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Topical Report

Fourier Transform Infrared (FTIR) Method Validation at a Natural Gas-Fired Internal Combustion Engine

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Environment and Safety Research
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In response to Title III of the 1990 Clean Air Act, the Gas Research Institute (GRI) is investigating air toxics emissions from natural gas industry sources. Included in this effort are measurements from internal combustion engines, one of the source categories targeted by U.S. Environmental Protection Agency (EPA). Formaldehyde and other aldehydes are potentially present in engine exhaust. Since there were no EPA-validated methods for quantifying reciprocating engine aldehyde emissions, GRI conducted a test to validate extractive Fourier Transform Infrared (FTIR) method using EPA Method 301. Due to the ability of FTIR to measure multiple species on a continuous and real-time basis, other compounds, NO_x, CO, CO_2, and moisture, were also included in this effort. Validation of formaldehyde, acetaldehyde, and acrolein was conducted using analyte spiking, while the validation of NO_x, CO, CO_2, and moisture was based on direct comparison to the applicable EPA reference methods.

On July 21, 1995, the U.S. EPA approved the test results presented in this report and indicated that the results *"can be considered valid according to Method 301 for this source and similar sources"* and the proposed FTIR test protocol based on the validation testing results *"may be used at any gas-fired facility"*.

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RESEARCH SUMMARY

TITLE	Fourier Transform Infrared (FTIR) Method Validation at a Natural Gas-Fired Internal Combustion Engine
CONTRACTOR	Radian Corporation GRI Contract Number: 5091-254-2293
PRINCIPAL INVESTIGATORS	Gunseli Sagun Shareef, Larry D. Ogle, and Jeffrey P. LaCosse
REPORT PERIOD	May 1994 - July 1995
OBJECTIVE	To develop and validate effective measurement technologies for pollutants of potential concern in internal combustion engine exhaust.
TECHNICAL PERSPECTIVE	In response to Title III of the 1990 Clean Air Act, GRI is investigating air toxics emissions from natural gas industry equipment, including internal combustion engines. Formaldehyde and other aldehydes are potentially present in engine exhaust. GRI and member companies have plans to collect air toxics emissions data to advance the information base. Such data could also facilitate industry participation in EPA's Maximum Achievable Control Technology (MACT) based standard development for the engines source category. To ensure acceptability of such data, there is a need to use validated methods for measuring emissions of pollutants of concern. However, there were no EPA-validated methods for quantifying formaldehyde and other aldehydes potentially present in engine exhaust.
TECHNICAL APPROACH	Testing was conducted to validate extractive FTIR method for measurement of formaldehyde, acetaldehyde, and acrolein according to the EPA Method 301 -- Field Validation of Pollutant Measurement Methods from Various Waste Media. Since FTIR is capable of measuring multiple species on a continuous and realtime basis, other compounds, NO$_x$, CO, CO$_2$, and moisture, were also included in this validation effort. For validation of aldehydes, the analyte spiking procedure was used, while the validation of the other compounds was based

TECHNICAL APPROACH (Continued)

on direct comparison to the applicable EPA reference methods (Methods 7E, 3A, 10, and 4 for NO_x, CO_2, CO, and moisture, respectively).

The validation test was conducted on July 11-15, 1994 at a GRI member company's facility in the Midwest. Samples were taken from a Cooper-Bessemer GMV-10TF engine rated at 1,100 hp. Engine operating parameters were monitored during the validation testing; however, no attempt was made to optimize engine performance or minimize emissions.

A Nicolet Model RS-3 FTIR bench equipped with a gas cell adjusted to a path length of 10.8 meters was used to obtain maximum sensitivity for the compounds of interest while minimizing interferences from high concentrations of moisture and carbon dioxide. The cell had a 32-inch mirror spacing inside a 4-inch ID stainless steel tube (Model 4-32-AU, Infrared Analysis). The spectral data were recorded using a flow-through cell maintained at 365° F. The cell pressure was monitored continuously during the measurements. Instrumental resolution was set at 0.5 cm^{-1} for all validation and reference spectra measured. Quantitation of the spectral data was based on classical least squares and band area techniques.

RESULTS

Based on the calculational procedures in EPA Method 301, the FTIR data met the precision and bias criteria in the method for all of the target compounds. EPA also made available a draft, revised Method 301 which includes revised statistical procedures. Calculations performed according to the revised procedures indicated that the FTIR data met the revised method criteria as well.

The results of this validation testing were submitted for EPA's review and approval in mid-1995. On July 21, 1995, EPA, in a letter to GRI, indicated that the test results "*can be considered valid according to Method 301 for this source and similar sources*" and the draft FTIR test protocol based on the validation testing results "*may be used at any gas-fired facility*".

PROJECT IMPLICATIONS

There is a need to develop and validate effective measurement technologies for quantifying air toxics emissions of potential concern from natural gas industry equipment. With EPA's MACT rule development for the internal combustion engines source category targeted for the year 2000, GRI and member companies have plans to collect air toxics emissions data to advance the information base. These data could facilitate industry participation in EPA's MACT development effort. Since there was no EPA-validated method for measuring aldehydes in engine exhaust, the FTIR method developed and validated by GRI provides an EPA-approved measurement tool for the gas industry.

The validation testing also included measurements of NO_x, CO, CO_2, and moisture in engine exhaust. Therefore, the FTIR test protocol serves as a single measurement approach with which the industry can monitor air toxics and criteria pollutant emissions from engines simultaneously.

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Executive Summary

Under Title III of the 1990 Clean Air Act, the U.S. Environmental Protection Agency (EPA) is developing air toxics regulations for various source categories. The target promulgation dates for the oil and gas production industry and for the stationary internal combustion (IC) engines source category are 1996 and 2000, respectively. Because these regulations could have large economic and operational impacts on the gas industry, Gas Research Institute (GRI) initiated an air toxics research program. A survey of the air toxics emissions data in the first phase of this program identified critical research needs for field measurement of key emission sources and development of effective measurement technologies, with preliminary field measurements in Phase II of the study indicating IC engine air toxics emissions to be a potential concern.

GRI and its member companies have plans to continue to collect air toxics emissions data to advance the information base. In addition, such data could facilitate industry participation in EPA's maximum achievable control technology (MACT) based regulation development. To ensure acceptability of such data, there is a need to use validated methods for measuring emissions of the pollutants of concern. However, there are no EPA-validated sampling and analytical methods available for measuring formaldehyde and other aldehydes which are potentially present in the engine exhaust. Measurement methods exist for these compounds in other sources, such as boilers and industrial furnaces firing hazardous waste, but the methods have not been validated for gas industry related sources. Therefore, GRI conducted a study for validating the extractive Fourier Transform Infrared (FTIR) spectroscopy method according to EPA Method 301--"Field Validation of Pollutant Measurement Methods from Various Waste Media." Method 301 is a set of procedures to be followed in validating a proposed test method for a particular emission source/category; it is not a measurement method.

The target compounds for the validation testing are shown below:

- Acetaldehyde;
- Acrolein;
- Formaldehyde;
- Carbon Monoxide (CO);
- Carbon Dioxide (CO_2);

- Oxides of Nitrogen (NO_x); and
- Moisture.

Since FTIR is capable of measuring multiple species on a continuous and realtime basis, NO_x, CO, CO_2, and moisture were also considered in this validation. Field validation testing was conducted on July 11-15, 1994 at a GRI member company's compressor station facility in the Midwest. Samples were taken from a Cooper-Bessemer GMV-10TF 2-cycle engine rated at 1,100 horsepower. Engine operating parameters were monitored during the validation testing; however, no attempt was made to optimize engine performance or minimize emissions.

Based on the calculational procedures in EPA Method 301, the FTIR data meet the criteria specified in the method for all of the target compounds. EPA also made available a draft, revised Method 301 which includes revised statistical procedures. Calculations were performed according to the revised procedures, which also indicated that the FTIR data meet the revised method criteria. The following tables present a summary of results, with precision and bias acceptability information and correction factors (where applicable) calculated according to both versions of Method 301.

Table S-1

Validation Results Summary -- Analyte Spiking[a]

Parameter	Formaldehyde		Acetaldehyde		Acrolein	
	301	DR301	301	DR301	301	DR301
Precision Acceptable?	Yes	Yes	Yes	Yes	Yes	Yes
Bias Statistically Significant?	No	Yes	No	Yes	Yes	Yes
Correction Factor	--	0.90	--	0.95	1.14	1.14
Meet Validation Criteria?	Yes	Yes	Yes	Yes	Yes	Yes

[a]301 = Method 301.
DR301 = Draft Revised Method 301.

Table S-2

Validation Results Summary -- Paired Sampling[a]

Parameter	NO_x		CO		CO_2		Moisture	
	301	DR301	301	DR301	301	DR301	301	DR301
Precision Acceptable?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Bias Statistically Significant?	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Correction Factor	1.02	1.02	0.98	0.98	0.98	0.98	--	--
Meet Validation Criteria?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

[a]301 = Method 301.
DR301 = Draft Revised Method 301.

The EPA has reviewed the results presented in this document and indicated in a July 21, 1995 letter to GRI that the results *"can be considered valid according to Method 301 for this source and similar sources"* (see Appendix A).

Additionally, the EPA stated that the proposed FTIR test protocol drafted based on the validation testing results *"may be used at any gas-fired facility"* (see Appendix B for the FTIR test protocol).

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1.0 INTRODUCTION

1.1 Background

In the 1990 Clean Air Act Amendments (CAAA), Congress included provisions to reduce emissions of hazardous air pollutants (HAPs) considered to pose a risk to human health and the environment. The U.S. Environmental Protection Agency (EPA) defined a schedule for developing air toxics regulations for various source categories. The accelerated schedule includes a target promulgation date of mid-1996 for the oil and natural gas production industry. In addition, air toxics regulations for stationary internal combustion (IC) engines are scheduled for promulgation in 2000. Additionally, several states have air toxics regulatory initiatives underway that will impact the natural gas industry.

Because these regulations could have large economic and operational impacts on the gas industry, the Gas Research Institute (GRI) contracted with Radian Corporation to conduct a multi-phase research program to determine potential sources of air toxics emissions, the quantities emitted, individual species present at each source, and the potential risk they pose. A survey of the air toxics emissions data in Phase I of this program identified critical research needs for field measurement of key emission sources and development of effective measurement methodologies. Among the key emission sources are IC engines used for compression and transmission of natural gas in the industry.

Preliminary testing on natural gas-fired engines performed during the first three field campaigns (late 1993 and early 1994) showed potentially significant emission levels of formaldehyde from some engines. In these tests, extractive Fourier Transform Infrared (FTIR) spectroscopy and manual methods [SW-846 Method 0011 and California Air Resources Board (CARB) Method 430] were used for measurement of the aldehyde species.[1,2] Differences between the FTIR method and the manual methods were observed in some of the test results. Additionally, high variability was observed in

CARB Method 430 triplicate measurements during test runs. Both manual methods are based on derivatization of the aldehydes with 2,4-dinitrophenylhydrazine (DNPH) in impinger solutions. In several cases where aldehydes were observed using the FTIR, they were not observed in the analysis of the manual method samples, although trace amounts were found in the field blanks. Impinger solutions were observed to be clear instead of the orange color typically associated with DNPH, indicating a potential cross-reaction which consumed the derivatizing reagent. Recent results reported in literature indicate potential interferences may be caused by nitrogen dioxide (NO_2) present in the exhaust gas.[3,4]

Similar problems were observed with the manual methods in laboratory studies under controlled conditions. However, laboratory spiking studies and line loss tests conducted using the FTIR method consistently resulted in recoveries at or greater than 90 percent for the spiked aldehydes (formaldehyde, acetaldehyde, and acrolein).

1.2 Objective

GRI and its member companies have plans to participate in EPA's MACT regulation development by continuing to collect air toxics emissions data. To ensure acceptability of such data, it is critical to use validated methods and procedures for measuring emissions of pollutants of concern. Currently, there are no EPA-validated measurement methods available for quantifying formaldehyde and other aldehydes potentially present in the engine exhaust. Measurement methods exist for these compounds in other sources, such as boilers and industrial furnaces firing hazardous waste, but the methods have not been validated for gas industry related sources. As described above, problems were observed using the DNPH-based methods for characterizing the exhaust from some engines.

