conducted in TMF Tuesday through Thursday: a) path length calibration b) audit gas standards c) system checks 3) U/G operations transported FTIR trailer to middle of east side of Room 1, Panel 1. Vendors and WIPP facility personnel set up FTIR system.
June 10, 1996	1) Conducted u/g prototype testing in Room 1, Panel 1: a) tracer gas tests b) electromagnetic interference (EMI) test c) vibration testing d) auto-restart of system after power outage e) remote access of instrument 2) Sampled with canisters for comparison testing. 3) Borrowed partially full nitrogen dewar from WIPP analytical lab. 4) On-hands training with instrument: a) change out of liquid nitrogen dewar b) manually evacuating and filling sampling cells c) configuration of FTIR parameters 5) Liquid nitrogen dewar delivery and change out.
June 17, 1996	1) Concluded tests with optimized sampler location tests 2) Restationed FTIR inlet sampling lines at S-1600 and S-1950 drifts. 3) VOC monitoring personnel conducted canister sampling at Stations VOC-1, 2, 8, and 9.
June 24, 1996	1) Continued to maintain normal operation of FTIR system. 2) Moved FTIR trailer while Geotechnical Engineering detensioned roof bolts in Room 1; system down 1 ½ days. 3) FTIR vendor optimized FTIR analysis method for the proper water vapor reference (can change remotely on FTIR). 4) Worked on liquid nitrogen dewar delivery schedule with the supplier.

Table 4. Time Line of FTIR Prototype Test Activities (continued)

Week of:	Activities:
July 01, 1996	1) Changed liquid nitrogen dewar on Monday. 2) Collected raw and processed data on 270 MB cartridge disk. Removed raw data from FTIR computer to free space on hard drive.
July 08, 1996	1) Check of liquid nitrogen dewar on Monday; over 65% full. 2) Collected raw and processed data on 270 MB cartridge disk. Removed raw data from FTIR computer to free space on hard drive. 3) Conducted remote checks of system daily throughout the week via modem.
July 15, 1996	1) Change out of liquid nitrogen dewar on Monday. Dewars appear to last more than two weeks. 2) Collected raw and processed data on 270 MB cartridge disk. Removed raw data from FTIR computer to free space on hard drive. 3) Conducted remote checks of system daily throughout the week via modem.
July 22, 1996	1) Conducted remote checks of system daily throughout the week via modem. 2) Downloaded processed data via modem at the end of the week.
July 29, 1996	1) Continued to maintain normal operation of FTIR system. 2) Streamlined process of restationing FTIR during scheduled roof bolt detensioning in Room 1. **Note:** System down only 3 ½ hours versus 1 ½ days the week of June 24, 1996 3) Traveled to FTIR vendor location to conduct "humid" gas standard tests, learn the reporting software, and work out schedules/deliverables. 4) During trip to FTIR vendor location, changed sampling and analysis times remotely on the FTIR system. System sampling three samples/hour upstream (S-1950) and downstream (S-1600).
August 5, 1996	1) Noted there was a WIPP weekend power outage. FTIR data indicates UPS supplied power until 8:30am Sunday when the batteries were depleted. At 8:00am, Monday morning, FTIR system restarted successfully when power was reintroduced to the panel. 2) Collected raw and processed data on 270 MB cartridge disk. 3) Removed raw data from FTIR computer to free space on hard drive. 4) Disconnected FTIR from uninterruptible power supply.

7.0 Facility Support

The extractive FTIR prototype system has required the following minimal underground facility support:

- 115 Volt AC power, 40 amperes
- Surge protection
- An air compressor or access to facility plant air
- Forklift support for change out of nitrogen dewars
- A tractor to move FTIR system trailer when needed

It was determined that prototype testing could best be conducted in Room 1, Panel 1. Other locations considered for deployment of the extractive FTIR system were the E-300 drift and the intersection of S-1600 and East 140 drift (E-140). Because Underground Mining Operations personnel were conducting maintenance of the back to these drifts, access was restricted until the end of September 1996. Room 1, Panel 1 has existing power and access to underground plant air. Room 1 also has lighting that would be helpful when conducting some of the prototype tests.

Underground Facility Operations support was timely and effective. During the first three months of on-line operation, the extractive FTIR system has required minimal operational maintenance and facility support. This facility support has been provided with minimal impact to normal underground operations. The main support requirement for continued operation of the extractive FTIR system is the change out of the 180-liter liquid nitrogen dewars. Originally, it was projected that weekly dewar change out support would be required. Operating knowledge revealed that in the WIPP mine environment, the 180-liter liquid nitrogen dewars last 18-21 days. Liquid nitrogen from the local supplier can, therefore, be curtailed by 50-66%.

8.0 Prototype FTIR Test Plan and Results

The FTIR vendor provided a test plan that addressed the requirements outlined in the statement of work for the lease of an FTIR system for prototype testing.

8.1 Test Descriptions

In order to demonstrate the performance of the FTIR monitoring system, several different types of tests were required. First, tests of the instrument itself were required to demonstrate that the FTIR system and the analysis methods were performing adequately. Second, tests of the gas handling system were necessary to determine if the lines or cell would have any unwanted effect upon the sample extracted. Third, the overall system was tested to demonstrate long term performance and immunity to the harsh conditions in the underground. The first two sets of these tests were performed above ground to demonstrate basic system performance. The long term operational tests were then conducted underground. The various tests required are outlined in section 8.2 through 8.4. Detailed descriptions of the procedures that were followed in making each of the measurements are presented in Section 8.5.

8.2 Above Ground Tests

After the instrument was delivered to the WIPP site several tests were performed to demonstrate that the instrument and gas handling systems were performing properly before the unit was transported to the underground. These tests that were performed were the following:

- Background (I_o) generation
- Detector linearity
- Line shifts
- Spectral resolution
- Path calibration
- Minimum Detectable Concentrations (MDCs) for target compounds
- Signal-to-noise tests
- Line loss tests

8.3 Underground Tests

Once the instrument was in place underground, additional tests were conducted to determine optimum operational conditions, to demonstrate long term system performance, and to demonstrate system immunity to the harsh conditions of the underground. The additional tests included the following:

- Tracer gas tests
- Duration and salt loading tests
- Power outage tests
- Data completeness evaluations
- Electromagnetic interference

8.4 Tests Performed at FTIR Vendor Facility

The following additional tests were performed at the FTIR vendor facility to address the issue of adsorption of VOC samples in the sampling cells over time:

- VOC accuracy tests
- Cell losses
- Method validation tests

8.5 Detailed Description and Results of Tests

This section presents the detailed procedures followed in conducting the prototype tests at the WIPP site and the results of these tests. The above ground tests were conducted the week of June 3, 1996, with the FTIR housed in a building above ground at the WIPP facility. At the conclusion of these tests the FTIR system was moved to Room 1, Panel 1 in the underground. The underground tests were then conducted the following week in Room 1. Concurrent with the operation of the FTIR system in the underground, additional tests were conducted at the FTIR vendor facility July 1-2, 1996, using a similar system.

8.5.1 Background (I_o) Generation

A background (I_o) spectrum is simply a single beam spectrum collected under conditions in which no (or minimal) molecular absorption is present. This single beam spectrum is essentially the instrument response function showing the spectral variability of the signal due exclusively to the optics, detector, and electronics. In a closed path system, collection of the background spectrum is straightforward because the cells can be evacuated and the optical transfer bench purged. A new I_o must be generated every time the instrument is moved to a new sampling location. This establishes the basic system response function that is required to produce absorbance spectra from the raw interferogram or single beam data. Consequently, this test was performed both at the surface and once the instrument was placed underground. The system has the capability of producing automated I_o functions at regular intervals (e.g., every midnight).

To collect the background or I_o spectrum, the optical transfer bench itself must be free of all molecular contaminants. To assure this, the bench was purged with zero air from the air filter at high flow rate until no further reduction in the water (H_2O) or CO_2 absorption was observed. The purge was then continued for one hour at the normal rate prior to initiating data collection. Both cells were then evacuated to less than 1 torr, and this evacuation was maintained during data collection. Once the cells were evacuated and the bench adequately purged, single beam spectra were collected at the 0.5 cm^{-1} resolution in each cell. This was done using an averaging time of five minutes to achieve an optimum signal-to-noise ratio. The single beam spectra were then used directly as the background or I_o spectra for each cell. The files produced in this process were:

Table 5. Background Files Stored

Cell	File Name
#1	bkgc164a.spa
#2	bkgc264a.spa

8.5.2 Detector Linearity

Detector linearity checks are necessary after relocating the device because alignment changes can cause changes in the total throughput of the instrument, which in turn can influence linearity. These checks can be performed quickly, and the adjustment of linearity (if necessary) is relatively straightforward. Linearity was, therefore, checked both at the surface and after positioning the instrument underground. It was not anticipated that a linearity adjustment would be required at either place.

The detectors used in the FTIR system are MCT quantum detectors. These detectors can be non-linear with input intensity. The electronics built into the detector preamplifier linearize the detector response, but this circuit must be set initially to assure that the system is linear for the conditions in which the system is set up. A characteristic result of non-linearity in the detector is the production of erroneous frequencies in the interferogram. After transformation, these erroneous frequencies give rise to innacurate spectral features. The easiest way to note these features is to observe the opaque regions of strongly absorbing bands or the regions beyond the cutoff of the detector, in which the system signal should be zero.

To check for nonlinearity and set the linearity circuits of the preamplifier the FTIR was put into continuous-scan mode, and the single beam spectrum was observed in the "Collect" and "Optical bench setup" menu item of the FTIR control and setup software. When this menu item is selected the software displays the real-time single beam spectrum at low resolution during scanning. The wavenumber extents for this display was in the 0 cm^{-1} to 400 cm^{-1} region. This range was beyond the response of the MCT detector where the signal should be exactly zero. The linearity setting on the preamplifier was then adjusted to bring the signal in this region to as low a value overall as possible. Once this was done, the baseline through this zero region, and zero signal regions in the CO_2 bands near 2350 cm^{-1} and the H_20 bands at 3700 cm^{-1} or 1600 cm^{-1}, were inspected. These regions all defined a straight line at zero volts, thereby indicating that the system was linearized.

8.5.3 Line Shifts

Line shifts can occur due to FTIR or cell alignment changes. Alignment changes cause the instrument to transmit slightly different portions of the total available energy, and this can in turn cause slight line shifts. Line shift is an issue primarily because it can cause a mis-match between the reference spectra and the sample data. Absolute wavelength accuracy is not critical, but invariance of shifts and agreement between the line positions of the sample spectra and the reference spectra is critical.

To demonstrate line position accuracy, HDO (deuterated water) lines in the 3205 cm^{-1} to 3225 cm^{-1} region were used. At approximately 4:00 pm on June 4, 1996, a cell was filled with ambient air and a series of spectra collected throughout the night. The single beam spectrum collected at 5:02 pm (a6156r02.sgl) was used to test line shift. This single beam spectrum was converted to absorbance using the previously collected background or I_o and the FTIR analysis software. The absorbance spectrum was then displayed with the full screen encompassing the 3205 to 3225 cm^{-1} region. The reference spectrum for water to be used in the analysis method (0515wpc1.h2o) was then loaded and displayed along with the spectrum collected on site. These spectra are shown in Figure 7. Inspection of these spectra shows only very minor line shifts between the two spectra.

As a result, no shifts of either the reference or the sample spectra were performed.

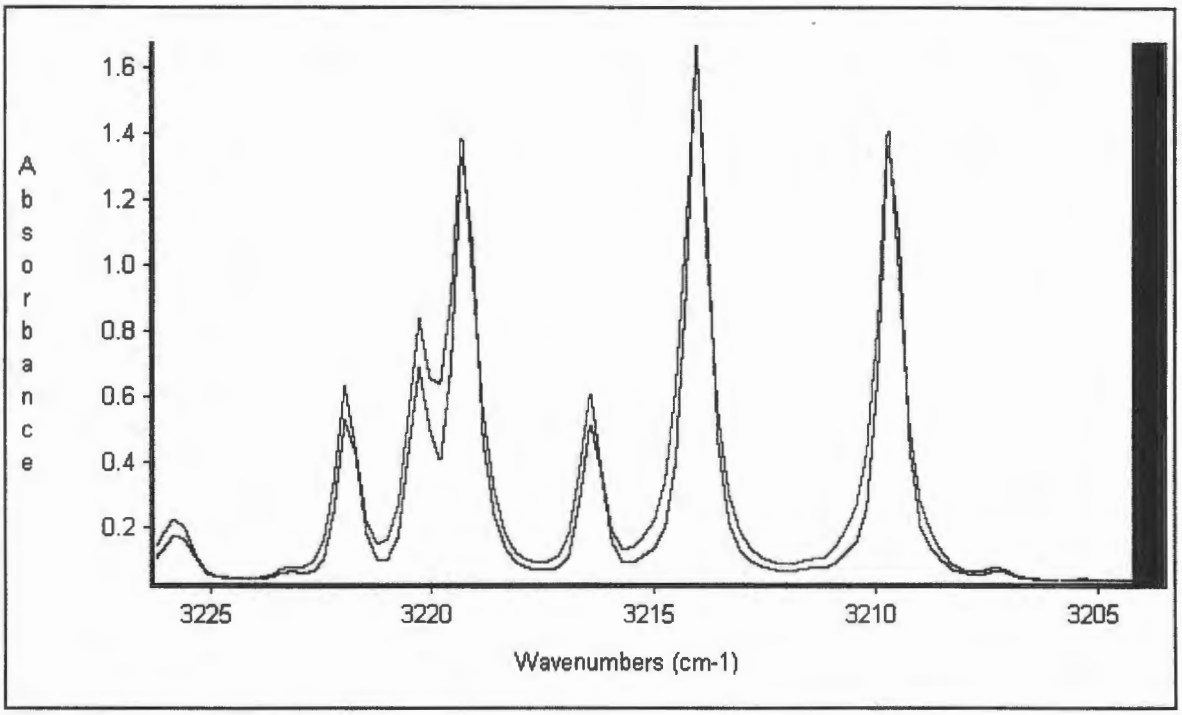

Figure 7. Comparison of Water Reference Spectrum to Collected Ambient Air Spectrum in the HDO Region.

8.5.4 Spectral Resolution

Spectral resolution is also a function of overall system alignment. To demonstrate that the system was truly supporting 0.5 cm^{-1} resolution during data collection, the resolution was verified before the system was transported to the underground. The resolution was checked quickly after transport to the underground to verify that it had not changed. Any observed change would be corrected through FTIR or optical system realignment.