Based on the data collected during the preliminary testing and the laboratory study, GRI conducted a field test (July 11-15, 1994) to validate the extractive FTIR method for formaldehyde, acetaldehyde, and acrolein. Since FTIR is capable of measuring multiple species on a continuous and realtime basis, oxides of nitrogen (NO_x), carbon monoxide (CO), and carbon dioxide (CO_2) were also considered in this validation. The comparison between FTIR and the EPA reference method results for these species was made on a dry basis, necessitating collection of moisture data for this correction. Therefore, validation of moisture measurements using FTIR was also undertaken during this testing effort. The target compounds are summarized below:

- Acetaldehyde;
- Acrolein;
- Formaldehyde;
- Carbon Monoxide (CO);
- Carbon Dioxide (CO_2);
- Oxides of Nitrogen (NO_x); and
- Moisture.

1.3 Approach

In validating the extractive FTIR method for measurement of the pollutants listed above, the procedures outlined in Method 301--"Field Validation of Pollutant Measurement Methods from Various Waste Media" were followed (see Appendix C). A test plan was submitted for EPA's review and comment before the field testing. For validation of the aldehydes, the analyte spiking procedure from Method 301 was used, as consistent with the validation testing conducted by EPA on a coal-fired boiler.[5] For validation of NO_x, CO, CO_2, and moisture using FTIR, a paired sampling system was employed since EPA reference methods exist for measuring these compounds (Method 7E, 10, 3A, and 4, respectively).

Field measurements were based on extraction of a slip-stream of the IC engine exhaust through a heated transfer line and delivery of a portion of this sample stream to the analytical instruments for concentration measurements. FTIR analysis of this extracted sample was performed on a hot/wet basis, as removal of moisture can result in losses of aldehydes. Conditioning of the gas sample was necessary for CO, CO_2, and NO_x measurements using the EPA reference methods. For a direct comparison between the reference methods and FTIR, the FTIR data were converted to a dry basis. Moisture in the gas stream was measured using EPA Method 4, as well as a direct measurement with the FTIR method.

The testing was broken into two separate periods which were performed over two days in the field. On July 13, 1994, validation testing was performed for formaldehyde, acetaldehyde, and acrolein. The testing for CO, CO_2, NO_x and moisture was conducted on July 14, 1994.

2.0 SITE DESCRIPTION

2.1 Test Site

The sampling site for the testing was a GRI member company's compressor station facility in the Midwest. The engine selected for the validation testing was a Cooper-Bessemer GMV-10TF, 2-cycle unit rated at 1,100 horsepower. This engine is considered to be representative of 2-cycle engines used in the natural gas industry. In addition, measurable levels of the target compounds listed in Table 1-1 were present in its exhaust.

Engines at this site were housed inside a building with the individual exhaust duct passing through the building wall into a vertical muffler and tailpipe. All engines were fueled with the same gas which was supplied from a common header pipe. Since the engines also shared common suction and discharge lines, the load on each engine was a function of the station suction and discharge pressures and the number of engines on-line at any given time.

The engine used for the validation tests was tested approximately one month before the validation tests. Results from that effort were used to determine calibration and spike levels for the validation testing. The formaldehyde, acetaldehyde, and acrolein levels measured during the validation testing were very similar to those observed previously. The NO_x, CO, and CO_2 levels were slightly different, with NO_x concentrations having the largest deviation from previous test results.

2.2 Engine Operation

An engine analyst was on-site during testing to ensure the engine was operating at steady conditions, to measure and confirm load conditions, and to be available should any maintenance be required during testing. No attempt was made to tune the engine to optimize efficiency or to minimize emission levels.

Process data were collected during the testing to document the operating conditions (see Appendix D). In general, the operation was steady throughout the testing. An upset was experienced during the aldehyde spiking on July 14, when another engine which was on common suction and discharge lines went out of service. This event changed the load conditions on the engine being tested and caused some rapidly changing concentrations of the target compounds. Data collected during this upset period were not used in the calculations, and additional test runs were made to ensure sufficient data were available to perform the necessary calculations.

3.0 SAMPLING PROCEDURES

3.1 Analyte Spiking

The validation for the target aldehyde compounds consisted of dynamic spiking of a slip-stream of the exhaust gas stream with the target compounds as close to the sample probe tip as possible. The spike gas stream volume comprised about 23 percent of the sample gas volume extracted from the stack. For formaldehyde, acetaldehyde, and acrolein, the spike levels were approximately 2X, 3X, and 8X the concentrations in the exhaust gas stream before spiking, respectively.

The tests consisted of 32 separate test runs involving one FTIR instrument (24 test runs, 12 spiked and 12 unspiked are required by Method 301). Four of the paired runs (eight test runs) were not used in the Method 301 calculations due to an engine upset during data collection.

Measurements consisted of monitoring the unspiked sample stream for a period of five minutes as a complete run followed by monitoring the spiked sample stream for five minutes. A single composite FTIR spectrum, consisting of 185 scans, was generated for each 5-minute test run. Sufficient time (five minutes) was allowed between runs to thoroughly flush the FTIR cell before data collection was begun for the next run. FTIR spectra were monitored during the 5-minute flush period to ensure the cell was completely flushed and had reached steady conditions in the time interval between the spiked and unspiked sample analyses. The cell was observed to reach steady conditions within two minutes of the 5-minute flush period, indicating the adequacy of this procedure to ensure no overlap between spiked and unspiked samples occurred.

3.2 Paired Sampling (NO_x, CO, CO_2, and Moisture)

A total of nine sets of replicate samples were collected for the NO_x, CO, CO_2, and moisture data validation (nine sets are required by EPA Method 301). Each test run (1-hr duration) consisted of simultaneous collection of data using the EPA reference methods and FTIR. An average concentration over the test run was calculated for all methods. The FTIR data for NO_x, CO, and CO_2, were corrected for moisture for comparison to the data collected using the respective EPA reference methods.

3.3 Sampling/Dynamic Spiking System

During the validation testing, samples of the engine exhaust were extracted through 3-inch ports in the horizontal section of the exhaust duct (12-inch ID) by inserting a sample probe (see Figure 3-1). The sample ports were located three stack diameters upstream of the muffler and 14 diameters downstream of the 90° elbow in the exhaust duct. As illustrated in Figure 3-2, the sample from the engine exhaust for both the reference method analyzers and the FTIR was collected with the same shielded, sintered stainless sample probe and extraction system. Samples were extracted continuously at a single point in the exhaust stream and delivered via a 100-ft heated Teflon® line to the monitoring trailer for measurement of the target analytes.

3.3.1 Sample Delivery/Conditioning

Located immediately after the sample probe was an insulated orifice meter connected to a Magnahelic for periodic measurement of the extracted gas flow rate. The total gas flow rate was monitored on a continuous basis using the calibrated heated rotameter inside the mobile laboratory.

Immediately after the orifice meter was a calibration tee assembly used to periodically introduce calibration gases into the sample line as close to the probe tip as practical. Calibration gas introduction was controlled remotely using an electric 3-way solenoid valve.

The sample gas was directed through a heated (280°F) Teflon® sample line to a heated head diaphragm pump. This pump provided a pressurized sample to a flow

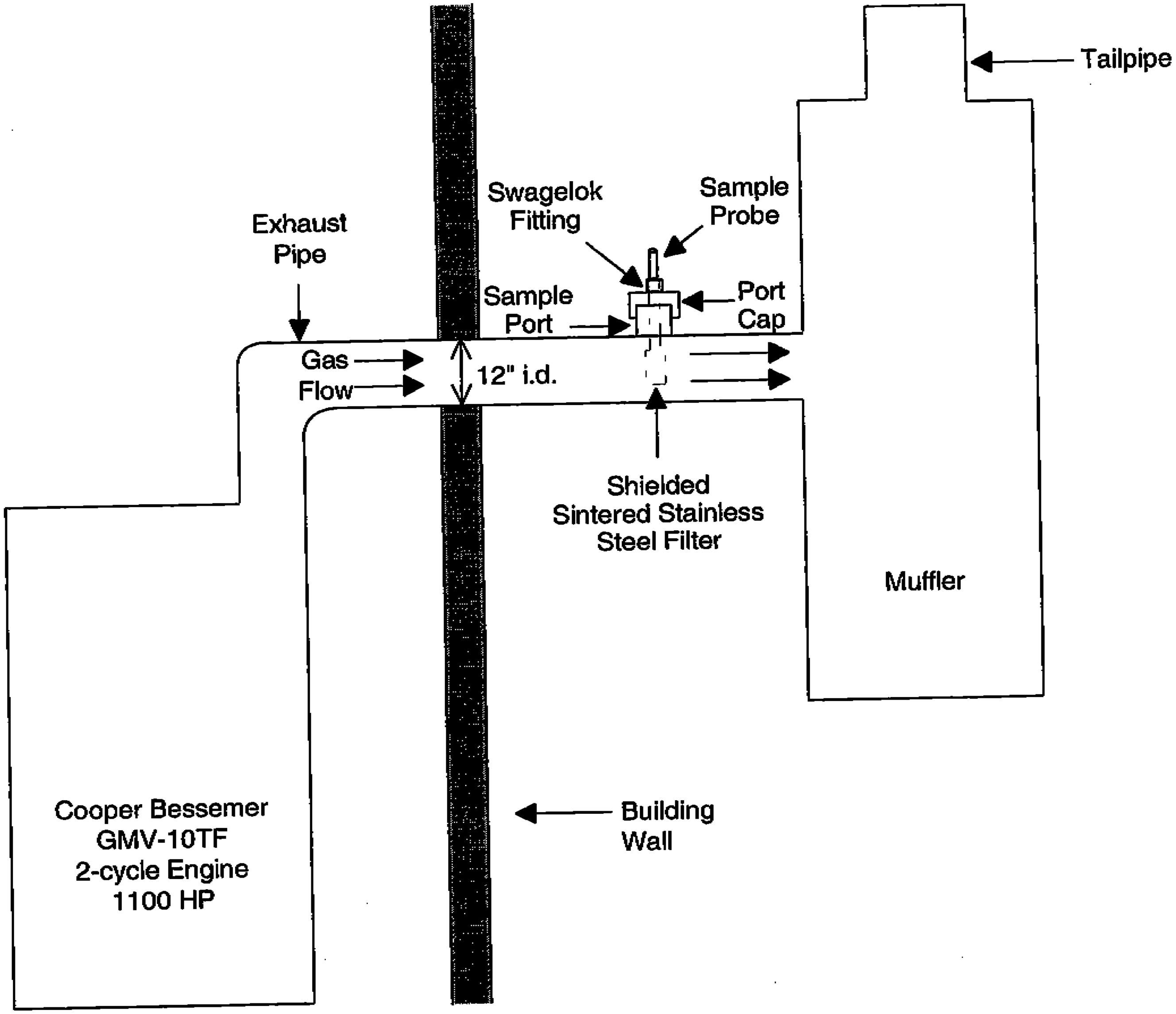


Figure 3-1. Sampling Location

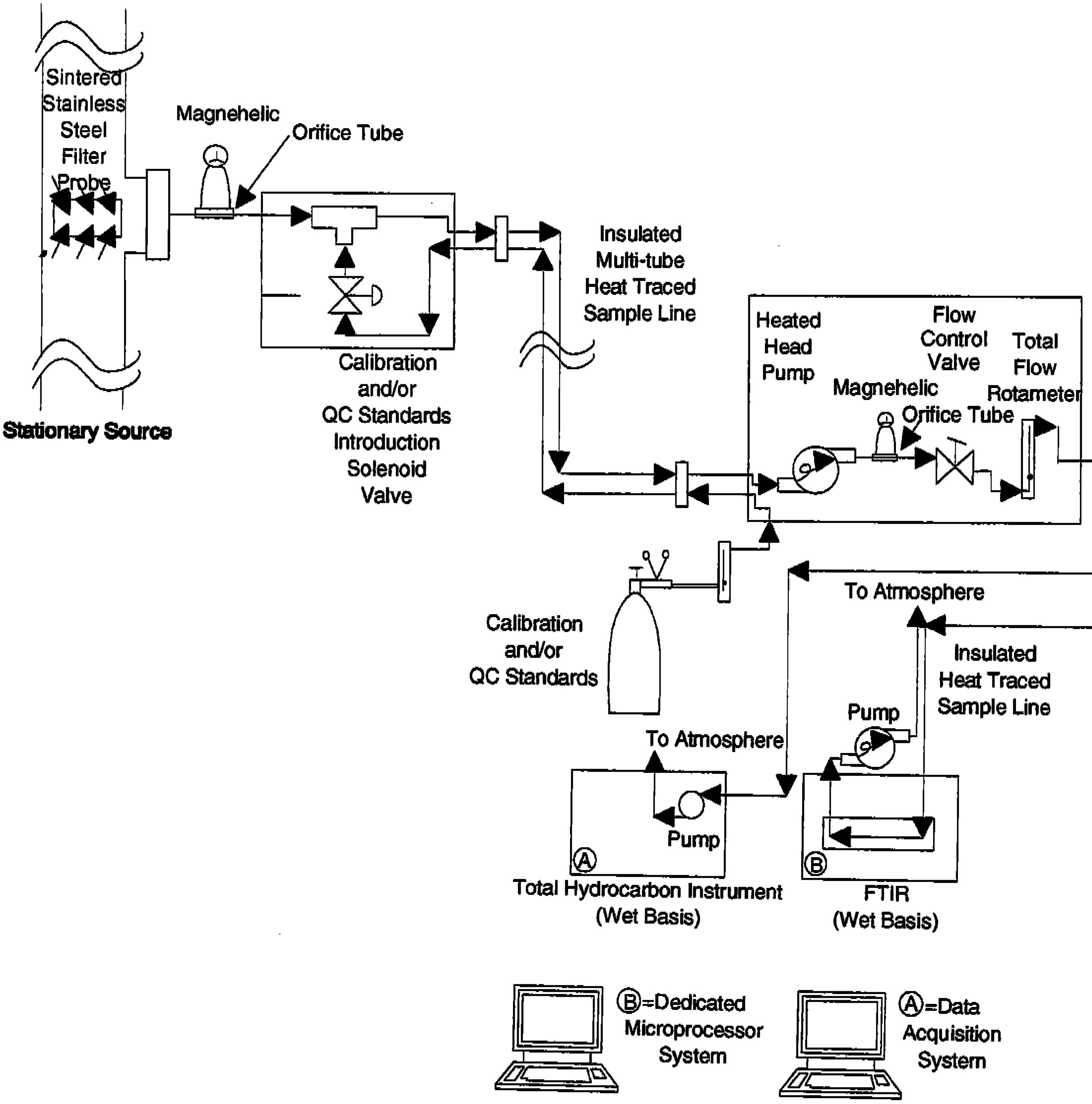
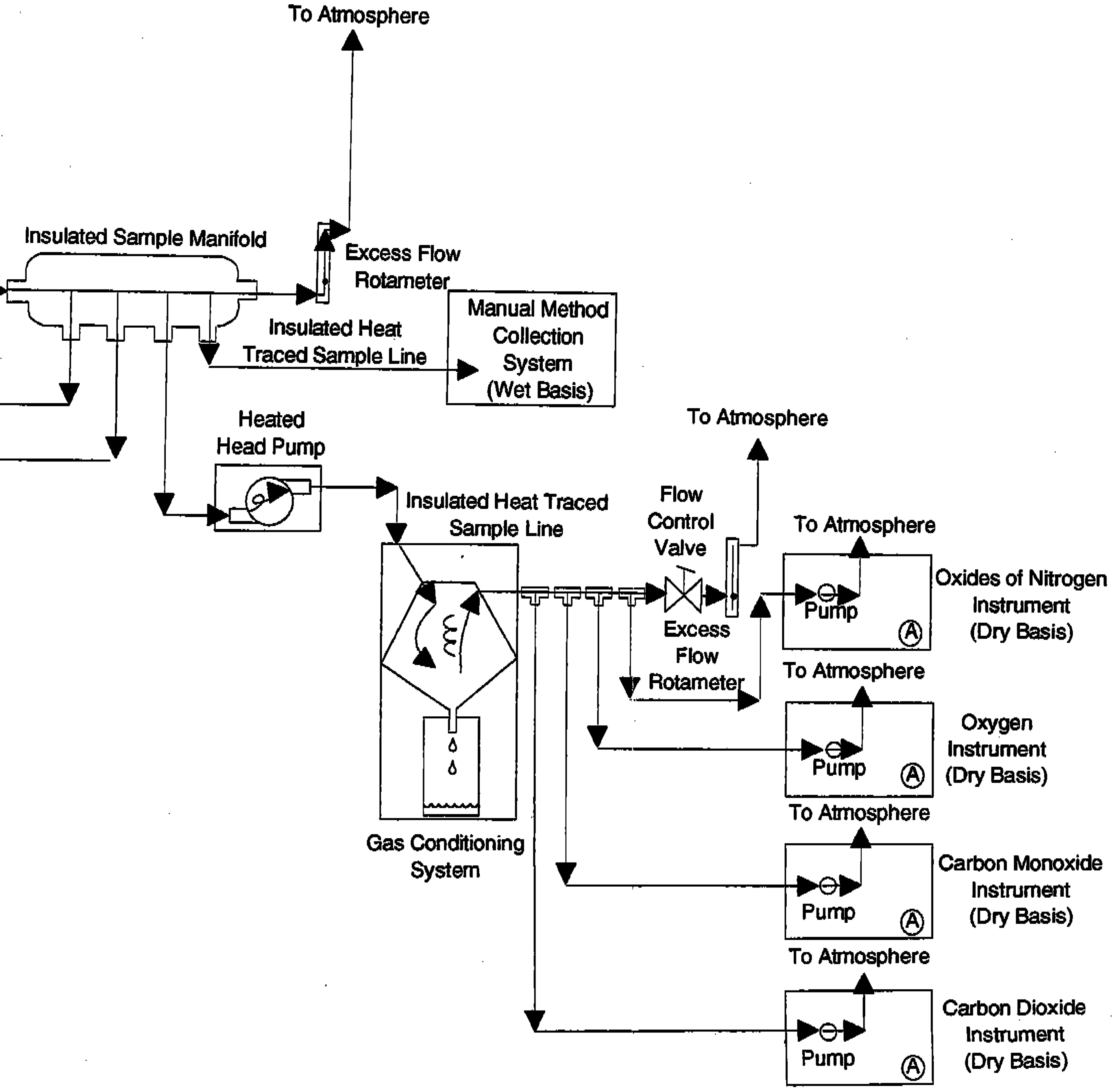


Figure 3-2. Sampling and



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Analysis System Schematic

controller metering the sample stream to a heated glass manifold. Sample gas flow rate was maintained at a constant rate of approximately 15 standard liters per minute (lpm) during the entire testing period.

After entering the glass manifold, the exhaust gas was split into separate streams; one directed to the NO_x, CO, CO_2, and O_2 analyzers, a second directed to the FTIR analyzer, a third directed to the total hydrocarbon analyzer (data collected, but not used in the validation effort), and a fourth to a moisture train. The sample stream for the NO_x, CO, CO_2, and O_2 analyzers was sent to a gas conditioning system designed to remove both fine particulate matter and moisture prior to introduction into the analyzers. Moisture removal was achieved using chilled condensers maintained at 35 ± 2°F, with continuous condensate removal to minimize any losses due to absorption (e.g., NO_2).

The sample stream to the FTIR instrument was transferred through a heated line from the glass manifold to prevent moisture condensation, and directed through the 7-liter FTIR cell using a heated head diaphragm pump. Sample cell pressure was monitored to allow corrections based on the absolute pressure of the cell. The FTIR cell was heated with a blanket (tube) heater controlled at 365°F (185°C) to avoid condensation of water and higher molecular weight organic compounds. (Note: All reference spectra used in this validation effort were developed at this temperature.)

Moisture samples were collected inside the mobile laboratory as close to the FTIR instrument as possible. A heated line from the glass manifold system was used to deliver sample to a Method 4 moisture train. Samples were collected at a flow rate of approximately one liter per minute into a midget impinger-based collection system.

All supporting information (e.g., flow rate data, calibration data, and raw data sheets for moisture measurements, gas cylinder certification sheets) is documented in Appendix E.

3.3.2 Spiking System Design

The dynamic spiking system was designed to allow simultaneous generation of known concentrations of the target aldehyde compounds. The spiking gas stream was generated through dynamic dilution of a certified multi-component standard contained in a high pressure cylinder for acetaldehyde and acrolein. Formaldehyde spiking was performed by continuous volatilization of a liquid solution of formalin at a known concentration. Figure 3-3 presents the schematic of the spiking system.

3.3.3 Spiking System Operation

The target spiking concentrations for each of the aldehyde compounds were calculated based on the native concentrations measured in the engine exhaust. Flow rates of the gaseous standards being spiked were set using flow controllers and were monitored with mass flowmeters calibrated using a National Institute of Standards Technology (NIST) traceable bubble meter.

A formalin solution with a formaldehyde concentration of 380 μg/mL was prepared from a stock formalin solution of 37 percent formaldehyde. This formalin solution was injected into a heated block [482°F (250°C)] for vaporization and was swept into the extracted exhaust stream using the gaseous standards of the other target aldehydes. Its flow rate was maintained nominally at 1.0 mL/min using a High Performance Liquid Chromatography (HPLC) pump. A calibrated balance was used to confirm the formalin solution flow rate by measuring weight loss from the container as a function of time. Laboratory tests were conducted with this volatilization system to ensure that a consistent spike level of formaldehyde could be delivered. Additional tests were conducted in the field using ambient air before the validation testing began.

The HPLC pump/balance assembly and the heated injection block were positioned on scaffolding next to the exhaust manifold to minimize the distance the formalin solution was pumped and to avoid condensation of the vaporized stream prior

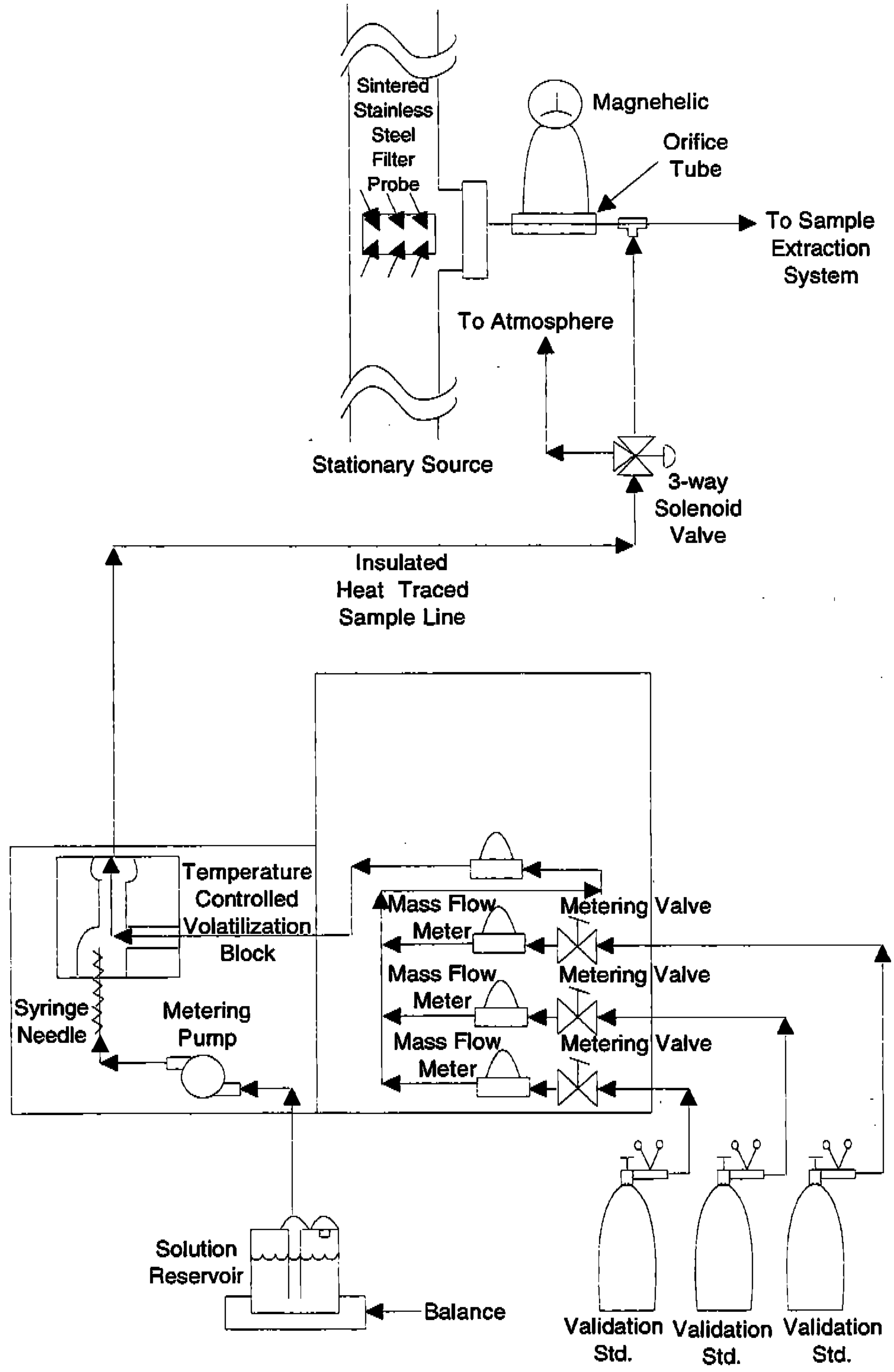

Figure 3-3. Dynamic Spiking System

to spiking into the exhaust flow. As previously described, a 3-way valve was used to start spike gas flow into the extracted exhaust gas stream to allow the concentrations to reach steady conditions and to completely flush the FTIR cell. The spike gas was vented to the atmosphere via a remotely actuated 3-way valve during collection of unspiked sample spectra. A 5-minute time interval was maintained between diverting the spike gas flow to the atmosphere and measurement of the unspiked native aldehyde concentrations.