Demonstrating the spectral resolution of the instrument is difficult because every observed spectral line has some width of its own. Therefore, to assess instrument resolution, one must look at either low pressure lines or account for the finite width of the lines observed. The latter is easier to perform because full pressure cell fills can be used and weaker lines easily observed. Therefore, the line width expected, based upon computed instrument effects and known line widths, is compared to that observed to verify instrument resolution. The expected line width is the convolution of the instrument function of the FTIR with a pressure broadened (Lorentz) line. This yields the width that should be observed for specific spectra because the convolution integral accurately represents the distortion of the spectral lines by the instrument. A good approximation to the convolution integral is:

$$\gamma_{obs} = r^2/2 + ((r^2/4 + \gamma_l))^{1/2},$$

where γ_{obs} is the half width of the spectral line that should be observed with an instrument if that

instrument has a resolution of r and the line being observed has a half-width of γ_l (obtained from literature values). This equation predicts that the line widths of Table 6 should be observed for the two specific H_2O lines at 1187 cm^{-1} and 1149.5 cm^{-1}. These two lines are isolated enough to allow for resolution verification. To evaluate the half-width of the observed lines, one spectrum gathered in each cell (a6156r02.sgl and b6156r08.ifg) was used. These spectra were expanded around the two line positions, and the full width at half-peak absorbance was measured using the FTIR analysis software. The half-widths observed are shown in Table 6. A value falling between 0.9 to 1.1 times the expected value is considered acceptable, as shown in Table 6, all measurements fell well within this range.

Table 6. Measured and Predicted Line Widths For the FTIR System

Line Type Position (cm^{-1})	Actual Line Width (cm^{-1})	Predicted Line Width (cm^{-1})	Observed* Line Width (cm^{-1}) Cell #1	Observed* Line Width (cm^{-1}) Cell #2
H_2O 1187.02	0.0835	0.513	0.491	0.497
H_2O 1149.46	0.0687	0.0510	0.515	0.522

* Cell #1 data file: a6156r02.sgl; Cell #2 data file: b6156r08.ifg

Resolution was also visually verified by observing the methane line at 2917 cm^{-1} as shown in Figure 8. This plot is from the same Cell #1 spectrum described above. This methane "line" was actually a set of four lines clustered together, three of which appear to be resolved. The first two lines are just resolvable if the instrument has a resolution of 0.5 cm^{-1}. If the lines are resolved, a dip should be seen between them at 2916.60 cm^{-1}. If the lines are not resolved, no dip will be seen, and the set of lines will appear as a doublet with only the dip at 2917.31 cm^{-1} being visible. As seen in Figure 8, the dip was clearly visible in the field spectrum, further supporting the 0.5 cm^{-1} resolution of the instrument.

8.5.5 Path Calibration

Before measurements can be performed with the FTIR, the actual path of the multi-pass cells must be verified. This calibration was accomplished by filling the cells with a calibration gas of known concentration and then deducing path length from the resulting absorbance spectrum. This test was performed above ground when the instrument was first delivered to the site, and it would not be required again unless the alignment of the cells was altered.

8.5.6 Minimum Detectable Concentrations for Target Compounds

The Minimum Detectable Concentrations (MDCs) for target compounds was expected to improve at the WIPP site as compared to the tests performed at the FTIR vendor location. The very low humidity provides a more desirable measurement environment, and, therefore, the interferences from water are reduced. As a result, MDC checks will be performed using ambient air as the cell charge to determine expected detection limits for conditions at the WIPP site. These tests were not repeated underground.

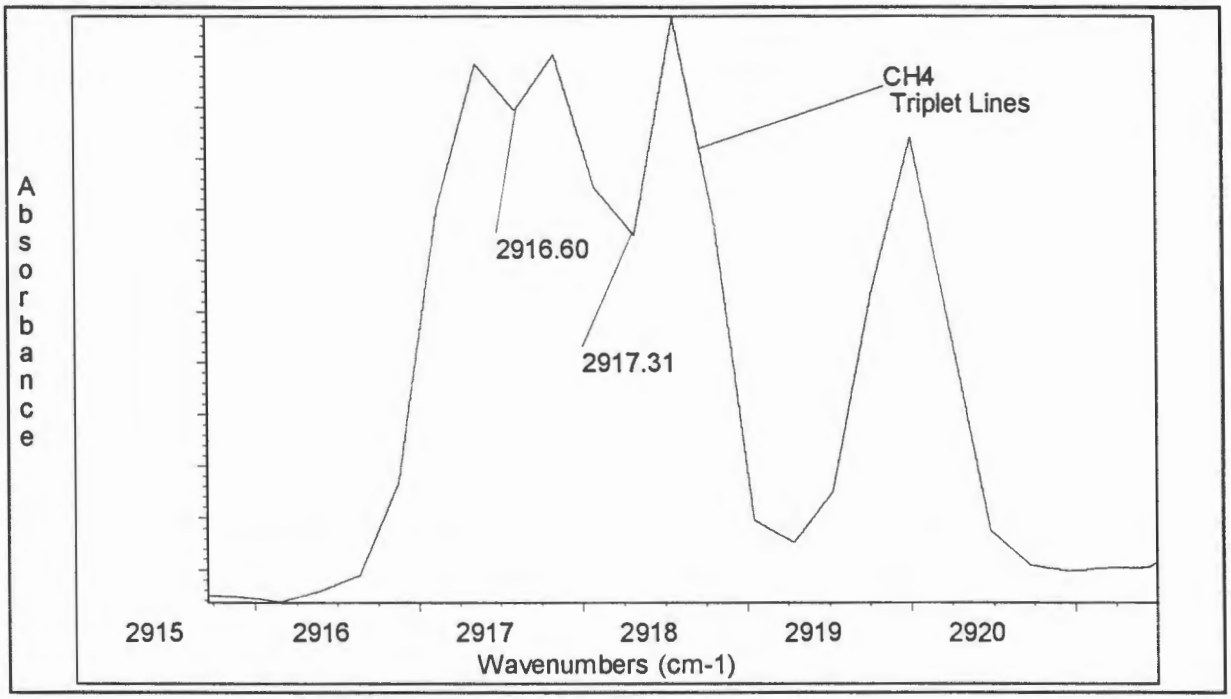

Figure 8. Triplet Methane (CH4) Line at 2917 cm^{-1} Demonstrating Spectral Resolution of 0.5 cm^{-1}

To determine the MDCs observable with an FTIR, analysis methods which utilize Classical Least Squares (CLS) have been developed to look for all target compounds. These methods are then used to analyze a series of spectra with all major interferents present but none of the analytes present. This is the most stressful case in that the analyte concentrations are at a minimum (zero) while the interferents are at values expected for the test environment. When the analytical method is used to analyze a series of 10 spectra of this type, the correct value to be returned by the method is zero. In reality, the result is a series of values scattered about some mean value. If, for a given compound, this mean value is zero, the method has no bias for that compound. On the other hand, if it averages to a non-zero value, there is bias, and this bias must be corrected using the manual or automated bias correction methods developed by the FTIR vendor. The scatter itself is the important characteristic for deducing MDC because it represents the minimum deviation that could be attributed to a detected compound versus that caused by system interference and noise. Three times this standard deviation (σ) is usually taken as the detection limit (represents a 99% confidence limit).

To evaluate MDCs at the WIPP facility, the flow system was first checked for leaks by evacuating the system to two torr, valving off the pump, and watching the pressure rise. The rise was much less than 1 torr per minute and was, therefore, deemed to be adequate. A purge was maintained from the air filter through both the FTIR system and the optics transfer box for the duration of the data collection period to assure minimum influence from the ambient air. Prior to filling the cell for the MDC analysis, new background files were generated for both cells. The cell conditions for the measurements and the background files used are shown in Table 7.

Table 7. Background Files Used for the MDC Data Files

Cell	Cell Pressure Cell Temperature Cell Path length Co-adds	File Name	Interferogram Peak to Peak (volts)
1	2 torr 29 C 115 m 178	BKGC164A.SPA	+8.65 v, -6.29 v
2	2 torr 29 C 115 m 178	BKGC264A.SPA	+8.69 v -6.11 v

To ensure that the gas handling system filled the cells with clean air, both cells were filled to 400 torr with ambient air and then pumped out to less than 5.0 torr. The cells were then filled again to one atmosphere for the measurements and a series of ten (10) spectra were collected at 0.5 cm^{-1} resolution. The initial conditions of the fills for both cells are shown in Table 8. All actual conditions during measurement were written into the header record of the individual spectral data files generated by the FTIR analysis software.

Table 8. Fill Conditions and File Names for the Series Files Used to Evaluate MDC Values

Cell	Cell Pressure Cell Temperature Cell Path length Co-adds	File Name	Interferogram Peak to Peak (volts)
1	667 torr 29.0 C 115 m 188	a6157b28.spa to a6157bd19.spa	+8.60 v, -6.28 v
2	669 torr 29 C 115 m 188	b6157b34.ifg to b6157d25.ifg	+4.65 v -6.16 v

The 10 spectra collected in each cell were then post-processed to absorbance and quantitated. Using the 10 spectra from each cell, the standard deviation and the MDC was computed for all target compounds. This was performed for two cases: 1) for the raw data as collected and 2) for the data after bias correction. The results of these computations are shown in Tables 9 and 10 for each cell along with the average annual reporting levels from Table 1. As shown in Tables 9 and 10, the only target compound whose MDC is not below the average annual reporting level is 1,2 - dichloroethane. This MDC must be lowered by further optimizing the quantitation method.

Table 9. Minimum Detectable Concentrations (MDCs) for Bias Corrected and Uncorrected Data in Cell #1

	Uncorrected (ppbv)		Bias Corrected (ppbv)		Average Reporting Levels (ppbv)
Compound	**St. Dev.**	**MDC**	**St. Dev.**	**MDC**	
1,1 - Dichloroethylene	0.4	1.1	0.3	0.8	27
Carbon Tetrachloride	0.2	0.6	0.1	0.4	6
Methylene Chloride	1.5	4.5	1.3	3.8	326
Chloroform	0.2	0.7	0.2	0.7	5
1,1,2,2 - Tetrachloroethane	3.0	8.9	3.0	9.1	13
Chlorobenzene	2.5	7.6	2.6	7.8	2,300
Toluene	7.8	23.4	7.1	21.3	57,000
1,1,1 - Trichloroethane	1.3	3.8	1.2	3.5	600
1,2 - Dichloroethane	5.2	15.6	5.2	15.5	10

Table 10. Minimum Detectable Concentrations (MDCs) for Bias Corrected and Uncorrected Data in Cell #2

	Uncorrected (ppbv)		Bias Corrected (ppbv)		Average Reporting Levels (ppbv)
Compound	**St. Dev.**	**MDC**	**St. Dev.**	**MDC**	
1,1 - Dichloroethylene	0.9	2.8	1.0	2.9	27
Carbon Tetrachloride	0.1	0.4	0.1	0.4	6
Methylene Chloride	1.8	5.3	1.6	4.9	326
Chloroform	0.3	1.0	0.3	1.0	5
1,1,2,2 - Tetrachloroethane	3.3	9.8	2.8	8.3	13
Chlorobenzene	2.9	8.7	3.0	9.0	2,300
Toluene	4.6	13.8	4.6	13.8	57,000
1,1,1 - Trichloroethane	1.5	4.5	1.6	4.7	600
1,2 - Dichloroethane	9.0	27.0	8.9	26.6	10

8.5.7 Signal-to-Noise Tests

The signal-to-noise ratio, or the Noise Equivalent Absorbance (NEA) for FTIR systems, can be a limiting factor on MDCs. NEA is strongly influenced by system alignment and total system energy throughput. Consequently, the NEA was measured above ground to demonstrate that it was within specification. This test was repeated whenever the alignment of the system was altered significantly (this is usually characterized by a significant increase or decrease in total signal strength, as reflected in the interferogram peak-to-peak signal).

The objective of the signal-to-noise tests is to measure the inherent system noise as a NEA and show that it is smaller or equal to the desired level of $5x10^{-4}$ with five minute averaging and 0.5 cm^{-1} resolution. The NEA represents the noise level below which no measurements can be made. It will dictate the smallest observable absorbance and, hence, the smallest concentration observable for a given compound. To conduct the NEA test, the FTIR bench and transfer optics were purged with zero air from the Balston air filter until no further reduction in H_2O and CO_2 absorption was observed. The two cells (Cell #1 and Cell #2) were then pumped to less than 1 torr and held at this low pressure throughout the tests to eliminate all atmospheric absorption from the spectra. Two tests were then conducted on each cell:

- Test at 4 cm^{-1} resolution using 32 co-added spectra
- Test at 0.5 cm^{-1} resolution using 188 co-added spectra (five minute averaging)

To perform these measurements, a single beam background spectrum was gathered, and this was immediately followed by collection of a single beam sample. These two single beam spectra were then ratioed and the absorbance generated in the normal fashion. The ratioing of the two spectra canceled out all absorption from ambient air constituents remaining in the bench or cells, leaving only the system noise. The peak-to-peak and root-mean-square (rms) noise was determined using the noise analysis function within the FTIR analysis software. Noise values were assessed in two regions, one from approximately 900 to 1100 cm^{-1} and one from approximately 2400 to 2500 cm^{-1}. These regions were adjusted slightly to avoid any residual absorption in the spectrum arising from incomplete pumping of the cells or purging of the bench. The results of these measurements are shown in Table 11. All values met or exceeded the specification of $5x10^{-4}$.

Table 11. Signal-to-Noise Levels (NEA) Measured in Both Cells of The Extractive System

Cell No.	Resolution	NEA 1000 to 1100 cm^{-1}	NEA 2405 to 2500 cm^{-1}	File Name(s)
1	4 cm^{-1} 32 scan	$1.4x10^{-4}$ pk-pk $3.6x10^{-5}$ rms	$8.3x10^{-5}$ pk-pk $2.3x10^{-5}$ rms	NEAC14CM.spa
2	4 cm^{-1} 32 scan	$2.3x10^{-4}$ pk-pk $5.8x10^{-5}$ rms	$1.4x10^{-4}$ pk-pk $3.5x10^{-5}$ rms	NEAC24CM.spa
1	0.5 cm^{-1} 179 scan.	$4.5x10^{-4}$ pk-pk $7.3x10^{-5}$ rms	$2.6x10^{-4}$ pk-pk $3.8x10^{-5}$ rms	NEAC15CM.spa
2	0.5 cm^{-1} 179 scan	$4.6x10^{-4}$ pk-pk $8.9x10^{-5}$ rms	$2.5x10^{-4}$ pk-pk $5.5x10^{-5}$ rms	NEAC25CM.spa

8.5.8 Line Loss Tests

Line losses can be a problem with long extraction lines. This problem is usually significant when monitoring polar compounds such as hydrogen fluoride or hydrogen chloride. It is rarely an issue with the compounds being monitored at the WIPP facility. However, to assure that the lines would not influence the results in any way, line loss tests were performed above ground prior to relocating the FTIR system to the underground. Once performed, these tests would not be repeated unless lines of a different material were used.

Two gas mixtures were used to test the analysis method for accuracy and to confirm that the extraction lines were not adsorbing any of the compounds of concern. To perform these tests, calibrated gas mixtures of the compounds to be detected were obtained from a gas supply company. These mixtures were obtained with a specified gravimetric accuracy of 5% and are typically prepared so all analytes are at concentrations five to ten-times above the minimum detection level for each compound. This assures that all measurements can be made at high accuracy so the effects observed can be unequivocally attributed to the lines or the cell and not to system precision. For the WIPP tests, the mixtures A and B shown in Table 12 were ordered and received. A pure sample of 1,1,2,2-tetrachloroethane was also ordered so a reference standard could be generated. The concentrations at which the samples were gravimetrically prepared are shown in Table 12.