Documentation of supporting information (e.g., flowmeter calibration data, formalin solution flow rate check) is provided in Appendix E.

4.0 ANALYTICAL PROCEDURES

4.1 Extractive FTIR System Description

For the validation testing, a Nicolet Model RS-3 bench with a cell path length of 10.8 meters was used to obtain maximum sensitivity for the compounds of interest while minimizing the spectral interferences due to the high concentrations of water and carbon dioxide. The spectral resolution of the FTIR instrument was 0.5 cm^{-1}. The cell had a 32-inch mirror spacing inside a 4-inch ID steel tube. Gold coated glass mirrors were utilized to prevent degradation of the mirror surface due to moisture or any acid gases in the exhaust stream.

The FTIR scans were recorded using a flow-through cell maintained at 365°F (185°C). The cell pressure was continuously monitored during the measurements.

4.1.1 FTIR Calibration Procedures

The FTIR instrument was calibrated for the target compounds by a two-step process: 1) measurement of the gas phase infrared spectrum at known concentrations and at the operating temperature of 365°F (185°C); and 2) development of a quantitation method for data processing where detection of target compounds is optimized and interference effects are minimized. These procedures are consistent with those found in the document, "Protocol for Performing Extractive FTIR Measurements to Characterize Various Gas Industry Sources for Air Toxics," prepared for GRI (see Appendix F; also included as part of the EPA-approved FTIR Test Protocol presented in Appendix B).

Calibrations were checked in the field by analyzing certified gas standards for all of the target compounds. During these checks, the cylinder gas mixtures were introduced into the instrument directly and/or at the sampling probe through the heat traced line. Line loss tests were conducted prior to the validation testing to confirm minimal sampling bias.

The formalin injection system used for introducing formaldehyde spike into the sample gas stream was checked for accuracy by injecting the solution into a heated ambient air stream and comparing the measured concentration versus the calculated concentration of formaldehyde.

4.1.2 FTIR Quantitation Procedures

Since concentration is a function of absorbance, the target compounds were quantitated by ratioing the field-measured spectrum to the reference spectrum using a classical least squares (CLS) technique. The basis of the CLS method is to scale each reference spectrum so that its spectral features match the magnitude of the corresponding field spectrum as closely as possible. The least-squares criterion is used to determine the best match for all spectral features in the analysis, where the sum of the squared residuals over the spectral analysis region is minimized. The scaling factor used for each spectrum is then converted to a concentration. It is assumed that the spectral lines obey Beer's law, which states that the line intensity is linearly proportional to the concentration of the species (and pathlength).

The CLS method allows the computation of concentrations using spectral features which may overlap with features from interfering species. Compounds that possess moderate to strong spectral features in a particular sampling environment (i.e., H_2O, CO_2, and CO in combustion exhaust) usually have features which are free of interferences, and can be analyzed by band area/height methods without resorting to interference corrections. The remaining target compounds (i.e., formaldehyde, acetaldehyde, acrolein, and NO_x) are subject to interferences, particularly from the compounds listed above and were quantitated using algorithms developed by Radian to compensate for these interferences.

Nonlinear behavior is expected for low molecular weight compounds such as CO, which exhibit sharp spectral features. Correction curves that cover the range of concentrations observed during this effort were used for CO, NO, and CO_2 to account for this nonlinear behavior.

Spectral analysis regions used for the target compounds in this study are shown in Table 4-1. A relatively weak absorbance band was used for the quantitation of moisture. By using a weaker band, any problems with nonlinearity or saturation caused by the relatively high levels of moisture present in the exhaust gas stream were avoided.

Table 4-1

FTIR Target Compound Spectral Analysis Regions

Target Compound	Analysis Region (cm^{-1})
Acetaldehyde	2665 - 2834
Acrolein	920 - 995
Formaldehyde	2665 - 2834
CO	2164 - 2185
CO_2	1009 - 1083
NO	1818 - 1931
NO_2	1598 - 1600
Moisture	870 - 886

Modifications were made to the FTIR analysis method to correct for an observed loss in resolution. This loss was due to a temperature increase in the mobile laboratory resulting from increasing ambient temperatures. Compounds with very sharp spectral features, such as water and CO, were affected and quantitated low during this time period. The instrument was realigned after Run No. 6 resulting in much better agreement for water and CO. The data collected during Runs 2 through 6 were requantitated using band areas in order to correct for the loss of resolution.

4.1.3 FTIR Data Handling

All FTIR raw and processed data were stored on a computer hard disk. Each day, all data were transferred onto backup storage media (e.g., optical drive) which was stored in a secure location. In addition, all quantitation routines developed for the data were backed up on floppy diskette and on hard drive.

4.2 Instrument Based Reference Method Analyzers

Table 4-2 lists the analyzers used for continuous emissions monitoring (CEM) during this testing effort, with the operating ranges indicated.

Table 4-2

Reference Method Analyzers

Target Compound	Instrument	Range Employed	Measurement Principle
CO_2	Beckman 865	0-20%	Nondispersive infrared
NO_x	TECO 10AR	0-2500 ppm	Chemiluminescence
CO	TECO 48	0-500 ppm	Gas filter correlation
O_2	Servomex 1100	0-25%	Electrocatalysis

4.2.1 Data Acquisition

The NO_x, CO, CO_2, and O_2 data were collected electronically using an analog to digital (a/d) converter and a computer system. The a/d converter and the computer were the primary components of a data acquisition system (DAS) designed to complete a full cycle of data collection and processing at least 10 times every minute. Data processing included calculation of average values based on operator-specified intervals. The DAS system also permitted periodic, on-demand calibrations of the analyzers. The calibration data presentation format indicated the calibration response for the analyzers before and after application of appropriate correction factors for any calibration drift which may have occurred between calibrations. All calibration and emissions data were stored on magnetic media at the conclusion of each test day.

4.2.2 Calibration Procedures

Prior to sampling on the first test day, a three-point (zero plus two upscale points) calibration was performed on each instrument to provide a linearity response check. The calibration gases were introduced at the sampling probe to determine analyzer calibration error during the tests. Immediately after each test run, zero and upscale cylinder gases were introduced through the entire sampling system to determine calibration drift during each test run.

4.2.3 Data Handling

All data were stored on a computer hard disk, with hard copy printouts. Additionally, the data were backed up on floppy diskettes.

4.3 Manual Method Procedures

Moisture in the exhaust gas was measured during the NO_x, CO, and CO_2 validation testing using EPA Method 4 for comparison with FTIR measurements. Moisture measurements were conducted in the mobile laboratory on a slip stream of the hot/wet sample measured by the FTIR. The balance used to weigh the moisture collected in the impingers was calibrated with type "S" weights prior to deployment in the field; it was checked with standard weights in the field. All other equipment (e.g., dry gas meter) used in Method 4 data collection were calibrated according to procedures described in the method.

4.4 Data Reduction

Data reduction was conducted on-site. FTIR data reduction was based on predetermined quantitation routines developed for similar sources. Minor modifications of the quantitation routines were necessary to tailor the FTIR analysis to the particular exhaust gas and observed interferences. Calculations of aldehyde compound spike rates and stream composition were performed on-site and compared with measurement results on a continuous basis. In this manner, any problems observed due to differences between calculated and measured concentrations of the spiked compounds were identified and resolved immediately.

5.0 RESULTS

5.1 Validation of Formaldehyde, Acetaldehyde, and Acrolein

Key spiking data are summarized in Table 5-1. Formaldehyde, acetaldehyde, and acrolein were dynamically spiked into a slip stream of the engine exhaust gas. Prior to the initiation of spiking, native levels of these compounds were determined in the unspiked exhaust gas stream. Spiking levels for formaldehyde and acetaldehyde were designed to result in a factor of two to three increase in concentration above the native levels. The spiking level for acrolein was similar to that of acetaldehyde since the two compounds were in the same cylinder at approximately the same concentrations. Acrolein was present at a lower concentration than acetaldehyde in the unspiked stack gas, resulting in spiked gas acrolein concentrations about eight times the native acrolein concentration.

5.1.1 Spiked Gas Concentrations

Formaldehyde concentration in the spiking solution was determined from seven individual measurements, with triplicate measurements made before and quadruplicate measurements made after the validation testing. These measurements were based on DNPH derivatization followed by laboratory HPLC analysis. The average concentration in the spiking solution was determined to be 380 μg/mL.

Since the extracted gas sample was diluted during spiking (23.1 percent), the total concentration of the target compound present in the spiked total sample gas was calculated using the native amount in the unspiked exhaust (corrected for dilution) plus the amount spiked corrected for total gas flow. The concentration of formaldehyde in the spiked total sample gas was calculated using the following expression:

Table 5-1

Aldehyde Spiking Data

Sample Gas Characteristics	
Total sample gas flow rate	14.62 L/min
Diluted acetaldehyde and acrolein gas flow rate	2.04 L/min
Vapor flow rate (from formalin solution)	1.34 L/min
Total spiked gas flow rate	3.38 L/min
Percentage of extracted gas in total sample gas	76.9
Spike Solution/Cylinder Gas Concentrations	
Formalin solution	380 μg/mL
Acetaldehyde	48.0 ppm
Acrolein	55.2 ppm
Spiked Gas Concentrations	
Formaldehyde	20.8 ppm
Acetaldehyde	6.7 ppm
Acrolein	7.7 ppm

$$C_{F,\ spike} = \frac{(C_{soln} \times Q_{spike\ soln} \times \frac{1}{MW_F} \times 24.04) \times 10^6}{Q_{total}} \qquad (5\text{-}1)$$

where:

$C_{F,\ spike}$ = Concentration of formaldehyde in spiked total sample gas (ppm)
C_{soln} = Concentration of formaldehyde in spiking solution (μg/mL)
$Q_{spike\ soln}$ = Flow rate of spiking solution (mL/min)
MW_F = Molecular weight of formaldehyde (μg/μmole)
Q_{total} = Flow rate of spiked total sample gas (L/min)

The constant 24.04 μL/μmole in Equation 5-1 is the volume occupied by one μmole of gas. An example calculation is shown below:

$$C_{F,\ spike} = \frac{\left[380 \frac{\mu g}{mL} \times 1 \frac{mL}{min} \times \frac{1}{30} \frac{\mu mole}{\mu g} \times 24.04 \frac{\mu L}{\mu mole} \times 10^6\right]}{14.62 \frac{L}{min}}$$

$$= 20.8 \text{ ppm}$$

For acetaldehyde and acrolein, the following expression was used to calculate spiked gas concentrations in the spiked total sample gas:

$$C_{i,\ spike} = C_{i,\ cyl} \times \frac{Q_i}{Q_{total}} \qquad (5\text{-}2)$$

where:

$C_{i,spike}$ = Concentration of compound "i" in spiked total sample gas (ppm)
$C_{i,cyl}$ = Concentration of compound "i" in cylinder (ppm)
Q_i = Flow rate of cylinder gas containing compound "i" (L/min)

For acetaldehyde, the spike gas concentration was calculated as 6.7 ppm:

$$C_{A,\ spike} = \frac{48 \text{ ppm} \times 2.04 \frac{L}{min}}{14.62 \frac{L}{min}}$$

$$= 6.7 \text{ ppm}$$

5.1.2 Validation Data

Table 5-2 presents the data collected during the validation of formaldehyde, including the unspiked native concentration, the corrected native concentration, the total spiked concentration which includes the spike amount added to the corrected native amount, and the concentrations measured by the FTIR instrument. A calculation of the total concentration measured as a percentage of the spiked amount is also shown.

A total of 16 spiked/unspiked paired runs were made. As previously mentioned, an engine upset condition was observed during Runs 1 through 4. Therefore, the data from these runs are not included in the calculations.

The data for acetaldehyde and acrolein measurements are shown in Tables 5-3 and 5-4, respectively. Acrolein was consistently measured at levels higher than those spiked. Direct measurement of the acrolein spike cylinder gas also showed a similar trend. Values reported in Table 5-4 reflect corrected concentrations based on recertification of the spiking cylinder (see Section 6.1.1 for additional discussion).

5.1.3 Validation Results

The concentration data measured for the three aldehydes were used to calculate precision and bias as detailed in Section 6.3 of Method 301 (Part 63 of CFR Vol. 57, No. 250, dated Tuesday, December 29, 1992, with the corresponding errata). A calculation spreadsheet was retrieved from the EPA bulletin board for performing these calculations and used to determine if the proposed method results pass the criteria for validation. A summary of Method 301 calculations for formaldehyde, acetaldehyde, and acrolein is shown in Table 5-5. The criteria for precision is that the relative standard deviation shall not be greater than 50 percent. Bias is established by comparing the proposed method results against a reference value (i.e., calculated value of the spike level) using a t-test. Bias may be eliminated by employing a correction factor based on the validation data, with bias correction factors outside the 0.7 to 1.3 range considered

Table 5-2

FTIR Validation Data for Formaldehyde

Run No.[a]	Unspiked Native Conc (ppm)	Corrected Native Conc (ppm)[b]	Total Native Plus Spiked Conc (ppm)	Total Measured Conc (ppm)	Measured/ Spike (%)[c]
5	24.01	18.46	39.26	42.15	107.4
6	23.27	17.89	38.69	37.16	96.0
7	22.58	17.36	38.16	35.29	92.5
8	19.5	15.00	35.80	39.76	111.1
9	19.47	14.97	35.77	38.79	108.4
10	19.8	15.23	36.03	36.28	100.7
11	20.11	15.46	36.26	38.74	106.8
12	19.96	15.35	36.15	41.74	115.5
13	20.02	15.40	36.20	37.35	103.2
14	19.78	15.21	36.01	39.38	109.4
15	19.83	15.25	36.05	42.62	118.2
16	19.71	15.16	35.96	39.74	110.5
Mean	20.67	15.90	36.70	39.08	106.6

[a] Runs 1 through 4 were not used due to engine upset conditions.

[b] Corrected for dilution (e.g., 18.46 = 24.01 x 0.769).

[c] Recovery [e.g., 107.4 = (42.15/39.26) x 100].

Table 5-3

FTIR Validation Data for Acetaldehyde

Run No.[a]	Unspiked Native Conc (ppm)	Corrected Native Conc (ppm)[b]	Total Native Plus Spiked Conc (ppm)	Total Measured Conc (ppm)	Measured/ Spike (%)[c]
5	5.47	4.21	10.90	11.45	105.0
6	5.33	4.10	10.80	11.10	102.8
7	5.22	4.01	10.71	10.38	96.9
8	4.04	3.11	9.80	10.16	103.7
9	4.00	3.08	9.77	10.40	106.4
10	3.68	2.83	9.53	9.73	102.1
11	3.90	3.01	9.70	10.06	103.7
12	4.08	3.14	9.84	10.28	104.5
13	3.90	3.00	9.70	9.86	101.6
14	3.85	2.96	9.66	10.24	106.0
15	3.78	2.91	9.60	10.00	104.2
16	3.35	2.58	9.27	9.96	107.4
Mean	4.22	3.24	9.94	10.30	103.7

[a] Runs 1 through 4 were not used due to engine upset conditions.

[b] Corrected for dilution.

[c] Recovery.

Table 5-4

FTIR Validation Data for Acrolein

Run No.[a]	Unspiked Native Conc (ppm)	Corrected Native Conc (ppm)[b]	Total Native Plus Spiked (ppm)	Total Measured Conc (ppm)	Measure/ Spiked (%)[c]
5	1.50	1.15	8.86	7.79	87.9
6	1.41	1.08	8.79	7.71	87.7
7	1.47	1.13	8.83	7.71	87.3
8	1.36	1.05	8.75	7.65	87.4
9	1.32	1.02	8.72	8.08	92.7
10	1.00	0.77	8.47	7.52	88.8
11	1.41	1.08	8.79	7.92	90.1
12	1.34	1.03	8.73	7.69	88.1
13	1.33	1.02	8.73	7.74	88.7
14	1.52	1.17	8.87	7.68	86.6
15	1.47	1.13	8.83	7.64	86.5
16	1.35	1.04	8.76	7.66	87.4
Mean	1.37	1.06	8.76	7.79	88.3

[a] Runs 1 through 4 were not used due to engine upset conditions.

[b] Corrected for dilution.

[c] Recovery.

Table 5-5

Results Summary - Analyte Spiking (Method 301)

Parameter[a]	Formaldehyde	Acetaldehyde	Acrolein	Method Criteria
S_m	39.08	10.30	7.79	--
M_m	20.67	4.22	1.37	--
SD_s	2.46	0.26	0.38	--
SD_u	0.92	0.38	0.12	--
RSD_s	6.3	2.5	4.8	≤50
RSD_u	4.5	9.0	8.9	≤50
B	2.39	0.36	-0.96	--
Bias Statistically Significant?	No	No	Yes	t ≤2.201
CF	--	--	1.14	0.7 ≤ CF ≤ 1.3
Meet Validation Criteria?	Yes	Yes	Yes	--

[a]S_m = Measured mean of the spiked samples.
M_m = Measured mean of the unspiked samples.
SD_s = Standard deviation of the FTIR spiked values.
SD_u = Standard deviation of the FTIR unspiked values.
RSD_s = Relative standard deviation of the FTIR spiked values.
RSD_u = Relative standard deviation of the FTIR unspiked values.
B = Bias at the spike level.
t = t-statistic.
CF = Correction factor.

unacceptable. As indicated in the table, FTIR data for all three compounds meet the precision and bias criteria (see Appendix G for spreadsheet printouts).

5.1.4 Draft Revised Method 301

In addition to the method published in the Federal Register, Radian has received from EPA a draft revision of Method 301 including a spreadsheet (see Appendix H). The revised methodology was evaluated for formaldehyde, acetaldehyde, and acrolein. Results of the revised calculations are presented in Table 5-6 documenting that FTIR data for all three target compounds meet the criteria specified in the draft revised method as well (see Appendix I for spreadsheet printouts).

5.2 Validation of NO_x, CO, and CO_2

The target compounds, CO, CO_2, NO_x including moisture were validated using the paired train procedure for comparison to reference methods. Concentrations of these compounds were measured by both the reference method and by FTIR and averaged over a period of one hour. The results of these paired measurements were then compared using the Method 301 calculation methodology.

5.2.1 Validation Data

A total of nine paired tests were performed on July 14, 1994. Engine operation was relatively stable across this entire period. However, some variation was observed, primarily due to changes in suction pressure, which affected the load on the engine. These excursions can most easily be observed by reviewing the NO_x data presented in Appendix J or in the data summary shown in Table 5-7.

Table 5-7 contains average values determined from the EPA reference methods and FTIR for the nine 1-hr runs. All FTIR data were corrected to a dry basis using the EPA Method 4 results.

Table 5-6

Results Summary - Analyte Spiking (Draft Revised Method 301)

Parameter[a]	Formaldehyde	Acetaldehyde	Acrolein	Method Criteria
S_m	39.08	10.30	7.79	--
M_m	20.67	4.22	1.37	--
SD_s	2.46	0.26	0.38	--
SD_u	0.92	0.38	0.12	--
SD_{pooled}	1.86	0.33	NA	--
RSD	9.0	7.7	4.8	≤50
B	2.39	0.36	-0.96	--
Bias Statistically Significant?	Yes	Yes	Yes	t ≤ 2.228
CF	0.90	0.95	1.14	0.7 ≤ CF ≤ 1.3
Meet Validation Criteria?	Yes	Yes	Yes	--

[a]S_m = Measured mean of the spiked samples.

M_m = Measured mean of the unspiked samples.

SD_s = Standard deviation of the FTIR spiked values.

SD_u = Standard deviation of the FTIR unspiked values.

SD_{pooled} = Pooled standard deviation.

B = Bias at the spike level.

RSD = Relative standard deviation.

t = t-statistic.

CF = Correction factor.

NA = Not applicable (see Appendix I).

Table 5-7

Validation Data Summary for NO_x, CO, CO_2, and Moisture

Run No	NO_x (ppm, dry)		CO (ppm, dry)		CO_2 (%, dry)		Moisture (%)	
	CEM	FTIR[a]	CEM	FTIR[a]	CEM	FTIR[a]	Manual	FTIR
1	447.94	446.76	103.14	106.51	4.17	4.22	9.63	9.55
2	520.17	492.92	103.27	103.51	4.24	4.29	10.60	10.37
3	538.31	519.40	103.32	103.01	4.22	4.26	10.20	10.07
4	566.99	543.70	103.10	101.66	4.20	4.26	10.10	10.13
5	506.61	474.12	103.91	101.07	4.17	4.24	10.60	10.32
6	768.43	724.36	101.55	99.38	4.27	4.36	10.10	10.58
7	763.77	773.39	102.99	109.17	4.29	4.47	10.40	10.24
8	724.54	724.91	100.08	106.80	4.25	4.41	9.90	9.99
9	662.93	681.21	99.60	111.76	4.24	4.47	10.95	10.02
Mean	611.08	597.86	102.33	104.76	4.23	4.33	10.28	10.14

[a] Conversion of FTIR data from wet to dry basis based on Method 4.

5.2.2 Validation Results

A summary of the validation results is given in Table 5-8 based on Method 301 calculations. The acceptance criteria for precision requires the precision of the proposed method to be the same or better than that of the validated reference method as determined by an F-test. Significance of bias between the results from the proposed and the validated reference method is determined using a t-test. Bias correction factors outside the range 0.9 to 1.1 are considered unacceptable. Table 5-9 summarizes the results using the draft revised Method 301 procedures. As indicated in both tables, the FTIR data for all four compounds meet the specified criteria. A brief description of the calculations is included below, with detailed spreadsheet printouts provided in Appendices G and I.

NO_x: The standard deviation for the reference method was obtained by converting the precision or the relative standard deviation (RSD) value into standard deviation using the mean of the Method 7E measurements. The RSD of Method 7E is 2.16 percent in the range of 100 to 1,000 ppm, as presented in the stack measurement precision data obtained from EPA (see Appendix K).

Method 7E measures NO_x as a combination of NO and NO_2 while the FTIR measures NO and NO_2 individually. The NO and NO_2 concentrations were added to get a total concentration which was directly compared to the concentrations from the reference method. In these measurements, NO_2 comprised less than 2.5 percent of the total NO_x measured.

CO: Since EPA has not included precision data for Method 10 in the summary provided in Appendix K, the precision indicated in the method (2 percent of span) was applied in the calculations, as suggested by EPA.

CO_2: Precision data available from EPA were used in the comparison of the two methods (see Appendix K).