Table 12. Mixtures Used in Performing VOC Spiking and Line Loss Test

Compound	Expected MDC (ppbv)	Mixture	Nominal Concentration (ppbv)
1,1 - Dichloroethylene	5	B	621
1,1,1 -Trichloroethane	10	B	523
1,1,2,2 - Tetrachloroethane	10	separate	322
1,2 - Dichloroethane	15	A	2,030
Carbon Tetrachloride	5	A	1,180
Chloroform	8	A	730
Methylene Chloride	10	B	1,100

When the mixtures were received at the FTIR vendor facility, they were laboratory tested to verify they met specifications. All gases were at a lower concentration than expected, based upon the gravimetric mixing. This is shown in Table 13 which shows the nominal concentrations and those observed with the laboratory FTIR system. Two measurements are shown. These were the result of separate fills of the FTIR cell followed by separate measurements of the concentrations. The two results appear to agree well with one another but not with the nominal concentrations. This loss of sample is not unusual for gas samples if the shipping bottles have not been properly stabilized. Most VOCs will show wall adsorption effects that result in lower concentrations of the mixture. This can be overcome by long exposure of the cylinder to the gases or by treating the cylinders with a passivation agent prior to filling. This was apparently not done for the cylinders received at the WIPP facility. Because time did not permit the preparation of new samples, these mixtures were shipped to the WIPP facility, and it was assumed that the majority of the loss had already occurred and that the bottles would be stable enough to perform the line loss tests. However, because the absolute concentrations of these mixtures could not be verified, they could not be used to perform the analysis-method accuracy test. New bottles were ordered which were used to perform these tests separately.

Table 13. Measured Concentrations of the Gas Mixtures as Received at FTIR Vendor Facilities

Compound	Nominal Concentration (ppbv)	Assay Results Test #1 (ppbv)	Assay Results Test #2 (ppbv)
Mix #1 # CC79230			
Carbon Tetrachloride	1,180	400	390
Chloroform	730	380	380
1,2 - Dichloroethane	2,030	1,140	1,140
Mix#2 #CC74041			
1,1 - Dichloroethylene	621	480	480
Methylene Chloride	1,100	860	860
1,1,1 - Trichloroethane	523	430	430
Mix#3 #CC76916			
1,1,2,2 - Tetrachloroethane	322	0	0

To perform line loss tests, Cell #1 was evacuated and a new background spectrum collected (a6158l37.bkg). The gas bottle was then connected directly to the gas manifold through 10 feet of Teflon® tubing. To assure a clean fill, the cell was first filled to a pressure of 400 torr with gas mixture #2 and then pumped to less than 6 torr. The cell was then filled a second time to a total pressure of 664 torr at a temperature of 28.9° C and valved off. Successive measurements were then made of this gas mixture. One effect that was immediately observed was that the gas fills did not remain stable in the cell. This is demonstrated in Figures 9 and 10 which show the gas concentrations reported by the FTIR as a function of time after the initial fill for mixtures #1 and #2, respectively. Clearly, all compounds (particularly 1,2-dichloroethane) showed some loss with time.

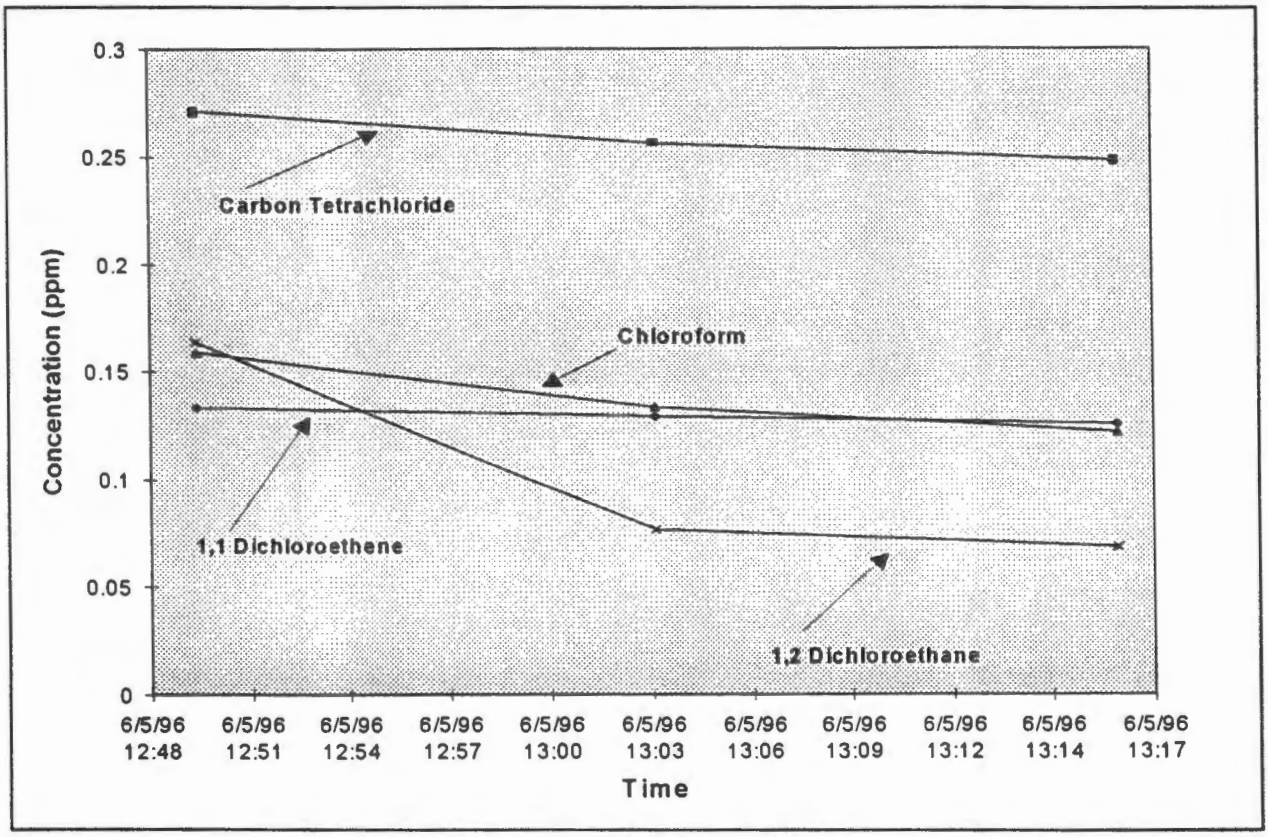

Figure 9. Plots of Observed Gas Concentrations In Cell #1 (gas Mixture #1) as a Function of Time.

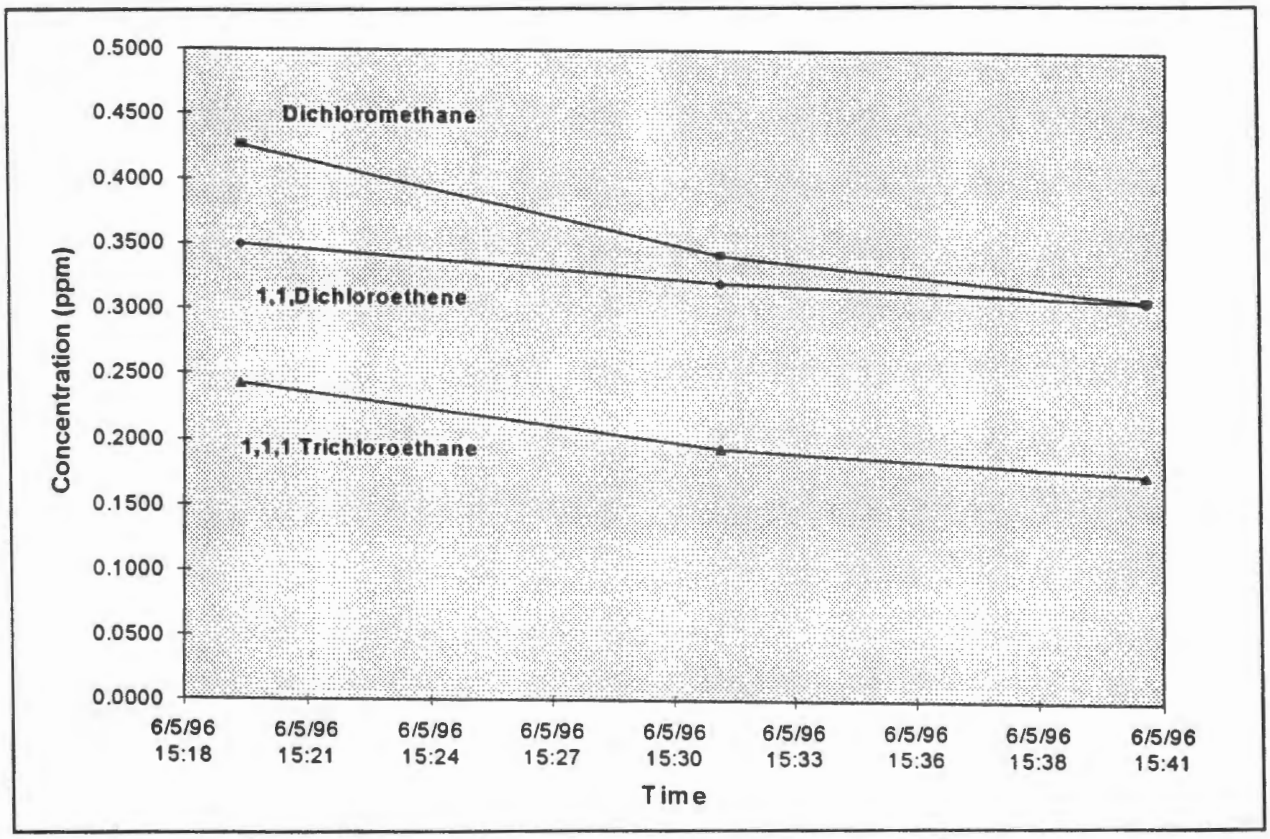

Figure 10. Plots of Observed Gas Concentrations In Cell #2 (gas Mixture #2) as a Function of Time

Because of the observed cell losses, it was decided to complete the line loss tests using the static cell fill approach only with mixture #2. After this test, the system was reconfigured to allow for continuous flow through the cell. This process eliminated any cell effects by flowing the gas mixture through the cell as long as necessary to condition it and achieve a stable gas charge. Typically, an asymptotic increase of the gas concentration to a final flat, invariant value is observed.

The results of the static line loss test for gas mixture #2 are shown in Table 14. The values labeled as "without extraction line" had a 10-foot section of Teflon® line coupling the gas bottle to the FTIR gas manifold, and the results are from spectral data file "mix2_1.spa". The observations labeled "with extraction line" had 100 feet of line between the gas bottle and the manifold; these results are from spectral data file "losc1m11.spa". The near equality of the two quantitated gas concentrations indicates that the lines were not producing any observable loss for the gases of mixture #2.

For gas mixture #1, dynamic gas fills were used to bypass the cell loss effects. In this case, gas was admitted to the cell through a short 10-foot line and flowed continuously until a stable unchanging reading was observed by the FTIR. A 100-foot section of Teflon® line was then inserted between the gas bottle and the FTIR manifold and the procedure repeated. The results of these tests are shown in Table 15. The measured concentrations of all compounds, with the

possible exception of 1,2-dichloroethane, were the same through and around the long Teflon® line. This indicates that there are no observable losses for any of these compounds. In the case of 1,2-dichloroethane, the observed 7.5% loss is probably significant since the FTIR precision is on the order of 2% to 3% and this is probably an actual loss. This is consistent with the observation described above that showed 1,2-dichloroethane as the most rapidly varying compound in the static fill tests.

Table 14. Concentrations Observed in Static Fill Mode With Gas Mixture #2 with and without the 100 Foot Teflon® Extraction Line

Compound	Without Extraction Line (ppbv)	With Extraction Line (ppbv)
1,1,1 - Trichloroethane	243	231
1,1 - Dichloroethylene	350	352
Methylene Chloride	426	427

Table 15. Concentrations Observed in Flow Through Mode With Gas Mixture #1 with and without the 100 Foot Teflon© Extraction Line

Compound	Without Extraction Line (ppbv)	With Extraction Line (ppbv)
Carbon Tetrachloride	336	333
Chloroform	299	292
1,2 - Dichloroethane	601	556
1,1 - Dichloroethylene	148	144

The analytical method validation tests could not be performed because of the instability of the gas mixtures received from the gas supplier. Also, these tests surfaced an apparent loss effect in the cells when used in a static filling mode. These two issues necessitated the running of a series of subsequent tests to resolve them. These subsequent tests were conducted at the FTIR vendor facility after return from the on-site acceptance tests. They were conducted with new gas calibration standards which were delivered in carefully pacified bottles. The results of these tests are presented in Section 8.5.14.

8.5.9 Tracer Gas Tests

The SF_6 tracer gas tests were conducted on June 11, 1996, in the underground at the WIPP facility. SF_6 is commonly used in tracer gas testing because it is not a carcinogen and is a relatively innocuous gas. The cylinder of SF_6 tracer gas was positioned in Panel 1, Room 7 a few meters from where it intersects the S-1950 drift. The locations of the FTIR inlet lines were just outside of Room 1 in the S-1950 drift (Cell #1, upwind) and in the narrow part of the S-1600 drift just west of Room 1 and VOC Sampling Station #9 (Cell #2, downwind). These positions provided a mixing path of approximately 350 meters between the point of release and the downwind measurement location and included a right angle in that path. The location of the downwind sampling line inlet was 5 feet 7 inches from the south rib (wall) and 5 feet 11 inches

from the floor.

The overall plan for the test was to inject SF_6 into the ventilation air stream in the drift after the upwind FTIR sampling location (S-1950). This injected concentration would then mix with the fresh air, thereby producing a diluted concentration for detection at the downwind FTIR sampling location (S-1600). The SF_6 injection rate could be controlled and monitored with a rotameter and the ambient air flow measured with a portable anemometer. These two rates would then dictate the concentration of SF_6 that should be observed at any point downwind of the injection point, provided the mixing with the air flow was complete. The input FTIR sampling location should "see" no SF_6 (assuming there is none in the air flow from the surface) while the output FTIR sampling location should see something close to the predicted concentration. This process allows for two tests to be performed: 1) a test of the overall FTIR monitoring system to determine if it returns the proper concentration for the simulated release from a disposal room and 2) a test to determine the optimum sampling location within the drift should non-homogeneous conditions exist in the drift. A recovery of 0.8 to 1.2 compared to the computed concentrations was considered acceptable (as in EPA Method 301 validation testing) particularly because of uncertainty in the homogeneity of the flow in the drift.

The first of these tests was conducted in the underground at the WIPP facility the week of June 10, 1996. The second test, that of determining optimum sampling locations, was not completed at the same time because of time restraints. This test was conducted by WIPP facility personnel the following week.

As expected, no SF_6 was detected by the FTIR instrument on the upwind leg at any time during the test. The only difficulty encountered in conducting the test itself was the variability in the air flow rate due to changing ventilation conditions in the mine. The conditions under which measurements were compared to expected (calculated) concentrations were as follows:

Drift size:	13.5 ft x 12.5 ft
Temperature:	81.5 °F
Pressure:	706 torr
SF_6 flow rate:	0.461 liters/minute

The volumetric air flow in the drift is given by:

$$Q = w\,h\,v,$$

where w=drift width, h=height, and v=air flow. For consistency with the SF_6 rotameter, which was calibrated at standard conditions (P_s = 1 atm, T_s = 70° F), the volumetric flow rate was converted to standard conditions as follows:

$$Q_s = (w\,h\,v)\,(P_a\,T_s)/(P_s\,T_a),$$

where the subscript, a, denotes the actual measurement conditions.

Figure 11 presents the results of expected and observed values. The SF_6 concentration was

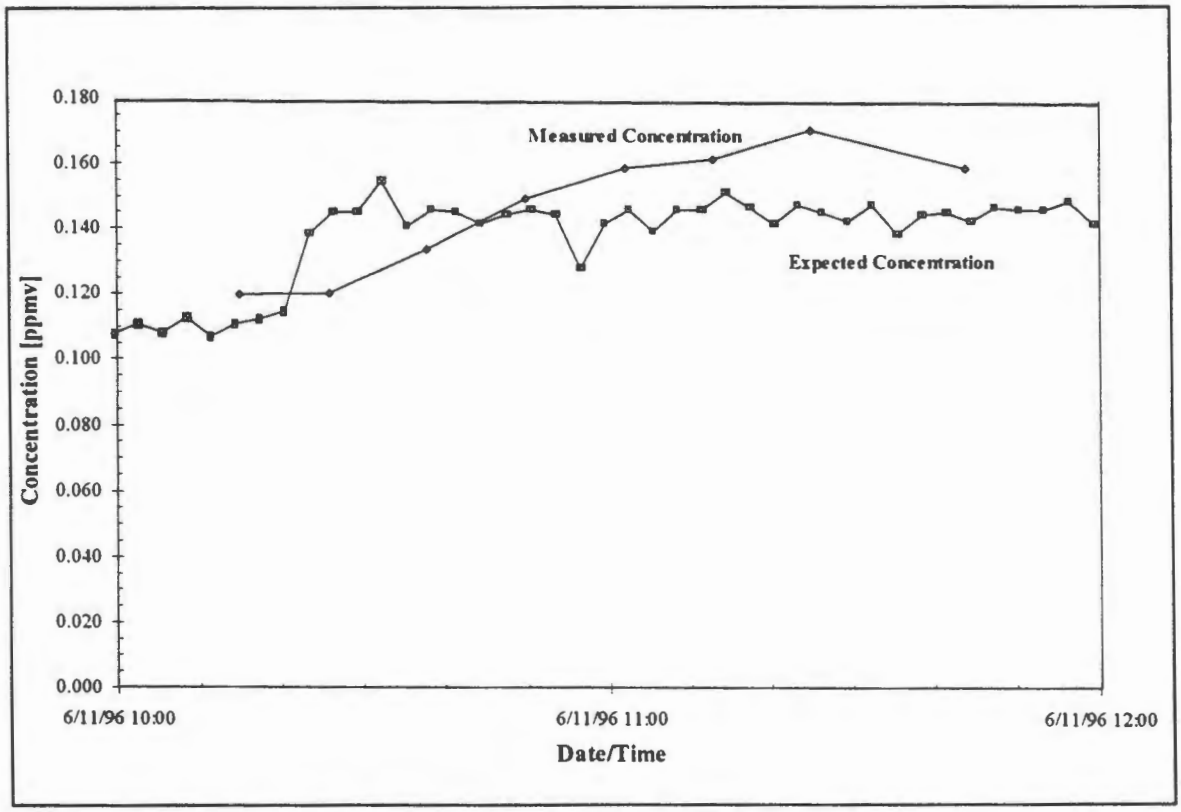

Figure 11. Plot of Expected and Observed SF_6 Concentrations in S-1600 During the Tracer Tests.

relatively stable for samples drawn into the cell from 10:57 am- 11:44 am with an average measured value of 162 ppb. This was 12.5% higher than the estimated expected concentration of 144 ppb. Considering the mixing and possible flow variability, this was considered to be an acceptable agreement. A canister sample was taken at 12:30 pm. The result of the canister analysis was 160 ppb for SF_6.

Testing for the optimized sampler location was conducted on Tuesday, June 18, 1996 and Wednesday, June 19, 1996. SF_6 would again be released and the objective would be to obtain an optimal location for the inlet sample lines, given that it would not interfere with normal underground operations through the drifts. Both inlet sample lines were moved to the S-1600 drift in the mine. One sample inlet was held in the center of the drift. This theoretically should have been the point with the highest air flow. The other inlet was positioned at various locations two feet away from the drift except for locations that would obstruct underground vehicles (i.e. two feet from the floor of the drift). Again, maintenance to the S-1600 drift may have impacted the dispersion of the tracer gas. It was noted that the measured concentrations of the SF_6 tracer gas measured closely enough between each sampler location that turbulent flow conditions appeared to allow for proper mixing in the drift. Therefore, any of the unobstructive sample inlet locations two feet from the S-1600 drift would yield similar results. Two feet below the center of the S-1600 back was chosen as the long-range inlet sample line location. The S-1950 sample line location was also positioned approximately two feet from the center of the back (ceiling).

8.5.10 Duration And Salt Loading Tests

The objective of the duration tests is to demonstrate the continuous operation of the FTIR monitor in the underground without intervention. A test was performed to evaluate the system for at least one continuous week of operation without intervention of any kind. One aspect requiring operator intervention is the replacement of sample filters. These filters were placed on the sample probes themselves to trap salt particles before they entered the extraction line. The system filters were estimated to last for five to seven day replacement cycles. Loading of the filters was easily tracked because the fill pressure of the cells decreases as the filters clog and produce resistance to the air flow. Once the filters clog to the point that the fill pressure decreases by 15% to 20% the system performance is compromised. The filter lifetime was, therefore, defined as the time at which this 20% reduction in cell fill pressure was observed. During the duration tests, the system was interrogated via telephone link to assess operation but it was not altered in any way.

The extractive FTIR prototype system was equipped with wool fiberglass filters at the inlet of each cell's sampling line to remove salt particulate. The following table shows the average daily pressures achieved in both cells at the beginning and end of a seven-week period:

Table 16. Cell Measurement Pressures

	June 11	July 31
Cell #1 Pressure (torr)	711	709
Cell #2 Pressure (torr)	709	705

The data indicates that although there was some accumulation of salt on the filters, there was no significant buildup which restricted air flow into the cells. The FTIR vendor indicated that the small accumulation of particulates may be handled by cleaning out the multi-pass cells with an optical solvent on an annual basis. This activity can be conducted in conjunction with other routine maintenance activities. The conclusion from this test is that the existing type of filters are adequate for long term use on the FTIR system. These filters do not require weekly replacement as originally estimated. It appears that even for preventative maintenance purposes, the filters can be used for a three to four month period prior to replacement.

8.5.11 Power Outage Tests

The FTIR system was initially set up with an uninterruptible power supply (UPS) system that decoupled it from the power line and provided backup power during the power failures. The FTIR system was also designed to reboot itself and resume normal operation if the power failed for an extended period. Both of these tests were performed after the system was installed in it's test location in the underground.

The tripping of a breaker elsewhere in the mine during the night of June 13, 1996, provided a test of the FTIR system's response to a power outage. The system operated continuously during the

of the FTIR system's response to a power outage. The system operated continuously during the night and was still collecting data when it was manually shut down on the morning of June 14, 1996. However, the pump, which was on a separate circuit not connected with the UPS, ceased to function, so all of the data taken overnight were collected on the same static air sample. As a result of this event, provisions were later made for the pump to be attached to the UPS as well. It appears that the UPS used with the system is adequate to maintain operation of the system for extended periods even with a full power failure. In addition, a power outage occurred sometime on Saturday, August 3, 1996. This outage affected the power to Room 1, Panel 1 and consequently the extractive FTIR prototype system. Because the vacuum pump was also connected to the UPS, the system depleted the batteries on Sunday August 4, 1996, at about 8:00 am. The UPS was able to support power to the FTIR system for greater than the goal of 15 minutes. Upon reapplication of power to the mine on Monday morning, August 5, 1996, the FTIR system booted up and restarted.

8.5.12 Data Completeness Evaluations

The goal for data completeness was that the system collect at least 75% of all possible data on a daily basis and 80% of all possible data on a monthly basis. "All possible data" refers to data that could be collected because the system should have been operating. Instances in which the system cannot collect data because of certain events such as total loss of power are excluded. Careful logs were kept by WIPP facility personnel so the periods of operation were known and periods in which data could not be collected were also known. The system itself logs all data with date and time stamps and if there is a power failure or other event causing the system to reboot, a new data file for each collection session is created. Given the logs and archived data, the percentage of data collected for each "day" of operation were compiled, and from this daily and monthly capture rates were computed.

The maximum daily number of expected data points from each cell of the FTIR monitoring system depends upon the cycle time set by the user in the FTIR analysis software, the time required for quantitations, and the time required for midnight spectral background acquisition. For the settings in effect during June and early July 1996, the number of spectra expected would have been 121 spectra per day. During the one-week period of June 29, 1996 through July 5, 1996, during which the system was left to operate unattended, 830 spectra were collected from Cell #1 out of a possible 847, for a capture rate of 98.0%. The corresponding figures for Cell #2 were 826 spectra and a capture rate of 97.5%. This exceeded the 75% daily target level as well as the 80% monthly value. After the initial on-site testing, the system parameters were changed to provide for longer cell pumpout times. As a result, 72 spectra are now expected to be captured each day from each cell.

Table 17 summarizes the daily and overall operational data recovery percentages from the interval of June 13 through August 9, 1996.

Table 17. Operational Data Recovery

Date	Percentage of data collected for day	Event (Either operator controlled or event external to FTIR system and computer)	Percentage of data collected not due to event
6/13/96	100.00%	None: Startup at 14:56	100.00%
6/14/96	91.67%	Diagnostics on FTIR	100.00%
6/15/96	100.00%		100.00%
6/16/96	100.00%		100.00%
6/17/96	93.33%	Setting up FTIR for testing	100.00%
6/18/96	98.33%	Setting up FTIR for testing	100.00%
6/19/96	98.33%	Going through startup/shutdown sequence	100.00%
6/20/96	100.00%		100.00%
6/21/96	78.30%	Dewar depleted of coolant due to supplier mixup	100.00%
6/22/96	100.00%		100.00%
6/23/96	100.00%		100.00%
6/24/96	95.00%	Setting up FTIR under direction of vendor	98.33%
6/25/96	35.80%	Powered down FTIR - Rm1 Roofbolt detensioning	95.56%
6/26/96	36.67%	Roofbolt detensioning finished at 14:30	100.00%
6/27/96	100.00%		100.00%
6/28/96	91.67%	Downloaded raw data to cartridges, cleared up hard drive	100.00%
6/29/96	100.00%		100.00%
6/30/96	100.00%		100.00%
7/1/96	100.00%		100.00%
7/2/96	100.00%		100.00%
7/3/96	100.00%		100.00%
7/4/96	100.00%		100.00%
7/5/96	100.00%		100.00%
7/6/96	100.00%		100.00%
7/7/96	100.00%		100.00%
7/8/96	93.75%	Downloaded raw data to cartridges, cleared up hard drive	100.00%
7/9/96	100.00%		100.00%
7/10/96	96.88%	Went through maintenance steps with vendor on phone	100.00%
7/11/96	97.92%	Note: FTIR vendor may have changed water vapor ref.	97.92%
7/12/96	100.00%		100.00%
7/13/96	100.00%		100.00%
7/14/96	100.00%		100.00%
7/15/96	66.14%	Operator stopped data collection-cell 1. Auto Reset next day.	100.00%
7/16/96	100.00%		100.00%
7/17/96	100.00%		100.00%
7/18/96	53.13%		53.00%
7/19/96	67.19%	System off 3 hrs while training operator on shutdown procedure	73.40%
7/20/96	100.00%		100.00%
7/21/96	100.00%		100.00%
7/22/96	100.00%		100.00%
7/23/96	100.00%		100.00%
7/24/96	95.83%	Going thru more training of personnel on FTIR system	100.00%
7/25/96	98.96%	FTIR vendor downloading daily data	100.00%
7/26/96	100.00%		100.00%
7/27/96	100.00%		100.00%
7/28/96	100.00%		100.00%
7/29/96	100.00%		100.00%
7/30/96	86.25%	System shut off while roofbolt detensioning	100.00%
7/31/96	98.63%	At FTIR vendor and made changes to analysis time of FTIR	100.00%
8/1/96	100.00%		100.00%
8/2/96	100.00%		100.00%
8/3/96	100.00%		100.00%
8/4/96	40.30%	Power outage u/g during weekend. UPS lasted over one day.	100.00%
8/5/96	95.80%	Disconnected FTIR from UPS. Still connected to line condtnr.	100.00%
8/6/96	100.00%		100.00%
8/7/96	100.00%		100.00%
8/8/96	100.00%		100.00%
8/9/96	98.63%	FTIR vendor downloaded data	100.00%
Average:	**93.25%**	**Average including events:**	**98.59%**

8.5.13 Electromagnetic Interferences

Electromagnetic Interferences (EMI) tests were performed after relocating the FTIR system in the underground. Since radios are not used underground, radio frequency interference was not expected to be an issue. However, there was a concern about heavy electrical equipment running in the immediate vicinity of the FTIR and/or tied on to the same electrical circuit.

An examination of the system response to electromagnetic interference was carried out on June 12, 1996 using a power drill as an EMI noise source. The drill was placed at several locations in close proximity to the FTIR to evaluate possible system degradation. The following table presents the peak-to-peak noise equivalent absorbances (NEA) measured in the long-wavelength region during the test. The tests were carried out using Cell #1 under vacuum. The data indicate that there was no decrease in system performance from the work tool used.

Table 18. NEAs Measured During EMI Test

	NEA (pk-pk) (894 - 1011 cm^{-1})
No Noise	2.5×10^{-4}
Drill before UPS	2.2×10^{-4}
Drill after UPS	3.1×10^{-4}
Drill on computer outlet	2.7×10^{-4}

8.5.14 VOC Accuracy Tests, Cell Losses and Method Validation Tests

As discussed in Section 8.5.8, the dual-cell system was tested at the WIPP site using the 100 meter cell filled directly from cylinders that contained several gases at sub-ppm levels mixed with nitrogen. During these tests, it was observed that the fills were not stable and that the concentrations dropped with time. In subsequent discussions with EPA technical experts, it was learned that when very dry samples are admitted to various containers, they are adsorbed on the wall surfaces and the partial pressures of these substances are seen to decrease with time. However, EPA also indicated that if moisture is admitted with or prior to the admission of the dry samples, then the water vapor will be preferentially adsorbed and the organics admitted to the cell will show essentially no loss. To further investigate these effects, additional tests were conducted using a dual cell FTIR system at the FTIR vendor facilities that was identical to that installed at the WIPP site. For these tests, four gas mixtures were obtained from a preferred gas standards supplier with analytical accuracy stated to be +/- 5 %. The mixtures used were identical to those originally tested at the WIPP site and they are also shown in Table 19. To be assured of mixture stability in the bottles, the FTIR vendor had its analytical laboratory take samples of the mixtures and analyze them in their analytical laboratory. The results of these analyses are shown in Table 19.