Table 5-8

Results Summary - Comparison with Validated Methods (Method 301)

Parameter[a]	NO_x	CO	CO_2	Moisture	Method Criteria
d_m	13.21	-2.43	-0.10	0.14	--
SD_v	13.20	10.00	0.11	0.23	--
SD_d	20.91	5.05	0.07	0.39	--
SD_p	7.71	3.57	0.05	0.16	--
Precision Acceptable?	Yes	Yes	Yes	Yes	$F \leq 1.0$
Bias Statistically Significant?	Yes	Yes	Yes	No	$t \leq 1.397$
CF	1.02	0.98	0.98	--	$0.9 \leq CF \leq 1.1$
Meet Validation Criteria?	Yes	Yes	Yes	Yes	--

[a]d_m = Mean of the paired sample differences.
SD_v = Standard deviation provided with the validated method.
SD_d = Standard deviation of the paired sample differences.
SD_p = Standard deviation of the FTIR measurements.
F = F-statistic.
t = t-statistic.
CF = Correction factor.

Table 5-9

Results Summary - Comparison with Validated Methods (Draft Revised Method 301)

Parameter[a]	NO_x	CO	CO_2	Moisture	Method Criteria
d_m	13.21	-2.43	-0.10	0.14	--
SD_v	13.20	10.00	0.11	0.23	--
SD_d	20.91	5.05	0.07	0.39	--
SD_p	21.43	2.84	0.06	0.35	--
SD_{pooled}	17.80	4.01	0.09	0.29	--
Precision Acceptable?	Yes	Yes	Yes	Yes	$F \leq 4.03$
Bias Statistically Significant?	Yes	Yes	Yes	No	$t \leq 1.397$
CF	1.02	0.98	0.98	--	$0.9 \leq CF \leq 1.1$
Meet Validation Criteria?	Yes	Yes	Yes	Yes	--

[a] d_m = Mean of the paired sample differences.
SD_v = Standard deviation provided with the validated method.
SD_d = Standard deviation of the paired sample differences.
SD_p = Standard deviation of the FTIR measurements.
SD_{pooled} = Pooled standard deviation.
CF = Correction factor.
F = F-statistic.
t = t-statistic.

Moisture: In the spreadsheet, a value of 0.23 percent was used for the standard deviation of the reference method (see Appendix K). Since the FTIR and Method 4 moisture results are very similar, correction of the FTIR NO_x, CO, and CO_2 concentrations by the FTIR moisture data has no impact on the validation results.

6.0 QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

6.1 Reference Spectra

A number of quality control procedures were initiated during the validation of formaldehyde, acetaldehyde, and acrolein. The standard spectrum for formaldehyde was developed from a certified cylinder gas purchased from Scott Specialty Gases. This spectrum was generated according to the procedures in the EPA document "Protocol for Applying Fourier Transform Infrared (FTIR) Spectrometry in Emission Testing", Draft Version S7, March 31, 1992.

The formaldehyde cylinder used to generate the reference spectrum was measured by direct introduction into the FTIR cell a number of times to assess measurement reproducibility. This data set is presented in Table 6-1 with the difference between measured and certified cylinder concentrations expressed as a percent of the certified concentration.

Table 6-1

FTIR Measurements of Formaldehyde Master Cylinder

Certified Concentration (ppm)	Measured Concentration (ppm)	Error (%)
4.7	4.65	-1.06
4.7	4.63	-1.49
4.7	4.61	-1.92

Acetaldehyde and acrolein reference spectra were generated from certified gaseous standards obtained from Scott Specialty Gases using procedures similar to those described in the draft EPA protocol referenced above. All spectra were measured at a cell temperature of 365°F (185°C).

Before the validation testing, ambient air was pulled through the heated sample lines and spiked with formalin solution to determine recovery of formaldehyde from a solution of known concentration and spike rate in a stream with no measurable amount of formaldehyde. Acetaldehyde and acrolein were also spiked into the ambient air stream from the certified gas cylinder. These results are presented in Table 6-2, where the average error based on four measurements was 13.5, -3.0, and 15.6 percent for formaldehyde, acetaldehyde, and acrolein, respectively.

Table 6-2

Spiked Ambient Air Measurements for Target Aldehydes

Compound	Calculated Spike Amount (ppm)	Measured Concentration (ppm)				Average Measured Conc. (ppm)	Average Error (%)
		Run a	Run b	Run c	Run d		
Formaldehyde	20.8	23.4	25.0	21.8	24.0	23.6	13.5
Acetaldehyde	6.7	6.5	6.6	6.4	6.6	6.5	-3.0
Acrolein	7.7	6.7	6.4	6.4	6.3	6.5	-15.6

As previously described, the cylinder used to introduce acetaldehyde and acrolein was measured by direct introduction into the FTIR cell. Acetaldehyde was reportedly present at a concentration of 55.4 ppm in the cylinder, but was measured at 49.5 ppm. Recertification of this cylinder showed that acetaldehyde concentration was 48.0 ppm, indicating an error of 3.1 percent in the field. All acetaldehyde results reported in this document have been corrected to the recertified concentration.

The acrolein concentration from the certified gas cylinder was measured at 68.3 ppm by FTIR, within 23.7 percent of the certified concentration of 55.2 ppm. Recertification of the acrolein cylinder confirmed the 55.2 ppm concentration in the cylinder. Since the reference spectrum was generated from another certified Scott cylinder of 50 ppm concentration, one of the certifications was considered to be incorrect. Subsequent analysis of a master standard gas provided by Scott Specialty

Gases has shown that the concentration of the original gas cylinder used to generate the reference spectrum was in error. The acrolein data in this report have been corrected for this difference of 23.7 percent. Regardless of this discrepancy between the standard cylinders, the FTIR acrolein results meet the Method 301 criteria.

The reference spectra for NO, NO_2, CO, and CO_2 were generated from certified gaseous standards while the reference spectra for moisture were generated by vaporizing known quantities of water into a nitrogen stream.

6.2 Functionality Check

Ethylene and CO gases were analyzed on a daily basis during validation testing. Ethylene was used as a functionality check standard in a manner consistent with that employed by Entropy Environmentalists, Inc. for the validation FTIR at a coal-fired boiler. The CO results were used as a functionality check in a similar manner, but since CO has sharper spectral lines than ethylene, analysis of this cylinder on a regular basis was used to determine if degradation of instrument performance had occurred. The results from the measurement of both gases are shown in Table 6-3. For ethylene measurements, the average error was -1.7 percent, while the error for CO measurements averaged -3.2 percent for the 99.7 ppm gas.

Table 6-3

Results from FTIR Analysis of Ethylene and CO Gases

Compound	Certified Concentration (ppm)	Measured Concentration (ppm)			Average Measured Concentration (ppm)	Average Error (%)
		July 13	July 14	July 15		
Ethylene	100	97.5 97.1	97.4 101	99.7 97.0	98.3	-1.7
Carbon Monoxide	99.7	91.3	100.6	99.4 94.7	96.5	-3.2
Carbon Monoxide	350[a]	361			361	+3.1

[a] CEM QC gas.

6.3 Comparison to EPA Reference Spectra

Reference spectra for formaldehyde, acrolein, and acetaldehyde were retrieved from the EPA bulletin board and compared to the Radian reference spectra. The spectra were converted to the proper format using a Galactic SpectraCalc™ software package before the comparison.

One of the two reference spectra for formaldehyde (spectral file 086b4snB) included on the bulletin board was used in this comparison. It was not possible to compare the acetaldehyde spectrum due to the presence of impurities. The two acrolein spectra from the bulletin board were also included in this analysis. Table 6-4 presents the results of this comparison, using the EPA reference spectra to quantify the results from the Radian reference spectra. Using the EPA spectrum, the Radian formaldehyde reference spectrum was quantitated high (about 6 percent), while the acrolein spectrum was quantitated low (14 to 19 percent). The acrolein spectra comparison also indicates the original certified cylinder used to create the Radian reference spectrum was incorrect (see Section 6.1.1). Correction of the Radian values by 23.7 percent as previously discussed results in values within 10 percent of those determined from the EPA spectra.

Table 6-4

Comparison of Radian Reference Spectra to EPA Reference Spectra

Compound	Radian Reference Spectra Certified Concentration (ppm)	Quantitation Results Using EPA Reference Spectra (ppm)	
Formaldehyde	4.7	5.0	
Acrolein	50.0	40.6	42.8
Acrolein (corrected)	38.2	40.6	42.8

6.4 Blank Check

When analyte spiking was performed, dry nitrogen gas was purged through the sample line as a blank to check for contamination in the sample lines. The results of this blank analysis are shown in Table 6-5. None of the target compounds were identified in the blank on July 13, 1994.

Table 6-5

Nitrogen Blank Analysis Results by FTIR

Compound	Concentration (ppm)
Formaldehyde	0.01 ± 0.05
Acetaldehyde	0.14 ± 0.24
Acrolein	-0.51 ± 0.53
Moisture	-298 ± 558
CO	-0.05 ± 0.10
CO_2	-79.1 ± 145
NO	0.10 ± 0.22
NO_2	0.07 ± 0.11

6.5 Instrumental Analyzer Method Quality Control Procedures

For the NO_x analyzer, the NO_2 to NO conversion efficiency was determined prior to field sampling by using a certified NO_2 calibration gas cylinder. The converter efficiency was determined to be greater than 90 percent. The same gas cylinder was analyzed using the FTIR instrument to verify the NO_2 concentration analysis. The FTIR quantitated both NO and NO_2, with NO_x calculated as the sum of the individual measurements of these two compounds.

Leak checks of the entire sample system, including the extraction and standard injection system, were conducted by capping the lines at the probe and at the injection tee and turning on the sample pump system. Leaks through the sample line were monitored using the oxygen analyzer and the pressure transducer on the FTIR cell. In addition, during the measurement of the nitrogen blank, the oxygen analyzer was monitored to determine if leakage had occurred. No leaks were found in the sample collection and conditioning system.

The CEM analyzers were calibrated at the beginning of the test day. Zero, mid-range and span gases were introduced at the outlet of the sample probe to determine calibration error. As shown in Table 6-6, the calibration error was within ±2 percent of the span for all calibration gases. The introduction of calibration gases through the entire sampling system eliminated any sampling system bias in the measurements. Immediately following each test run, zero and high-range cylinder gases were introduced into the analyzers through the entire sampling system to determine the drift during each run. As summarized in Table 6-7, the error was well within ±3 percent of span.

The NO_x analyzer was operated at a range of 2500 ppm, considerably greater than the concentrations measured during the validation effort. The selection of this range and the levels of NO_x calibration gases used was based on previous measurements on this engine where much higher NO_x concentrations were measured. Only one cylinder of NO_x calibration gas was available in the NO_x concentration range observed in the engine exhaust during the validation testing. However, this cylinder had insufficient pressure to analyze it more than two times on the day the validation was performed. As reported in Table 6-6, the results show a small positive bias at this concentration.

Calibration data from the previous day, July 13, 1994, was reviewed for additional analyses of the NO_x gas cylinder in the desired range. On July 13, calibration of the NO_x analyzer was conducted in the same manner as on July 14 when the validation was completed. The 509 ppm NO_x standard was analyzed three times on July 13 with values of 531, 537, and 535 ppm being recorded. Averaged with the two analyses of this standard on July 14, a positive bias of 6.05 percent was obtained. Correction of the data

Table 6-6

CEM Calibration Error Check

Run No.	Analyzer	Concentration Level	Units	Actual Concentration	Measured Concentration	Calibration Error (% of span)
A	Oxygen	Zero	%v	0	0.0	0.0
		Mid	%v	3.0	3.1	0.4
		Span	%v	20.9	20.9	0.0
	CO	Zero	ppmv	0	0	0.0
		Mid	ppmv	99.7	99	-0.2
		Span	ppmv	500	502	0.4
	CO_2	Zero	%v	0	0.0	0.0
		Mid	%v	3.49	3.5	0.1
		Span	%v	18	18.0	0.0
	NO_x	Zero	ppmv	0	0.0	0.0
		Mid	ppmv	509	539	1.2
		Span	ppmv	2005	2005	0.0
B	Oxygen	Zero	%v	0	0.0	-0.1
		Mid	%v	3.0	3.1	0.3
		Span	%v	20.9	20.9	-0.2
	CO	Zero	ppmv	0	0	0.0
		Mid	ppmv	99.7	98	-0.3
		Span	ppmv	500	498	-0.4
	CO_2	Zero	%v	0	0.0	0.0
		Mid	%v	3.49	3.5	0.0
		Span	%v	18.0	18.1	0.5
	NO_x	Zero	ppmv	0	1	0.1
		Mid	ppmv	509	557	1.9
		Span	ppmv	2005	1984	-0.8