Table 19. Cylinder Contents and Analyses

Mix #	Contents	Gas Supplier Analysis (ppbv)	FTIR Vendor Lab Analysis (ppbv)
1	Carbon Tetrachloride	1,090	824, 790
	Chloroform	2,090	1,820, 1,830
	1,2-Dichloroethane	2,000	2,080, 2,080
	Nitrogen		
2	1,1-Dichloroethylene	1,020	1,140, 941, 949
	Methylene Chloride	2,130	2,010, 1,860, 1,820
	1,1,1-Dichloroethane	1,050	935, 910, 863
	Nitrogen		
3	1,1,2,2-Tetrachloroethane	1,600	1,750, 1,510
	Nitrogen		
4	1,1,1-Trichloroethane	2,080	1,810, 1,790
	Nitrogen		

The first test series conducted at the FTIR vendor was a repeat of one of the tests conducted at the WIPP site to see if the same losses could be reproduced. To perform this test, Mix # 1 was admitted to an evacuated cell on a dry basis. Measurements were then made on this sample approximately five minutes apart for a little over one hour. Each data set represented one-minute of FTIR spectral co-adding. The results of the FTIR analyses for these measurements are shown in Table 20. It is seen that for Mix # 1, component concentrations steadily decrease with time just as they did during the on-site WIPP tests. This confirmed that these effects were not unique to the WIPP equipment nor to the WIPP environment.

For the second test set, room air (which contained water vapor) was admitted to the cell to a pressure of 651 torr. Three one-minute coadded data sets were then collected on this room air sample. The first of these spectra was used to construct a water vapor reference spectrum, which was used in all subsequent data analyses with the CLS routines. Gas Mixture # 1 was then added to the cell to a total pressure of 728 torr, which represented an addition of 77 torr of the pure gas mixture. Four data sets (one minute coadd each) were then collected every five minutes. The results of the analysis are shown in Table 21. It should be noted that the last row is the earliest data set collected and time increases upward. As may be seen from the table, the FTIR-reported concentrations rise slightly for the first three files (TST # 29 - 31) and then become stable (TST # 32). This initial rise is attributed to mixing and equilibration of the added sample within the cell.

#Quantitation Method = WIPP C2 05/27/96 Components = 22

Timestamp	H2O	error	CO	error	CO2	error	N2O	error	CH4	error	NH3	error	CH3OH	error	11DCE	error
7/31/96 14:55	155.6	97.16	0.2609	0.0021	0.7874	1.121	0.0013	0.0012	0.0088	0.0078	-0.0005	0.0018	0.0012	0.0019	0.0012	0.0011
7/31/96 14:37	144.3	98.48	0.2615	0.0021	1.045	1.104	0.001	0.0012	0.0107	0.0071	-0.0012	0.0018	-0.0006	0.0016	0.0006	0.0014
7/31/96 14:27	91.43	98.77	0.2611	0.0021	0.7152	1.069	0.0011	0.0012	0.0096	0.0078	-0.001	0.0018	-0.0004	0.0016	0.0012	0.001
7/31/96 14:22	109.3	103.8	0.2615	0.002	0.8418	0.9692	0.0007	0.0011	0.0136	0.0071	-0.0013	0.0019	-0.001	0.0019	0.0009	0.0013
7/31/96 14:17	102.7	102.7	0.261	0.0021	0.4433	1.119	0.0008	0.0011	0.0051	0.0078	-0.001	0.0019	0.0012	0.0017	0.0016	0.0005
7/31/96 14:12	75.24	107	0.2606	0.0021	0.134	1.172	0.0011	0.0012	0.0029	0.0075	-0.0013	0.002	0.0009	0.0019	-0.0003	0.0011
7/31/96 14:07	147	103.9	0.2609	0.002	0.3672	1.235	0.0007	0.0011	0.0072	0.0075	-0.0004	0.0019	0.0007	0.0018	-0.0001	0.0014
7/31/96 14:02	147.5	109.8	0.2606	0.0021	0.6415	1.191	0.0011	0.0012	0.004	0.008	-0.0016	0.002	-0.0007	0.0018	-0.0006	0.0011
7/31/96 13:57	114.5	120.2	0.2606	0.0021	0.4276	1.208	0.0008	0.0011	0.0056	0.0093	-0.0016	0.0022	0.0011	0.0018	0.0001	0.0011
7/31/96 13:52	75.75	128.6	0.2602	0.002	0.3306	1.211	0.001	0.0011	-0.0011	0.0084	-0.0018	0.0024	0.0009	0.002	0.0016	0.0014
7/31/96 13:46	81.07	140.1	0.2603	0.0021	1.016	1.446	0.0011	0.0011	0.0073	0.0096	-0.0029	0.0026	0.0024	0.0018	-0.0001	0.0014

MIX # =>	# 1				# 1								# 1			
Timestamp	CCL4	error	DCM	error	CHFRM	error	1122T	error	111TA	error	CHBNZ	error	12DCA	error		
7/31/96 14:55	0.9245	0.008	-0.2977	0.086	1.408	0.0134	0.2654	0.1346	-0.0037	0.0061	0.0251	0.0199	0.4245	0.0205		
7/31/96 14:37	0.9275	0.008	-0.3053	0.0859	1.426	0.0134	0.2666	0.1346	-0.0036	0.0061	0.0279	0.0211	0.4544	0.0202		
7/31/96 14:27	0.9288	0.0081	-0.3068	0.0874	1.44	0.0136	0.27	0.1368	-0.0039	0.0059	0.0239	0.0207	0.4735	0.0196		
7/31/96 14:22	0.9297	0.0081	-0.3108	0.0866	1.449	0.0135	0.2661	0.1356	-0.0063	0.0053	0.0228	0.0215	0.486	0.0177		
7/31/96 14:17	0.9302	0.0081	-0.3077	0.0868	1.459	0.0136	0.2652	0.136	-0.0059	0.0061	0.0317	0.0216	0.5018	0.0205		
7/31/96 14:12	0.9317	0.0081	-0.3074	0.0873	1.47	0.0136	0.2647	0.1368	-0.0051	0.0064	0.0254	0.0216	0.5201	0.0215		
7/31/96 14:07	0.9328	0.0082	-0.3138	0.0881	1.483	0.0138	0.2649	0.138	-0.0065	0.0068	0.0255	0.0208	0.5388	0.0226		
7/31/96 14:02	0.9342	0.0083	-0.3178	0.0887	1.504	0.0139	0.2677	0.139	-0.0064	0.0065	0.0336	0.0245	0.5895	0.0218		
7/31/96 13:57	0.9363	0.0083	-0.3239	0.0887	1.53	0.0139	0.2683	0.139	-0.0073	0.0066	0.0276	0.0259	0.6339	0.0221		
7/31/96 13:52	0.9389	0.0085	-0.3274	0.0907	1.57	0.0142	0.2652	0.142	-0.0095	0.0066	0.0278	0.0278	0.7112	0.0222		
7/31/96 13:46	0.9485	0.0087	-0.3499	0.0928	1.66	0.0145	0.2651	0.1454	-0.0086	0.0079	0.0357	0.0362	0.9122	0.0265		

Timestamp	C7H8	error	C2H4	error	O3	error	SF6	error	NO	error	NO2	error	SO2	error		TST #
7/31/96 14:55	-0.0128	0.0178	-0.0009	0.0026	0	0.0018	0.0002	0.0001	0.0156	0.0199	0.0137	0.0163	0.0133	0.012		14
7/31/96 14:37	-0.0169	0.0176	-0.0015	0.0026	-0.0005	0.0016	0.0003	0.0001	0.0122	0.0195	0.0184	0.0147	0.0112	0.0121		13
7/31/96 14:27	-0.0176	0.017	-0.0015	0.0026	0.0006	0.0015	0.0002	0.0001	0.0096	0.019	0.026	0.0161	0.0022	0.0114		12
7/31/96 14:22	-0.005	0.0154	-0.0017	0.0028	0.0009	0.0018	0.0003	0.0001	0.0129	0.0194	0.022	0.0148	0.0113	0.0116		11
7/31/96 14:17	-0.008	0.0178	-0.0018	0.0027	-0.0002	0.0016	0.0003	0.0001	0.0145	0.0191	0.0234	0.0162	-0.0006	0.0121		10
7/31/96 14:12	-0.008	0.0186	-0.002	0.0029	0	0.0018	0.0002	0.0001	0.013	0.0191	0.0194	0.0155	0.0107	0.0119		9
7/31/96 14:07	-0.0034	0.0196	-0.0023	0.0028	0.0008	0.0017	0.0003	0.0001	0.0134	0.0188	0.0315	0.0156	0.0061	0.0124		8
7/31/96 14:02	-0.0066	0.0189	-0.0012	0.0029	-0.0001	0.0017	0.0003	0.0001	0.0101	0.0192	0.0274	0.0166	0.0111	0.0122		7
7/31/96 13:57	-0.0112	0.0192	-0.0029	0.0032	0.0005	0.0017	0.0003	0.0001	0.0116	0.0195	0.0256	0.0193	0.0081	0.0121		6
7/31/96 13:52	-0.0089	0.0193	-0.0013	0.0034	-0.0009	0.0019	0.0003	0.0001	0.0105	0.0193	0.0125	0.0173	0.0083	0.0118		5
7/31/96 13:46	-0.0155	0.023	-0.0017	0.0037	-0.0017	0.0017	0.0003	0.0001	0.0102	0.0182	0.0156	0.02	0.0054	0.0125		4

Note 1: units are designated in ppmv

Note 2: error is +/- added to the measured value

Table 20. Analysis of Mix #1 with no Water Vapor Present in the Cell

	MIX # 1	Analysis													
#Quantitation Method = WP C2 AIR 08/01/96 Components = 21 (modified)															
Timestamp	AIR	error	CO	error	N2O	error	CH4	error	NH3	error	CH3OH	error	11DCE	error	TST #
8/1/96 15:34	637.2	3.957	0.0437	0.0042	0.011	0.0026	0.1593	0.0206	0.0051	0.001	0.0028	0.0024	0.0009	0.0009	32
8/1/96 15:29	641.5	4.099	0.0425	0.0041	0.0094	0.0025	0.1576	0.0188	0.0058	0.0011	0.0042	0.0022	-0.0009	0.0017	31
8/1/96 15:23	650.9	3.788	0.0409	0.004	0.0079	0.0025	0.14	0.0196	0.0049	0.001	0.0032	0.0022	0.0002	0.0012	30
8/1/96 15:18	661.6	4.109	0.0367	0.0044	0.0086	0.0027	0.1564	0.0231	0.0046	0.0011	0.0039	0.0023	-0.0001	0.0014	29
MIX added															
8/1/96 15:14	663.4	4.046	0.0162	0.0015	0.0191	0.001	0.1409	0.0146	0.0039	0.0011	0.0013	0.0025	0.0004	0.0013	28
8/1/96 15:09	673.3	3.421	0.0129	0.0012	0.0146	0.0007	0.1207	0.0139	0.003	0.0009	-0.0004	0.002	0.0007	0.0008	27
Exp Val =	0.106				0.222								0.212		
	CCL4	error	DCM	error	CHFRM	error	1122T	error	111TA	error	CHBNZ	error	12DCA	error	TST #
8/1/96 15:34	0.1025	0.0019	-0.063	0.0159	0.2026	0.0031	0.0797	0.0366	-0.0035	0.005	-0.0092	0.0115	0.2103	0.0132	32
8/1/96 15:29	0.1029	0.0019	-0.0573	0.0155	0.2034	0.003	0.079	0.0355	-0.0029	0.0046	-0.0075	0.0108	0.2134	0.0136	31
8/1/96 15:23	0.102	0.0018	-0.0611	0.0146	0.2009	0.0028	0.0813	0.0334	-0.0026	0.0048	-0.0086	0.0113	0.2091	0.0131	30
8/1/96 15:18	0.0769	0.0018	-0.0529	0.0148	0.1501	0.0029	0.0715	0.034	-0.0058	0.0048	-0.0026	0.0113	0.1549	0.0133	29
MIX added															
8/1/96 15:14	-0.0012	0.0016	-0.0111	0.0136	-0.0003	0.0026	0.0039	0.0312	-0.0018	0.0024	-0.0028	0.0056	0.0066	0.0078	28
8/1/96 15:09	-0.0007	0.0013	-0.0094	0.0107	-0.0002	0.0021	0.0001	0.0246	-0.0021	0.0023	0.0001	0.0054	0.0036	0.0065	27
	C7H8	error	C2H4	error	O3	error	SF6	error	NO	error	NO2	error	SO2	error	TST #
8/1/96 15:34	-0.1065	0.0859	0.0005	0.0015	0.0013	0.0023	0	0	0.0545	0.1055	0.0196	0.0212	0.0203	0.0202	32
8/1/96 15:29	-0.101	0.0808	-0.0006	0.0015	-0.0029	0.0021	0	0	0.0545	0.1074	0.0181	0.0193	0.0113	0.0196	31
8/1/96 15:23	-0.0926	0.075	0.0001	0.0014	-0.0011	0.0021	0	0	0.0559	0.1104	0.0105	0.0202	0.0152	0.0199	30
8/1/96 15:18	-0.09	0.0805	-0.0006	0.0015	0.0013	0.0021	0	0	0.0542	0.1193	0.007	0.0237	0.0119	0.021	29
MIX added															
8/1/96 15:14	-0.0736	0.066	-0.0013	0.0015	0.0003	0.0024	-0.0001	0	-0.0025	0.0372	0.0226	0.015	0.0366	0.0118	28
8/1/96 15:09	-0.0646	0.0542	-0.0007	0.0013	-0.0009	0.0019	0	0	-0.0006	0.0278	0.0217	0.0142	0.011	0.0126	27

Note 1: units are designated in ppmv

Note 2: error is +/- added to the measured value

Table 21. Analysis of Mix #1 with Water Vapor Present in the Cell

The Expected Values (Exp Val) given above the appropriate compounds in the table are values based on the Scott Analysis of the gas mixture and the pressure ratios of gas mixture and total cell pressure. It may be seen that the FTIR reported values are in good agreement with the values expected for all compounds, the percentage differences being 3.8% for carbon tetrachloride, 8.5% for chloroform, and 0.95% for 1,2 - dichloroethane.

Similar data were collected for gas Mixture # 2 and the results are shown in Table 23. Here the same type of behavior is seen with an initial rise of concentrations leveling off by the third or fourth measurement. Again, the agreement between the FTIR-reported value and that expected from pressure ratios is seen to be very good for 1,1 - dichloroethene and 1,1 - trichloroethane with percent deviations of 5.1% and 1.9% respectively. Methylene chloride (DCM) is the exception because it showed an error of 20%. This could be due to an inaccuracy in the calibration reference, and for that reason, comparisons of the FTIR vendor reference to others available in industry were performed.

Three other reference spectra for DCM were generally available: one from the commercial library of Infrared Analysis, Inc. (the Haunts Library), one from the FTIR library of DMA, Inc., and one from the EPA library generated by Entropy. For each of these spectra the quantity "Area/ppm*m" was calculated. This was essentially the integrated area under the absorbance spectrum of the compound divided by the concentration-pathlength. This should be an invariant quantity if the spectra were measured at the same total pressure and absolute temperature. The values obtained for each of the spectra compared to the FTIR vendor reference are shown in Table 22.

Table 22. Comparison of Four DCM Reference Spectra

	FTIR Vendor	Hanst	MDA	Entropy	AVG
Area/ppm*m	0.0186	0.0205	0.0226	0.0242	0.0215

If the average value of these spectra are assigned to the FTIR vendor reference for DCM (REF5049.SPA), the calculated concentration for DCM in Table 23 increases to 0.193 ppm from it initial value of 0.166. This is much better agreement with the Expected Value, producing a percentage deviation of only 7.6%.

The above two analyses indicated that admitting water vapor to the cell eliminated the adsorption problems encountered with dry samples. To study this phenomenon further, an overnight test was conducted. For this test, room air was first admitted to the cell to a pressure of approximately 101 torr. Mixture # 3 was then added to a pressure of 130 torr, followed by an addition of Mixture # 1 to a pressure of 162 torr; Mixture # 2 to a pressure of 198 torr; Mixture # 4 to a pressure of 241 torr; and finally air again to a total pressure to 731 torr. This provided a mixture with all compounds present which was then sealed in the cell while measurements were taken every 50 minutes throughout the night. The results of the FTIR analyses on this sample over the total measurement period, which lasted just under 13 hours, are given in Table 24. As before, the Expected Values are based on the Scott values and the pressure ratios. The intent of this test was to look for loss effects. The tests should not be viewed as a test of absolute accuracy but only in terms of loss effects with time. It may be seen that with the possible exception of 1,2 - dichloroethane, very little loss was observed after the initial equilibration.

	Mix # 2	Analysis													
#Quantitation Method = WP C2 AIR 08/01/96 Components = 21 (modified)															
Exp Val =>													0.098		
Timestamp	AIR	error	CO	error	N2O	error	CH4	error	NH3	error	CH3OH	error	11DCE	error	TST #
8/1/96 16:48	688.9	2.531	0.0218	0.0046	-0.009	0.0027	0.0358	0.0182	-0.0001	0.001	0.0032	0.0038	0.1034	0.0028	37
8/1/96 16:43	693.5	2.506	0.019	0.0044	-0.011	0.0026	0.0225	0.0155	-0.0004	0.0009	0.003	0.0036	0.1052	0.0031	36
8/1/96 16:38	702.9	2.78	0.0167	0.0043	-0.0122	0.0025	0.0158	0.015	-0.0006	0.0011	0.0049	0.0033	0.0985	0.003	35
8/1/96 16:33	714.4	2.919	0.0117	0.0046	-0.0109	0.0027	-0.0079	0.017	-0.0011	0.0011	0.0025	0.0029	0.0642	0.0027	34
Exp Val =>			0.209						0.103						
	CCL4	error	DCM	error	CHFRM	error	1122T	error	111TA	error	CHBNZ	error	12DCA	error	TST #
8/1/96 16:48	0.0029	0.0015	0.1664	0.0122	-0.0025	0.0023	0.0589	0.0279	0.1053	0.0065	-0.0013	0.0152	-0.0306	0.0153	37
8/1/96 16:43	0.0029	0.0015	0.1674	0.0123	-0.003	0.0024	0.0566	0.0282	0.1074	0.0064	-0.0013	0.015	-0.0328	0.0159	36
8/1/96 16:38	0.0028	0.0016	0.1641	0.0132	-0.0024	0.0026	0.0554	0.0304	0.0978	0.0065	-0.0031	0.015	-0.0361	0.0159	35
8/1/96 16:33	0.0027	0.0015	0.0995	0.0128	-0.0047	0.0025	0.0589	0.0294	0.06	0.0067	-0.0017	0.0156	-0.0329	0.0159	34
	C7H8	error	C2H4	error	O3	error	SF6	error	NO	error	NO2	error	SO2	error	TST #
8/1/96 16:48	-0.0242	0.0364	0.0008	0.0014	-0.0025	0.0036	0.0001	0	0.0719	0.1534	0.0188	0.0238	-0.0403	0.0263	37
8/1/96 16:43	-0.0173	0.0385	0.0016	0.0014	-0.0051	0.0034	0	0	0.0758	0.1559	-0.0077	0.0204	-0.0408	0.0249	36
8/1/96 16:38	0.0081	0.0419	0.0009	0.0015	-0.0054	0.0031	0.0001	0	0.0745	0.1592	0.0002	0.0197	-0.0438	0.0266	35
8/1/96 16:33	-0.0095	0.0396	0.001	0.0016	-0.0015	0.0028	0.0001	0	0.0664	0.1758	-0.0179	0.0222	-0.0489	0.0263	34

Note 1: units are designated in ppmv

Note 2: error is +/- added to the measured value

Table 23. Analysis of Mix #2 with Water Vapor Present in the Cell

The next morning, the cell was pumped out and refilled with mixture #4 (which contained only 1,1,1 - trichloroethane) in moist room air. Measurements were then taken in the same fashion as done for Mixtures #1 and #2. The results of these measurements are shown in Table 25. Here the same characteristic behavior is seen with the gas initially equilibrating with a corresponding rise in gas concentration after which the mixture stabilizes. The final concentration value reached for 1,1,1 - trichloroethane was 0.241, which was within 8% of the expected value of 0.222.

No analysis was conducted on Mix # 3 because of the lack of an appropriate reference spectrum for 1,1,2,2 - tetrachloroethane (1122T). The data obtained with this sample was used to create a reference spectrum for this compound. Unlike the other compounds, with 1122T the cell contents were not stable even with water vapor present (the measured concentration declined steadily). To obtain a stable sample for generation of a reference spectrum, the cylinder gas was allowed to flow continuously through the cell to establish a stable concentration. Once the concentration stabilized, the reference spectrum was collected.

It was verified that having water vapor present in the cell minimizes the effects of the adsorption of other compounds on the cell walls. In the analysis of the various mixes, most results agreed very well with the FTIR vendor reference values to within a few per cent. The exception was methylene chloride (DCM) for which all results were within 20 %. This was reconciled by correcting the calibration of the FTIR vendor reference through comparison with other references available in industry.

#Quantitation Method = WP C2 AUSTST 8/01-02/96 Components = 22

Timestamp	H2O	error	CO	error	N2O	error	CH4	error	NH3	error	CH3OH	error
8/2/96 6:43												
8/2/96 5:52	9860.5	22.33	0	0.0092	-0.0146	0.0055	0.0216	0.0085	0.0003	0.0004	0.0044	0.0036
8/2/96 5:01	9855.1	22.34	-0.0006	0.0092	-0.0151	0.0056	0.029	0.0111	0.0006	0.0004	0.0042	0.0036
8/2/96 4:10	9893.4	18.93	-0.0018	0.0092	-0.0151	0.0055	0.0146	0.0084	0.0006	0.0003	0.0034	0.0037
8/2/96 3:19	9899.4	22.01	-0.002	0.0091	-0.015	0.0055	0.0134	0.0088	0.0006	0.0004	0.0024	0.0038
8/2/96 2:28	9925.2	19.63	-0.0033	0.0093	-0.0167	0.0056	0.0109	0.0083	0.0002	0.0004	0.0028	0.0039
8/2/96 1:37	9918.8	20.47	-0.0036	0.0092	-0.0169	0.0056	0.0093	0.0085	0.0001	0.0004	0.0023	0.0039
8/2/96 0:46	9946.9	19.23	-0.0035	0.0092	-0.0174	0.0056	0.0041	0.008	0.0001	0.0004	0.0023	0.0039
8/1/96 23:54	9964.1	19.67	-0.0041	0.0094	-0.0191	0.0057	0.0009	0.0125	0.0002	0.0004	0.002	0.0038
8/1/96 23:13	10013.4	20.43	-0.0051	0.0092	-0.0189	0.0055	-0.0064	0.007	0.0002	0.0004	0.0019	0.004
8/1/96 22:22	10030.2	20.99	-0.006	0.0093	-0.0193	0.0056	-0.006	0.0088	-0.0001	0.0004	0.0012	0.004
8/1/96 21:31	10060.3	19.32	-0.0076	0.0093	-0.0203	0.0056	-0.0156	0.0088	-0.0007	0.0004	0.0006	0.0042
8/1/96 20:40	10105.6	19.53	-0.01	0.0093	-0.0214	0.0056	-0.0274	0.0083	-0.0006	0.0004	-0.0004	0.0041
8/1/96 19:49	10169.5	24.2	-0.013	0.0093	-0.0227	0.0056	-0.0376	0.0097	-0.0007	0.0004	-0.0005	0.0042
8/1/96 18:58	10249.2	26.77	-0.0155	0.0095	-0.0242	0.0057	-0.0498	0.0113	-0.0013	0.0005	-0.002	0.0043
8/1/96 18:07	10357.7	35.2	-0.0196	0.0095	-0.0268	0.0057	-0.0886	0.012	-0.0018	0.0006	-0.0018	0.0044
	10564.3	51.1	-0.0261	0.0095	-0.0328	0.0057	-0.1112	0.0132	-0.003	0.0009	-0.0036	0.0049

MIX # =>																
EST VAL =	# 2		# 1		# 2		# 1		# 3		# 2 + 4				# 1	
Timestamp	0.0517		0.0438		0.1081		0.0916		0.0836		0.1586				0.0877	
8/2/96 6:43	11DCE	error	CCL4	error	DCM	error	CHFRM	error	1122T	error	111TA	error	CHBNZ	error	12DCA	error
8/2/96 5:52	0.0704	0.0033	0.0429	0.0002	0.0839	0.0019	0.1031	0.0004	0.0438	0.003	0.1507	0.0012	0.0018	0.0028	0.0853	0.0199
8/2/96 5:01	0.0702	0.0032	0.0429	0.0003	0.0837	0.0026	0.1029	0.0005	0.0452	0.0042	0.1517	0.0016	-0.0004	0.0034	0.0881	0.0277
8/2/96 4:10	0.0705	0.0031	0.043	0.0003	0.0844	0.002	0.1029	0.0004	0.0456	0.0032	0.1522	0.0011	-0.0018	0.0024	0.0724	0.0135
8/2/96 3:19	0.0705	0.0033	0.0431	0.0002	0.0834	0.0015	0.1026	0.0003	0.0457	0.0024	0.152	0.001	-0.0013	0.0022	0.087	0.0194
8/2/96 2:28	0.0704	0.0032	0.0432	0.0002	0.0834	0.0018	0.1025	0.0004	0.0465	0.0028	0.1525	0.0012	-0.003	0.0028	0.0835	0.0125
8/2/96 1:37	0.0703	0.0032	0.0431	0.0002	0.0824	0.0017	0.1021	0.0003	0.0487	0.0026	0.1519	0.001	-0.0015	0.0023	0.0904	0.0133
8/2/96 0:46	0.0706	0.0033	0.0432	0.0002	0.0831	0.0016	0.102	0.0003	0.0485	0.0025	0.1512	0.0011	-0.0013	0.0025	0.0891	0.0126
8/1/96 23:54	0.0706	0.0034	0.0432	0.0004	0.0834	0.0026	0.1018	0.0006	0.0477	0.0045	0.1516	0.0019	-0.0024	0.0042	0.0836	0.0182
8/1/96 23:13	0.0707	0.0031	0.0432	0.0002	0.0827	0.0014	0.1014	0.0003	0.0502	0.0022	0.1514	0.0009	-0.0003	0.0019	0.0845	0.013
8/1/96 22:22	0.0702	0.0032	0.0432	0.0002	0.0808	0.0014	0.1009	0.0003	0.0512	0.0022	0.1508	0.0009	0.0013	0.0019	0.0863	0.0143
8/1/96 21:31	0.0701	0.0032	0.0431	0.0002	0.0799	0.0017	0.1003	0.0003	0.0533	0.0027	0.1502	0.001	0.0018	0.0021	0.0733	0.0113
8/1/96 20:40	0.0703	0.0035	0.0431	0.0003	0.079	0.0024	0.0996	0.0005	0.0547	0.0038	0.1504	0.0012	0.0012	0.0028	0.0773	0.0157
8/1/96 19:49	0.0703	0.0032	0.0431	0.0003	0.0793	0.0025	0.0994	0.0005	0.0553	0.004	0.1513	0.0014	-0.0007	0.003	0.0752	0.0155
8/1/96 18:58	0.0707	0.0033	0.0432	0.0005	0.0776	0.0036	0.0984	0.0007	0.0582	0.0058	0.1523	0.0019	-0.0027	0.0042	0.0783	0.0176
8/1/96 18:07	0.0706	0.0033	0.043	0.0005	0.0761	0.0041	0.0975	0.0008	0.0614	0.0086	0.1512	0.0022	-0.0002	0.0049	0.0828	0.0174
	0.0713	0.0036	0.0433	0.0006	0.0752	0.0045	0.0964	0.0009	0.0655	0.0071	0.1541	0.0027	-0.0054	0.0059	0.0941	0.0181