Table 6-7

Inter-Run CEM Calibration Check

Run No.	Analyzer	Concentration Level	Units	Actual Concentration	Measured Concentration	Calibration Error (% of span)
Post Run 1	Oxygen	Zero	%v	0	0.0	-0.1
		Upscale	%v	20.9	20.9	-0.2
	CO	Zero	ppmv	0	-0.1	0.0
		Upscale	ppmv	500	498	-0.4
	CO_2	Zero	%v	0	0.0	0.0
		Upscale	%v	18.0	18.1	0.5
	NO_x	Zero	ppmv	0	1.3	0.1
		Upscale	ppmv	2005	1984	-0.8
Post Run 2	Oxygen	Zero	%v	0	0.0	0
		Upscale	%v	20.9	20.9	0.1
	CO	Zero	ppmv	0	-0.1	0
		Upscale	ppmv	500	502	0.5
	CO_2	Zero	%v	0	0.0	0.1
		Upscale	%v	18.0	18.1	0.4
	NO_x	Zero	ppmv	0	0.9	0
		Upscale	ppmv	2005	2006	0
Post Run 3	Oxygen	Zero	%v	0	0.0	0
		Upscale	%v	20.9	20.8	-0.2
	CO	Zero	ppmv	0	0.1	0
		Upscale	ppmv	500	502	0.3
	CO_2	Zero	%v	0	0.0	0.1
		Upscale	%v	18.0	17.9	-0.4
	NO_x	Zero	ppmv	0	0.8	0
		Upscale	ppmv	2005	1998	-0.3
Post Run 4	Oxygen	Zero	%v	0	0.0	-0.1
		Upscale	%v	20.9	20.9	0.1
	CO	Zero	ppmv	0	-0.2	0
		Upscale	ppmv	500	496	-0.7
	CO_2	Zero	%v	0	0.0	-0.1
		Upscale	%v	18.0	18.1	0.6
	NO_x	Zero	ppmv	0	0.1	0
		Upscale	ppmv	2005	1993	-0.5

Table 6-7

(Continued)

Run No.	Analyzer	Concentration Level	Units	Actual Concentration	Measured Concentration	Calibration Error (% of span)
Post Run 5	Oxygen	Zero	%v	0	0.0	0.1
		Upscale	%v	20.9	20.9	-0.1
	CO	Zero	ppmv	0	0.1	0
		Upscale	ppmv	500	500	0.1
	CO_2	Zero	%v	0	0.0	0.1
		Upscale	%v	18.0	18.0	0.1
	NO_x	Zero	ppmv	0	0.7	0
		Upscale	ppmv	2005	1995	-0.4
Post Run 6	Oxygen	Zero	%v	0	0.0	-0.1
		Upscale	%v	20.9	20.9	-0.1
	CO	Zero	ppmv	0	-0.2	0.0
		Upscale	ppmv	500	497	-0.6
	CO_2	Zero	%v	0	0.0	0.1
		Upscale	%v	18.0	18.0	-0.2
	NO_x	Zero	ppmv	0	0.9	0.0
		Upscale	ppmv	2005	1990	-0.6
Post Run 7	Oxygen	Zero	%v	0	0.0	0.1
		Upscale	%v	20.9	20.9	-0.2
	CO	Zero	ppmv	0	0.1	0.0
		Upscale	ppmv	500	506	1.2
	CO_2	Zero	%v	0	0.0	0.0
		Upscale	%v	18.0	18.0	0.2
	NO_x	Zero	ppmv	0	0.0	0.0
		Upscale	ppmv	2005	2009	0.2
Post Run 8	Oxygen	Zero	%v	0	0.0	0.0
		Upscale	%v	20.9	21.0	0.3
	CO	Zero	ppmv	0	0.1	0.0
		Upscale	ppmv	500	499	-0.2
	CO_2	Zero	%v	0	0.0	-0.1
		Upscale	%v	18.0	18.1	0.4
	NO_x	Zero	ppmv	0	-0.1	0.0
		Upscale	ppmv	2005	2030	1.0

Table 6-7

(Continued)

Run No.	Analyzer	Concentration Level	Units	Actual Concentration	Measured Concentration	Calibration Error (% of span)
Post Run 9	Oxygen	Zero	%v	0	0.0	-0.1
		Upscale	%v	20.9	20.9	0.0
	CO	Zero	ppmv	0	-0.2	0.0
		Upscale	ppmv	500	489	-2.1
	CO_2	Zero	%v	0	0.0	0.2
		Upscale	%v	18.0	18.0	0.1
	NO_x	Zero	ppmv	0	-1.0	0.0
		Upscale	ppmv	2005	2031	1.0

for this apparent mid-range nonlinearity still provides data which meet the Method 301 validation criteria.

A comparison of the values measured using the CEM analyzers to those determined from the FTIR analysis is presented in Table 6-8. For CO measurements, the percent difference ranged from -2.2 to 1.2 for the CO analyzer, while the range for the FTIR measurements was -3.6 to 6.8 percent. For CO_2 measurements, the respective ranges for the CO_2 and the FTIR analyzers were -0.6 to 0.6 and -2.4 to 1.7 percent. The percent error for the NO_x analyzer ranged from -0.7 to 1.3. For the FTIR NO_x data, the range was -10.5 to 7.9 percent.

6.6 Analysis of EPA Audit Cylinder

An EPA audit cylinder was available for acetaldehyde for analysis by FTIR during the validation testing. The acetaldehyde audit cylinder was measured by direct introduction into the FTIR cell. Acetaldehyde was not observed in the duplicate analysis of the cylinder gas and was presumed to be at levels below the FTIR detection limit of 0.3 ppm (see Appendix L for letter submitted to Ms. Ellen Streib of EPA on audit result).

Table 6-8

Comparison of CEM/FTIR Measurements

Run No.	Component	Certified Concentration	Units	Measured Concentration		Percent Error[a]	
				CEM	FTIR	CEM	FTIR
Post Run 1	CO	500	ppm	502	525	0.4	5.0
Post Run 2	CO	500	ppm	503	519	0.6	3.8
	CO_2	18	%	18.09	17.83	0.5	-0.9
	NO_x	2005	ppm	2006	1900	0.0	-5.2
Post Run 3	CO	500	ppm	502	500	0.4	0.0
	CO_2	18	%	17.9	18.01	-0.6	0.0
	NO_x	2005	ppm	1998	1870	-0.3	-6.7
Post Run 4	CO	500	ppm	496	514	-0.8	2.8
	CO_2	18	%	18.1	18.02	0.6	0.1
	NO_x	2005	ppm	1993	1996	-0.6	-0.4
Post Run 5	CO	500	ppm	501	490	0.2	-2.0
	CO_2	18	%	18.0	17.56	0.0	-2.4
	NO_x	2005	ppm	1995	1815	-0.5	-9.5
Post Run 6	CO	500	ppm	497	508	-0.6	1.6
	CO_2	18	%	18.0	17.58	0.0	-2.3
	NO_x	2005	ppm	1990	1794	-0.7	-10.5
Post Run 7	CO	500	ppm	506	482	1.2	-3.6
	CO_2	18	%	18.0	17.75	0.0	-1.4
	NO_x	2005	ppm	2009	1998	0.2	-0.3
Post Run 8	CO	500	ppm	499	505	-0.2	1.0
	CO_2	18	%	18.1	18.3	0.6	1.7
	NO_x	2005	ppm	2030	2054	1.2	2.4
Post Run 9	CO	500	ppm	489	534	-2.2	6.8
	CO_2	18	%	18.0	17.98	0.0	-0.1
	NO_x	2005	ppm	2031	2163	1.3	7.9

[a] 100 (Measured - Certified)/Certified.

7.0 REFERENCES

1. Method 0011, Sampling for Aldehyde and Ketone Emissions from Stationary Sources, Methods Manual for Compliance for BIF Regulations, U.S. Environmental Protection Agency, Office of Solid Hazardous Waste, EPA/530-SW-91-010, December 1990.

2. Method 430, Determination of Formaldehyde and Acetaldehyde in Emissions from Stationary Sources, (Adopted: September 12, 1989; Amended: December 13, 1991), Stationary Source Test Methods, Volume III: Methods for Emissions Toxic Air Contaminants from Stationary Sources, State of California Air Resources Board, Monitoring and Laboratory Division, December 13, 1991.

3. Karst, U., A.H.J. Gromping, N. Bindings, U. Witting, and K. Cammann, Determination of Aldehydes, Ketones, and Nitrogen Oxides in Automobile Exhaust, American Environmental Laboratory, Vol. 7, No. 2, March 1995, pp. 32-33.

4. Scull, N., C. Kim, and D.E. Foster, Comparison of Unburned Fuel and Aldehyde Emissions from a Methanol-Fueled Stratified Charge and Homogeneous Charge Engine, SAE Paper 861543.

5. Fourier Transform Infrared (FTIR) Method Validation at a Coal-Fired Boiler, prepared by Entropy Environmentalists, Inc., Draft Report, U.S. EPA Contract No. 68-D2-0163, July 1993.

APPENDIX A

EPA COMMUNICATION

Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, Illinois 60631-3562
312/399-8100
FAX: 312/399-8170

GRI

May 26, 1995

Mr. William F. Hunt, Jr.
Director, Emissions, Monitoring and Analysis Division
MD-14
Office of Air Quality and Planning Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Subject: Request for Approval -- Validation of Extractive FTIR Method for Measurement of Select HAPs and Other Air Pollutants in Natural Gas Fired Engine Exhaust

Dear Mr. Hunt:

As discussed in the May 12, 1994 letter submitted to Mr. Robert G. Kellam, Acting Director, Technical Support Division, the Gas Research Institute (GRI) is investigating emissions from internal combustion engines, one of the source categories targeted by EPA for development of maximum achievable control technology (MACT) based regulations by 2000. Formaldehyde and other aldehydes are potential air toxics in engine exhaust. Since there is no validated measurement method currently available for quantifying these species, GRI conducted a field experiment on July 11-15, 1994 to validate an extractive Fourier Transform Infrared (FTIR) method for measurement of formaldehyde, acetaldehyde, and acrolein using U.S. EPA Method 301 procedures. Since FTIR is capable of measuring multiple species on a continuous and realtime basis, NO_x, CO, CO_2, and H_2O, were also included in this validation.

A test plan for the validation effort was prepared and submitted to the Agency for review on June 13, 1994. In preparing the test plan, we referenced the FTIR validation study conducted by EPA on a coal fired boiler, and also our discussions with Robin Segall, Lori Lay, and Gary McAlister of EPA. Their review comments were incorporated into the revised test plan as implemented in the field.

Based on the procedures in Method 301, the FTIR data collected during the testing meet the validation criteria specified in the method for all of the above compounds. The FTIR data also meet the revised criteria included in EPA's draft, revised Method 301. These results are described in detail in the enclosed summary report "Fourier Transform Infrared (FTIR) Method Validation at a Natural Gas Fired Internal Combustion Engine". Following EPA's suggestion, a test method entitled "Measurement of Select Hazardous Air Pollutants, Criteria Pollutants, and Moisture Using Fourier Transform Infrared (FTIR) Spectroscopy" is also enclosed for your review. In addition, the document "Protocol for Performing Extractive FTIR Measurements to Characterize Various Gas Industry Sources for Air Toxics" is included to provide supporting information. Please note that the result of the audit gas analysis was submitted to Ellen Streib of EPA on December 21, 1994.

GRI requests your review of this information package and approval of the extractive FTIR method for measuring formaldehyde, acetaldehyde, acrolein, NO_x, CO_2, CO, and H_2O in the exhaust of all natural gas fired, stationary internal combustion engines.

Please call me at (312) 399-8174, or contact Gunseli Sagun Shareef, the project manager from Radian Corporation, at (919) 461-1454 if you have questions or need additional information. We will follow up with you in late June to discuss your schedule for completing the review. Thank you for your time.

Sincerely,

James M. McCarthy
Senior Technology Manager
Air Quality Research

cc:
Jim Evans, GRI
Tom Roose, GRI
Conniesue Oldham, EPA/MD-19
Lori Lay, EPA/MD-19
Gary McAlister, EPA/MD-19
Gunseli Sagun Shareef, Radian/RTP

RECEIVED
JUL 28 1995
ENVIRONMENT & SAFETY

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

JUL 21 1995

Mr. James M. McCarthy
Senior Technology Manager
Air Quality Research
Gas Research Institute
Chicago, Illinois 60631-3562

Dear Mr. McCarthy:

The "Fourier Transform Infrared (FTIR) Method Validation at a Natural-Gas Fired Internal Combustion Engine," which was submitted by Radian Corporation, can be considered valid according to Method 301 for this source and similar sources.