Timestamp	C7H8	error	C2H4	error	O3	error	SF6	error	NO	error	NO2	error	SO2	error	CO2	error
8/2/96 6:43																
8/2/96 5:52	-0.0093	0.0097	0.0007	0.0006	-0.0046	0.0034	0	0	0.0564	0.0305	-0.0054	0.0093	0.0422	0.0153	609.8	0.4626
8/2/96 5:01	-0.013	0.015	0.0012	0.0006	-0.0043	0.0035	0	0	0.0463	0.0328	-0.0006	0.0122	0.052	0.0162	610.6	0.6407
8/2/96 4:10	-0.0066	0.0103	0.0008	0.0005	-0.0049	0.0035	0	0	0.0379	0.0302	-0.0057	0.0092	0.0471	0.0155	610.9	0.4816
8/2/96 3:19	-0.0053	0.0065	0.0004	0.0006	-0.0033	0.0036	0	0	0.0365	0.0284	-0.0109	0.0096	0.0429	0.0158	611.1	0.3585
8/2/96 2:28	-0.0082	0.01	0.0005	0.0005	-0.0045	0.0037	0	0	0.0292	0.027	0.0053	0.0091	0.0297	0.0154	611.8	0.43
8/2/96 1:37	-0.0122	0.0083	0.0006	0.0005	-0.0036	0.0037	0	0	0.0253	0.0267	-0.0018	0.0094	0.0419	0.0147	612.3	0.4032
8/2/96 0:46	-0.0039	0.0091	0.0007	0.0005	-0.0038	0.0037	0	0	0.022	0.0262	-0.0078	0.0087	0.0299	0.0149	613.1	0.3814
8/1/96 23:54	-0.0106	0.0171	0.0011	0.0005	-0.004	0.0038	0	0	0.0192	0.0512	-0.0103	0.0137	0.0415	0.0157	613.7	0.6819
8/1/96 23:13	-0.0017	0.0074	0.0003	0.0005	-0.004	0.0038	0	0	0.022	0.0266	-0.0033	0.0077	0.0266	0.0144	614.2	0.339
8/1/96 22:22	-0.0043	0.0087	0.0003	0.0006	-0.0035	0.0038	0	0	0.0224	0.025	0.0027	0.0076	0.0306	0.0144	614.1	0.3301
8/1/96 21:31	-0.0071	0.0078	0.0004	0.0005	-0.0038	0.004	0	0	0.0179	0.0241	0.0022	0.0075	0.0283	0.0149	614.6	0.4143
8/1/96 20:40	-0.0011	0.0135	0.0004	0.0006	-0.0041	0.0039	0	0	0.0195	0.0259	0.0004	0.0091	0.0273	0.0155	615.7	0.5766
8/1/96 19:49	-0.0063	0.014	0.0008	0.0006	-0.004	0.0039	0	0	0.0179	0.0262	0.0021	0.0106	0.0221	0.0155	617	0.8146
8/1/96 18:58	0.0005	0.0206	0.0009	0.0007	-0.0031	0.004	0	0	0.0199	0.0303	0.0033	0.0125	0.0226	0.0168	618.3	0.8877
8/1/96 18:07	-0.0025	0.0235	0.0009	0.0009	-0.0034	0.0042	0	0	0.0184	0.033	0.0011	0.0131	0.0113	0.0172	619.1	1.008
	-0.0019	0.0218	0.0009	0.0014	-0.0023	0.0046	0.0001	0	0.0135	0.036	-0.004	0.0144	0.0033	0.0188	621.5	1.088

Note 1: units are designated in ppmv

Note 2: error is +/- added to the measured value

Table 24. Analysis of Mixes #1-4 with Ambient Air

	MIX # 4	Analysis													
#Quantitation Method =	WP C2 AIR 08/01/96		Components = 21			(modified)									
Timestamp	AIR	error	CO	error	N2O	error	CH4	error	NH3	error	CH3OH	error	11DCE	error	TST #
8/2/96 10:02	680.6	3.5	0.0251	0.0045	-0.0058	0.0026	0.0731	0.0162	-0.0023	0.0011	0.0099	0.0114	0.0006	0.0013	43
8/2/96 9:57	686.1	3.491	0.0227	0.0045	-0.0077	0.0026	0.0598	0.0155	-0.0021	0.0011	0.0093	0.011	0.0015	0.0016	42
8/2/96 9:52	690	2.973	0.0203	0.0044	-0.0079	0.0026	0.0512	0.0154	-0.0011	0.0009	0.0096	0.0097	0.0007	0.0005	41
8/2/96 9:47	701.7	2.97	0.0168	0.0045	-0.0087	0.0026	0.0391	0.0139	-0.0013	0.0009	0.0059	0.0068	0.0009	0.0011	40
Exp Val =>									0.222						
	CCL4	error	DCM	error	CHFRM	error	1122T	error	111TA	error	CHBNZ	error	12DCA	error	TST #
8/2/96 10:02	0.0012	0.002	-0.0526	0.0169	-0.0089	0.0033	0.0903	0.0388	0.2407	0.0063	-0.0097	0.0148	-0.0113	0.0127	43
8/2/96 9:57	0.0012	0.0019	-0.0515	0.0158	-0.0089	0.003	0.0964	0.0361	0.2377	0.006	-0.0074	0.0141	-0.0114	0.012	42
8/2/96 9:52	0.0011	0.0018	-0.0494	0.0153	-0.0094	0.0029	0.0951	0.0351	0.2196	0.0057	-0.0103	0.0133	-0.0129	0.012	41
8/2/96 9:47	0.0014	0.0018	-0.0487	0.015	-0.01	0.0029	0.0924	0.0344	0.1772	0.0057	-0.0081	0.0132	-0.0166	0.0125	40
	C7H8	error	C2H4	error	O3	error	SF6	error	NO	error	NO2	error	SO2	error	TST #
8/2/96 10:02	-0.0858	0.0878	0.0016	0.0016	-0.007	0.0109	0.0001	0	0.0688	0.1433	-0.0114	0.0191	-0.0611	0.0252	43
8/2/96 9:57	-0.0343	0.0855	0.002	0.0016	-0.0071	0.0104	0.0001	0	0.0633	0.1461	-0.0163	0.0184	-0.0647	0.0229	42
8/2/96 9:52	-0.055	0.0779	0.002	0.0013	-0.0087	0.0093	0.0001	0	0.0686	0.1487	-0.0203	0.0183	-0.0577	0.0238	41
8/2/96 9:47	-0.0376	0.0801	0.0008	0.0013	-0.0076	0.0064	0.0001	0	0.0647	0.1563	-0.0295	0.0164	-0.0667	0.0233	40

Table 25. Analysis of Mix #4 with Water Vapor Present in the Cell

8.6 Additional Operational Observations

8.6.1 Unattended Duration

An ongoing examination of unattended FTIR operation has yielded some satisfactory results. One week of unattended operation was the original goal. The unattended operation was limited to the operator support that the extractive FTIR system required to swap out the nitrogen dewars. Originally, it was thought that the dewars needed replacement every 7-10 days. However, because the WIPP mine environment is dry and a constant temperature, the nitrogen dewars last 14-20 days. Another limiting condition is that every three to four weeks raw data must be downloaded from the computer and hard drive space must be cleared so that the computer hard drive capacity is not exceeded. Recently, the extractive FTIR system has undergone two weeks of unattended operation, thereby exceeding the original goals.

8.6.2 Remote Monitoring/Control

During the prototype testing in the underground, the ability to communicate directly with the FTIR data acquisition computer by a modem was demonstrated. After an initial startup delay due to configuring the communication software on the WIPP computers, daily remote monitoring of the instrument from above-ground may be practical. Other sites, according to the FTIR vendor, also use local area network connections which is traditionally a more reliable form of connection.

8.6.3 Comparison to Monthly Canister Sampling

A comparison was made with the July 15, 1996, canister sample taken at station VOC-8 which is located in the S1950 drift. The preliminary results of the canister analysis yielded nondetection for most of the target compounds. Methylene chloride was tentatively detected at .18 ppbv. Toluene was detected at .43 ppbv. From a summary of daily averaged values, the extractive FTIR system for Cell #1 bias corrected data read all compounds as nondetects. These results compare in that neither method returned any contrasting results with respect to reporting levels of any of the target compounds.

9.0 Quality Assurance and Quality Control Issues

Quality Assurance and Quality Control (QA/QC) issues fall into three areas: 1) those that are performed before monitoring to validate the instrument and analytical methods, 2) those that apply to the monitoring methodology itself, and 3) those related to post test validations of collected data. These areas are described individually below.

9.1 Prestart QA/QC Issues

Prestart QA/QC issues are related to the FTIR system performance. They focus on demonstrating that the instrument and its analytical methods are acceptable in providing the detection limits with the accuracy and precision required. Many of the tests discussed in Section 8.0 need to be performed to demonstrate that the instrument meets documented specifications. Of the tests discussed in Section 8, those that need to be performed prior to field testing include:

- EMI/RFI tests
- MDC tests
- Line-effects tests
- Resolution checks
- Linearity tests
- Accuracy and precision tests

These tests involve system characteristics or analytical method performance, and they will not change unless the configuration of the system is modified in some way. These tests are, consequently, performed at the beginning of a program and probably do not need to be repeated thereafter unless the system is altered.

9.2 QA/QC Tests Required During Measurements

System characteristics that can easily change based upon the system alignment or maintenance should be performed at the outset of all major test series and at regular intervals throughout tests of long duration. These tests, which were also discussed in Section 8.0, include the following:

- Signal-to-noise (NEA) tests
- Background (I_o) invariance
- Line shift tests

Generally, these tests should be repeated on a weekly basis to confirm system invariance and continued performance. If, during routine testing of these parameters, a significant change is observed that could influence the validity of the data, the system must be taken off-line and specific tests performed to determine the cause of the degraded performance. Appropriate repairs or adjustments must then be made to return the system to proper performance levels.

Other QA/QC activities required throughout routine testing periods include:

- Spot checking of data to confirm validity,
- Archival of all spectral and gas concentration data to assure proper custody, and
- Performance of routine maintenance to assure continued acceptable operation.

These are described individually in the subsequent sections.

9.3 Spot checks

The automated CLS routines analyze all spectra and report the gas concentration results. These methods work well provided they were developed properly at the outset and provided interferents are not present that the method is not prepared to handle. Therefore, throughout routine operation, spot checks should be made of all gas concentration data to identify any problems. This is done by first viewing plots of the concentration data with FTIR analysis software. In this review, trends in the data that are not expected, such as drifts in the quantitated values that never return to a low level or spikes in the data that appear simultaneously for a number of gases, are observed. For all data, the reported 95% confidence intervals are also viewed to ensure that they remain within acceptable bounds and are close to the expected minimum values.

If, in the review of the data, spikes or steps in gas concentrations are seen, these data sets are ideally suited for further "spot check" validations. These further validations are performed by retrieving the infrared spectra for the two measurement periods, just before and during a spike or step increase/decrease. By subtracting the two spectra, all features arising from gases that did not change will cancel. This leaves a very clean spectrum with features of only those compounds which changed between the two periods. This resulting "difference" spectrum can then be manually analyzed to quantitate all anomalies present. The quantitated values should agree with the difference in concentrations observed initially. If this agreement exists, the CLS values have been validated. If the manual and automated values do not agree, further investigation is necessary to identify and resolve the problem. Most often, it is an analytical method problem arising from interferences of unknown compounds.

If all data look reasonable, no further analysis is required. However, if any data look suspect, the infrared spectra must be retrieved and manually analyzed to determine if remedial action is necessary.

1) If a drift is observed, it is most frequently caused by bias induced by H_2O or CO_2. This bias can usually be confirmed by looking at the correlation plot between the analyte of interest and H_2O or CO_2. If a strong correlation exists, a bias is likely. This bias can be rectified by 1) generating a bias correction function based upon the data or 2) improving the match between H_2O/CO_2 references and the data.

2) If large error bars are observed, they are most often the result of interference by either

H_2O/CO_2 or by other non-naturally occurring compounds in the air. In either event, a modification to the analytical method will usually be required to eliminate it. The modification required is either a change in analysis regions/windows to eliminate the interference or the addition of the interferent to the method so it can be treated properly. The former action would be taken if the interferent is not of interest while the latter would be used if the interferent needs to be monitored along with the other compounds already in the method.

3) If any modifications are made to the analysis method, a permanent record of the changes made and the data impacted by the changes must be generated in the system log.

9.4 Archival of Data

An essential step during the data acquisition is the off-loading and archiving of all data as well as the generation of final "filtered" data files. This is a two-step process. First, all files need to be checked to verify that the file header contains all information necessary to uniquely identify the data. The normal parameters that the FTIR vendor software adds to the header include: date and time of the data collection, identification code for the system that collected the data, and a code indicating the specific cell used for collection. If these data are verified to be present in all files, the data are archived so at least two copies of all data are preserved at all times. Both the raw spectral data and the processed gas concentration data must be archived. The raw spectral data are the most critical since everything can be reproduced from it, if necessary, and it can be reprocessed with alternate analysis procedures yielding alternate compounds. Once the data have been validated and archived, filtered data sets can be generated using the FTIR vendor software filter functions. These filters allow data to be nulled if the signal voltage is insufficient for generation of valid data and allow for data to be flagged as a "no detect" if the concentration reported is less than a specified multiple of the error bar (usually two). These filtered files then become the data sets that will contain only the valid data.

9.5 Routine Maintenance

Instrument maintenance is critical to the continued collection of quality data. Several items that require continuous attention at different intervals include:

- Replacement of extraction line filters
- Replacement/refilling of the liquid nitrogen dewar
- Other filters

In addition, if an electric cryogenic cooler was ever used in place of liquid nitrogen dewars as the method for cooling the FTIR MCT detectors, typical service or replacement of this cryogenic cooler is estimated to be yearly.

9.5.1 Replacement of Extraction Line Filters

The exact interval for replacement of the extraction line filters has not been fully established. The filters were replaced after three months of continuous monitoring to observe the amount of visible salt particulate that had accumulated on the filter material. However, by appearance, the condition of the filters looked like they could still have lasted at least another month.

The operational check of the filter would be the primary indicator that a replacement filter is needed. As the filter gets clogged, the fill pressure in the cells will decrease. Because this is a parameter recorded with each data point collected, the pressure can be monitored and when it falls below a prescribed level (approximately 650 torr) the filter will need to be replaced.

9.5.2 Replacement/Refilling of the Liquid Nitrogen Dewar

The liquid nitrogen dewar lasts for two (or more) weeks before refilling is required. A regular schedule should be set up to change dewars or refill the underground dewar with at least 15% capacity remaining so data is not lost due to a lack of liquid nitrogen. The software records the fill times and duration for both detectors in the monitor. These times/durations can also be used as an indicator of the amount of liquid nitrogen being used. It is also a good way to assess the health of the detector dewars themselves since as these detector dewars loose vacuum the frequency of filling will increase. When the fill times become less than five to six hours apart, the detector dewars must be re-evacuated.

9.5.3 Other Filters

The air filters that remove H_2O and CO_2 from the sample inlet system of the FTIR spectrometer should also be replaced when the fill line filters are replaced. Also, once per year the oil and output filter of the vacuum pump must be replaced.

9.6 Poststart QA/QC Procedures

Once a test series is complete, all data must be archived as discussed above. A full set of spectral data should be backed up on optical disks, magnetic tape, or removable media hard drive disks. Since the gas concentration data are smaller in volume, they can be archived in any convenient manner. It is critical to archive the analysis method used, as well as all reference spectra used by the method, to ensure that the data can be reproduced from the spectra if necessary.

Because short-term checks are made of all data during the collection, the final data review should focus predominantly on long-term trends. Trends that are unexpected or abnormal are flagged, and the data scrutinized more thoroughly. A review of both the concentration data and its error bars are necessary as well as manual reprocessing of spectra to verify or negate specific data. If any data are modified, the reasons for the modification must be entered in the system log book so all activity can be traced and reproduced if necessary.

At the end of the measurement program, plots of all system parameter checks should also be made so the long term trends can be viewed. This would include data such as measured NEA, observed

line shifts, if any, and peak-to-peak interferogram signal. Reduced quality data, if any, should be flagged, noted, and reported with the data in an appropriate manner. Any unique events occurring during the test will also be documented and included in the appropriate data report.

9.7 Data Review/Interpretation

If concentrations are defined to be above the detection limit for a given target compound, the qualitative identification of the compound should be assessed in the following manner:

1) Examine the concentration plot of the compound for trends relative to levels of other atmospheric constituents (e.g., H_2O, CO_2, CO) and relative to instrument conditions (e.g., voltage, cell pressure). Concentration plots that follow trends in these other parameters may be suspect, indicating biases and/or false positives/negatives in the data.

2) To the extent possible, eliminate invalid data from the data file and save the censored data file under a new name. Data censoring may occur as a result of instrument or facility operating conditions or because remote or WIPP facility personnel activities interrupted data collection.

3) Assess whether observed concentration increases are accompanied by increases in total measurement error. This result may indicate that the observed concentration increases are not real.

4) For the data that exceed a compound-specific concentration of concern for each 24 hour averaging period, the difference spectrum should be generated by subtracting the upstream sampling data from the downstream sampling data. Then, a manual comparison can be made to the library reference spectrum for that compound. This will aid in assessing the reliability of the identification.

5) For reported negative concentrations smaller than the lower error bound, investigate potential causes for the results. The results may require comparison of spectral overlays of the sample spectrum relative to different reference spectra or consideration of other interfering variables (i.e., H_2O, CO, CO_2).

6) Once a final valid concentration data file is compiled, the results can be processed monthly for assessment relative to the concentrations of concern. Concentrations below the detection limit, and/or whose error bars include the detection limit, should be reported as the value of the detection limit.

7) If, in the judgment of the data reviewer, these checks support the identification of the target compound, the compound may be reported as detected. If the checks do not support the identification of the target compound, report the compound as the value of the detection limit.

9.8 Data Generation

If the sampling and analysis interval is set at 10 minutes, the amount of raw data generated is approximately nine megabytes a day. The files that contain the processed concentration data to be imported into a spreadsheet or database take up approximately 120 kilobytes per day. The method of long-term storage of the raw data itself is still under consideration. Presently, the raw data is stored on 3.5 inch 270-megabyte (MB) cartridge disks, the WIPPNET network, and archived onto 650 MB Compact Discs (CDs) using a CD recorder. Raw data may be stored in this manner for a period of about three years before recycling the storage disks. Alternatively, the processed data may be more easily managed on the present Syquest cartridge storage system. A 270-MB cartridge could hold 12.8 years worth of processed data with compression.

An emerging technology, slated for introduction at the end of this year, is digital video disc (DVD) which is a multi-layered Compact Disc-Read Only Memory (CD-ROM) technology purported to store between 8 gigabytes to 18 gigabytes of data. If this technology were used, then two year's worth of raw data could be stored (approx. 6.7 gigabytes) on one 5-inch DVD disk.

9.9 Data Handling and Records

The prototype testing period demonstrated that downloading, backups, and archiving of data are achievable. The processed data can be retrieved remotely by modem. On a bi-weekly basis, typically on the same trip when changeouts of the liquid nitrogen dewar are required, an operator downloads the raw data to 270 MB cartridges. The hard drive of the computer is then cleared of the raw data to allow for further data collection. Raw data is then copied onto a network drive. Another networked computer containing a CD-ROM recorder archives the raw data onto a primary CD and a secondary CD for backup. A CD will now hold about two and a half months of raw data without data compression and about five months with data compression. These CDs can then be considered a quality record because the processed data also contains the operating quality parameters of the system to verify the instrument was working correctly.

10.0 Summary

The WIPP extractive prototype FTIR system arrived the first week of June, 1996, and has been in operation since its initial deployment. Initial calibrations, alignments, and tests were conducted above ground in the Trupact II Maintenance Facility (TMF). The majority of tests including data recovery were conducted in the WIPP underground in and around Room 1, Panel 1. A summary of the notable results is as follows:

- A 95 percent (or better) data recovery rate was achieved during testing, which strongly supports the concept that this originally lab-oriented technology can be deployed to consistently function and report data in the WIPP underground environment.
- The extractive FTIR system functions properly during mining operations even though excess noise and vibration may be present.
- The extractive FTIR system can operate in the presence of EMI from small motors on the same circuit.
- Results from tracer gas tests compare favorably with canister sampling analysis results.
- Salt loading appears to have minimal impact on the operation of the extractive FTIR system, which is housed in a protective trailer and equipped with salt particulate filters on the inlet lines.
- While not completely validated by WIPP facility personnel, minimum detections on the majority of target compounds are suitable for compliance purposes (levels of regulatory concern can be detected).
- Method validation tests prove that the majority of target analytes can be identified and quantified using the classical least squares software. The remaining analytes will be the focus of future testing.

While the process for implementing quality assurance is not fully developed for the WIPP extractive FTIR prototype system, it appears that the development of a set of operational procedures will be straightforward.

When the FTIR system was challenged with "dry" gas standards, some VOCs adsorbed to surface(s) within the sampling cells. When ambient air was introduced in conjunction with the gas standards, water molecules would adsorb to the same surface within the sampling cells instead of the VOCs to allow for more accurate quantitation.

WIPP facility personnel have operated and collected data from the WIPP prototype extractive FTIR system for three months. During this time, facility support has been solicited and provided with minimal impact to normal underground operations. The only support and maintenance required for the FTIR system were:

- Bi-weekly nitrogen dewar transportation and change out
- Changing out the vacuum pump oil (has occurred once to date)

- Bi-weekly downloading of raw data to cartridge disks and clearing FTIR of computer hard drive space
- Downloading of processed data remotely by modem
- Use of a tractor with a hitch to temporarily move the FTIR trailer during roofbolt detensioning in Room 1 (approximately every five weeks), which indicates the system is somewhat mobile

WIPP facility personnel will continue to operate the extractive FTIR prototype system and collect data throughout FY 1997 for the purposes of resolving data quality issues and developing the appropriate operating procedures and quality assurance documentation.

11.0 RECOMMENDATIONS AND CONCLUSION

11.1 Program Personnel

The VOC monitoring personnel have demonstrated the ability to operate the extractive FTIR system, change out nitrogen dewars, download processed and raw data, and perform daily QA checks on instrument operation with minimal training. The cognizant engineers successfully solicited support for power, compressed air, nitrogen dewar transportation, and moving the FTIR system trailer when required. It is recommended that an analytical scientist or a spectroscopist be utilized in the future to perform data review and interpretation. Alternatively, these services could be obtained from an independent spectroscopist or the current FTIR vendor.

11.2 Computer Support

Because of the amount of data generated, appropriate computing power will be required to retrieve, store, and possibly post-process raw data. Technology is continually introducing higher processing power, storage options, and better organizational operating systems and software. The computer handling requirements of an FTIR system will become a more manageable task. Two Pentium™-class computers with three gigabytes or more of hard drive space, 270 MB cartridge drives, and a CD-ROM recorder is recommended to meet the requirements for fast and user-friendly data handling, data processing, and data archiving.

11.3 Future Effort

Future efforts will be focused on developing the quality assurance requirements from the initial sampling to the final reported concentrations. It is recommended that meetings with environmental regulators be initiated pending the acceptance of further use of this technology. The specific areas that require additional efforts are described in the subsequent sections.

11.3.1 Data Reduction and Reporting

Due to the quantity of data generated by the FTIR system each day, guidelines for evaluating measured data validity and reducing the data to an adequate level for reporting purposes (i.e., 24-hour averages) must be developed. A review of the data collected through mid-August 1996 was performed at the WIPP facility on August 16, 1996. The time series plots of the data indicated occurrences of baseline drift, potential intercorrelations between reported concentrations and other system variables, positive or negative data biases, and concentration variability.

For detected compounds, it is recommended that the 24-hour average be reported along with the maximum 10-minute average concentration measured over the 24-hour period, with associated total error. The summary report should indicate the detection limit for nondetected target compounds and provide the associated detection limit for each measurement day. For each valid 24-hour target compound concentration that exceeds a concentration of concern, the reported concentration shall be manually validated. Cell #1 and cell #2 concentrations should be reported separately, and the difference between upstream and downstream locations should be calculated

for each day. A daily average can be reported by averaging all concentrations measured over the 24-hour period (using the detection limit for BDL values) or by determining a concentration from a 24-hour, signal-averaged spectrum Use of a 24-hour signal-averaged spectrum may also be an appropriate tool to perform tentatively identified compound (TIC) searches.

11.3.2 Tentatively Identified Compounds

It may be possible to assess potential TICs by calculating a 24-hour, signal-averaged spectrum and subtracting out the water reference, background, and any detected target compounds. The peaks in the remaining difference spectrum may be compared to the library standard spectra for common VOCs (e.g., the EPA Target Compound List) to identify potential TICs. Concentrations can be estimated from the library reference standard concentrations with corrections for the cell length and pressure. It is recommended that this procedure for identifying TICs be included in the manual validation of reported target compound concentrations.

11.4 Conclusion

Although there are issues that will need to be thoroughly addressed before the FTIR technology can be considered the technology of choice for compliance purposes at the WIPP facility, this report demonstrates that FTIR technology can be supported by WIPP facility personnel in the WIPP mine environment.

There has been minimal impact to underground facility operations since deployment of the extractive prototype FTIR system at the WIPP facility. The main facility support required, that of transporting liquid nitrogen dewars for change-out purposes, has been coordinated to coincide with routine material trips at the waste and salt shafts.

Most of the performance tests described in Section 8 were successful in achieving their stated goals. The majority of target compounds had accuracies of less than 10 percent difference when gas standards were introduced into a similar extractive FTIR system at the FTIR vendor facility. The extractive prototype FTIR system at WIPP must be challenged with gas standards on a periodic basis to help maintain the accuracy of the system and to also aid in validating sampling data. The major issue that will require further testing and optimizing is the accuracy and minimum detectable concentration for 1,2 - dichloroethane. Sampling cell adsorption which leads to quantitative inaccuracies for a few target compounds, especially 1,2 - dichloroethane, is another area for improvement. Coating the walls of the sampling cells with a passivated material will be performed if cell losses cannot be improved by other operational means.

The QA/QC issues for validating the data appear to be on the same order, or less, than what is required for the canister sampling program. The major tradeoff benefit is the access to a larger statistical amount of data that can more accurately denote changes in concentrations of target compounds present during the disposal phase at the WIPP facility.

While the data generated is considerable by some standards, this system provides the ability to

continuously look at VOC emissions from Panel 1. Future compliance decisions can be made based on this larger set of statistical data. The majority of results described in Section 8 indicate that the WIPP extractive FTIR prototype system can function in the WIPP mine, provide on-line information that can be viewed and retrieved remotely, and operate unattended for weeks at a time, providing efficient measurements with high confidence.

REFERENCES

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ATTACHMENT 1

DRAFT OPERATING PROCEDURE CHECKLISTS DEVELOPED FOR WIPP PROTOTYPE EXTRACTIVE FTIR SYSTEM

Draft Checklist #1: Changing Out External Nitrogen Dewar with a Newly Filled Dewar

This activity shall be performed approximately every two weeks, after delivery of a newly filled liquid nitrogen dewar and when the external nitrogen dewar is reading less than 15% full.

Inside the FTIR Trailer

1) Turn off power to the two auto-fill control boxes by depressing the power button and noting that the display bulbs dim and extinguish.

External to the FTIR Trailer

2) Don the appropriate safety gear (Face shield and insulated gloves).
Note: Understand and follow the appropriate WIPP procedure on handling liquid nitrogen

3) Make sure the nitrogen dewar valve is completely closed.

4) Disconnect the liquid nitrogen dewar from the braided nitrogen line.

5) Inform fork lift operator to transport nitrogen dewar to the appropriate shaft to bring to the surface.

6) Ensure that the pressure gauge on the full nitrogen dewar reads approximately 22-25 psi.

7) Connect the dewar to the braided nitrogen line.

8) Open the valve to release liquid nitrogen.

Internal to the FTIR trailer

9) Turn both auto-fill control boxes on by depressing the power buttons.
Note: The system should auto-fill if it has been disconnected more than a few hours.

Draft Checklist #2: Relocation of FTIR Trailer

Internal to the FTIR Trailer

1) Stop the data collection process on the FTIR computer, exit Windows™, and power down the computer.

2) Power down the FTIR spectrometer (switch located in the back left corner of the FTIR spectrometer)

3) Power down the auto-fill control boxes.

4) Turn the control box switches (below the optical transfer box) to the bottom position (closed) position.

5) Carefully open the spectrometer cover, and fasten the foam plug to prevent the scanning mirror motor from locking during the transit of the FTIR trailer.

   Note: This step is not needed when relocating the FTIR trailer less than 30 feet and attention is made not to excessively jar the trailer.

6) Disconnect and pull out the sampling lines from inside the FTIR trailer.

7) Apply duct tape to ends of the sampling lines to prevent salt from entering the lines.

External to the FTIR Trailer

8) Power down and disconnect the vacuum pump located underneath the trailer, below the pull-down door area.

9) Disconnect the compressed air line.

10) Disconnect the power cords and/or extension cords from the outlets.

11) Don the appropriate safety gear, and following the appropriate WIPP procedure, close the valve on the nitrogen dewar, and then disconnect it.

12) Relocate the FTIR trailer and the liquid nitrogen dewar.

13) After relocation of the trailer and liquid nitrogen dewar to the original position, don the appropriate safety gear and reconnect the liquid nitrogen dewar to the FTIR system.

14) Open the valve of the nitrogen dewar.

Draft Checklist #2: Relocation of FTIR Trailer (continued)

Internal to the FTIR Trailer

15) Remove the foam plug internal to the spectrometer.

    Note: This step is not required if step 5 was not performed.

16) Reconnect the sampling lines to the appropriate connectors underneath the sampling cells.

17) Reconnect the compressed air line.

18) Reconnect the power lines and extension cords and restore power.

19) Turn the control box switches to the center (computer control) position.

20) Start up computer.

    Note: The system will automatically restart itself.

Draft Checklist #3: Monthly Check of the FTIR Noise Equivalent Absorbance on the FTIR

1) Open up the OMNIC® program window.

2) Choose the "Collect" option, then "Optical Bench Setup" pull down menu.

3) Set the setup to "32 scans" on the instrument.

4) Set the setup to "4 wavenumber" resolution.

5) Set the final format to "Absorbance" file format.

6) Set background handling to "before every sample."

7) Select "Okay."

8) Choose the "Collect Sample" option.

9) Select "Okay."

10) Select "Okay."

Note: The instrument is now taking a background sample.

11) Select "Okay."

12) Select "Yes" to add to window.

13) Look at the noise region in approximately the 1000 to 900 wavenumber range

14) Note the peak-to-peak value in Absorbance Units

Acceptable Range (Absorbance Units)	As Found (Absorbance Units)
5×10^{-4}	

15) Observe at the noise region in approximately the 2400-2500 wavenumber range.

Acceptable Range (Absorbance Units)	As Found (Absorbance Units)
5×10^{-4}	

16) Save this test file as _____.SPA and as a Quality Control Record.