The Emission Measurement Center noted that the proposed protocol "Measurement of Select Hazardous Air Pollutants, Criteria Pollutants, and Moisture Using Fourier Transform Infrared Spectroscopy" was somewhat different than the procedure used in the 301 validation.

The validation test used an in-stack filter. Spiking was performed after the primary (in-stack) filter and before a secondary filter. The protocol has one external filter. Spiking is performed before the external filter.

Technically, the protocol that has been proposed is different from the procedures used in the 301 validation test. However, we consider spiking before the filter more stringent; therefore, we consider the protocol acceptable. Also, the performance specifications listed in the proposed protocol are more stringent than Method 301 requirements. For future use of the submitted protocol, the burden of proof of a similar source is normally up to the facility. However, as long as these proposed performance specifications are met, we see no need for additional proof of the similar source requirement. Therefore, the protocol you have proposed may be used at any gas-fired facility.

It should also be noted that the Maximum Achievable Control Technology standard for this source category is not scheduled until the year 2000. Therefore, any data submitted will be considered when the Emission Standards Division (ESD) is in the data collection phase of the regulation. The contact person in ESD is Amanda Agnew. The Emission Measurement Center contact for this source category is Foston Curtis. They can be reached at 919-541-5268 and 919-541-1063, respectively.

Sincerely,

David C Misenheimer

for William F. Hunt, Jr.
Director
Emissions, Monitoring, and
Analysis Division

cc: Amanda Agnew (MD-13)
Foston Curtis (MD-19)
Lori Lay (MD-19)

APPENDIX B

FTIR TEST PROTOCOL

MEASUREMENT OF SELECT HAZARDOUS AIR POLLUTANTS, CRITERIA POLLUTANTS, AND MOISTURE USING FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

INTRODUCTION

This method describes the sampling and analysis procedures to be applied when using FTIR spectroscopy for measurement of select hazardous air pollutants, criteria pollutants, and moisture in the exhaust of natural gas-fired, stationary internal combustion (IC) engines.

The analytical procedures for FTIR measurements are described in the "Protocol for Performing Extractive FTIR Measurements to Characterize Various Gas Industry Sources for Air Toxics" which was prepared for the Gas Research Institute (GRI). The protocol document is included as an addendum to this method, with additional details provided in Reference 1.

1.0 SCOPE AND APPLICATION

1.1 Analytes. The analytes measured by this method and their CAS numbers are shown in Table 1.

Table 1. Target Analytes

Compound	CAS Number
Formaldehyde	50-00-0
Acetaldehyde	75-07-0
Acrolein	107-02-8
Carbon Monoxide	630-08-0
Carbon Dioxide	124-38-9
Nitric Oxide	10102-43-9
Nitrogen Dioxide	10102-44-0
Oxides of Nitrogen	Not Applicable
Moisture (Water)	7732-18-5

1.2 Applicability.

1.2.1 This method is for determination of the analytes listed in Table 1 for uncontrolled and controlled emissions from natural gas-fired, stationary IC engines. Suggested analysis regions are shown in Table 2.

Table 2. Analysis Regions

Compound	Analysis Region (cm^1)	Potential Interferants
Formaldehyde	2665-2834	water, methane
Acetaldehyde	2665-2834	water, methane
Acrolein	920-995	water
Carbon Monoxide	2164-2185	water, carbon dioxide
Carbon Dioxide	1009-1083	water
Nitric Oxide	1818-1931	water, carbon dioxide
Nitrogen Dioxide	1598-1600	water
Oxides of Nitrogen	--	--
Moisture (Water)	870-886	--

Formaldehyde, acetaldehyde, and acrolein are measured on a wet basis, and reported as parts-per-million volume (ppmV) on a wet or dry basis. Carbon dioxide (CO_2) is measured on a wet basis and reported on a dry basis as percent volume (%V) after correction for moisture. Carbon monoxide (CO), nitric oxide (NO), and nitrogen dioxide (NO_2) are measured on a wet basis and reported on a dry basis as ppmV after correction for moisture. The oxides of nitrogen (NO_x) concentrations are calculated as follows:

$$[NO_x] = [NO] + [NO_2] \tag{1}$$

where

[NO] = measured concentration of NO on a dry basis at a specific point in time;
$[NO_2]$ = measured concentration of NO_2 on a dry basis at the same point in time as [NO]; and
$[NO_x]$ = calculated concentration of NO_x on a dry basis.

Moisture (H_2O) is measured as %V. Correction of all target analyte concentrations to a dry basis is made using the following equation:

$$[Dry] = \frac{[Wet]}{1 - \frac{[H_2O]}{100}} \tag{2}$$

where

[Dry] = corrected dry concentration of the target analyte;
[Wet] = measured concentration of the target analyte on a wet basis, at a specific point in time;
[H_2O] = measured concentration of H_2O at the same point in time as [Wet].

1.2.2 This method does not apply when moisture condensation occurs in either the sampling system or the instrumentation (see Section 4.0).

1.3 Method Range and Sensitivity.

1.3.1 Range and sensitivity of the method are functions of the following factors:

- measurement cell pathlength;
- absorption coefficient of each target compound at the selected analytical frequency region;
- spectral resolution;
- interferometer sampling time;
- number of individual interferograms used to produce each time-averaged spectrum;
- detector sensitivity and response time;
- compounds comprising the sample matrix (i.e., H_2O, CO_2, and methane); and
- biases due to the sample collection and/or analysis system.

1.3.2 Measurement cell pathlength is the primary determinant of the range and sensitivity of the method. Appropriate pathlength of the measurement cell is determined by considering the following:

- the lowest expected concentration or the desired target detection limit of each target compound; and
- the concentration response characteristic of any interfering compound.

1.4 Performance Specifications.

1.4.1 The method performance specifications are presented in Table 3 for each analyte. These specifications are based on the validation test results and other tests conducted by GRI and can be achieved using an FTIR system with a spectral resolution of 0.5 cm^{-1} and a measurement cell pathlength of 10.8 meters (see Reference 1).

Table 3. Method Performance Specifications

Target Compound	Detection Limit	Precision (Percent RSD)	Accuracy (Percent Bias)[a]
Formaldehyde	0.25 - 1.0 ppmV	$\leq 10^b$	±10
Acetaldehyde	1.0 - 4.0 ppmV	$\leq 10^b$	±10
Acrolein	1.0 - 4.0 ppmV	$\leq 10^b$	±12.5
Carbon Monoxide	0.25 - 1.0 ppmV	≤5	±5
Carbon Dioxide	0.05 - 0.2 ppmV	≤2.5	±5
Oxides of Nitrogen	0.5 - 2.0 ppmV	≤2.5	±5
Moisture (Water)	0.05 - 0.20 %V	≤2.5	±5

[a] Accuracy = [(Concentration$_{(measured)}$ - Concentration$_{(actual)}$ / Concentration$_{(actual)}$] x 100

[b] Based on replicate measurements of spiked samples.

1.4.2 Prior to initial field application, an assessment of the specific sample collection and analysis system is recommended to ensure that the method performance specifications can be met (see Section 9.0).

1.5 Data Quality Goals. The Data Quality Goals (DQGs) are defined by the overall requirements for the intended use of the data. The DQGs for this method are considered the same as the performance specifications (refer to the addendum for additional discussion).

2.0 SUMMARY OF METHOD

2.1 Principle.

2.1.1 FTIR measurement is based on the absorbance of infrared energy by gas phase compounds. Most molecules absorb infrared energy at characteristic frequencies based on the molecular vibrational and/or rotational motion within the molecule. The absorption characteristics of a particular compound can be used to identify and quantitate the concentration of that compound. The concentration of a single target compound is related to its absorbance according to Beer's Law:

$$A(\nu) = a(\nu)bc \qquad (3)$$

where

$A(\nu)$ = absorbance at wavelength ν,
$a(\nu)$ = absorption coefficient at wavelength ν,
b = pathlength, and
c = concentration.

If more than one compound absorbs light at a given wavelength, then the total absorbance is found from a linear combination of Beer's law for each compound:

$$A_{total}(\nu) = b \sum_{i=1}^{N} a_i(\nu)\, c_i \qquad (4)$$

where

A_{total} = total absorbance at wavelength ν,
$a_i(\nu)$ = absorption coefficient for compound i at wavelength ν,
c_i = concentration of compound i,
N = total number of absorbing compounds, and
b = pathlength.

2.1.2 Compounds with very sharp spectral features such as CO can exhibit nonlinear analyzer response, requiring correction algorithms to accurately calculate concentrations. Correction algorithms are generated by measuring the spectrum of the compound at several different concentrations and fitting the resulting data to an appropriate correction curve.

2.1.3 Quantitation of each target compound is based on the application of a reference spectrum that is specific to that compound and is measured at a known concentration, temperature, and pressure. For the target compounds, quantitation is performed by selecting characteristic absorbance regions that have minimal interferences from other compounds present in the gas stream. The classical least squares (CLS) method is applied to fit the reference spectra to the sample spectrum, with the resulting scaling factors used to calculate concentrations. The CLS method finds the set of concentrations that minimizes the residuals in the analysis region and provides a confidence interval for each concentration calculated. The confidence interval is used as a diagnostic to determine how well the CLS method fit was accomplished. It is used to assess instrument performance and to alert the user to review the data for the presence of new or elevated concentrations of interferants in the sample.

2.2 Sampling and Analysis.

2.2.1 Sample gas is extracted from a point in the exhaust pipe before or after the muffler assembly, depending on the length of the exhaust pipe sections and the distance from the nearest upstream and/or downstream disturbances. A heated external filter attached to the outlet of the sample probe is used to remove any particulates in the exhaust stream.

2.2.2 The stack flow may be pulsed, consistent with the movement of mechanical components. A velocity traverse is performed according to EPA Method 1 to ensure that the sample probe is located at a representative point in the sample stream.

Typically, the exhaust flow pattern from IC engines is turbulent, providing for a well-mixed, non-stratified profile.

2.2.3 Sample gas is continuously extracted from the exhaust stream at a flow rate of 15-20 liters/minute via a sample probe and a temperature controlled Teflon transfer line using a high-capacity, heated head pump. The sample gas stream is then delivered to a heated distribution manifold within the mobile laboratory. A portion of the sample gas is continuously extracted from the distribution manifold, through a temperature controlled Teflon transfer line, and the FTIR measurement cell at a flow rate of 7-10 liters/minute using a lower capacity heated head pump (see Figure 1).

2.2.4 Analyte/surrogate spiking is used for quality assurance (see Section 9.0).

2.3 Operator Requirements. To effectively operate the sampling equipment and FTIR system and to perform the procedures presented in the method, the operator must have a working knowledge of FTIR spectroscopy, continuous emissions monitoring, and source sampling.

3.0 DEFINITIONS

Definitions of terms are presented in Appendix A.

4.0 INTERFERENCES

4.1 Analytical Interferences. Compounds present in the sample exhaust gas stream that could interfere with the accurate measurement of the target compounds include CO_2, H_2O, and methane. These interferants have absorption features that can overlap the absorption features of the target compounds. The degree of interference is dependent upon the spectral absorbance region used to measure each target compound, the concentration of the target compound, spectral resolution, and the associated sample matrix. The effect of interferences is minimized by selecting appropriate quantitation regions specific to each target compound (see Reference 1 for additional discussion).

4.2 Background Interferences. Interferences in the FTIR spectral background can be caused by condensation of organic or inorganic material on the cell windows or mirrors. Monitoring of the background spectra is required to avoid these interferences (see Section 8.0)

4.3 Sampling System Interferences. Potential interferences include the loss of the target analytes in the sampling system or contributions from the sampling system which may interfere with sample analysis. Cold spots in the sample line can result in moisture condensation and loss of water soluble compounds such as the aldehydes.

5.0 SAFETY

5.1 Prior to field application of the method, a site-specific Health and Safety Plan must be prepared. General safety precautions include the use of steel-toe boots, safety glasses, hard hats, and work gloves. In certain cases, facility policy may require the use of fire-resistant clothing while on-site. Since the method involves monitoring at high-temperature sampling locations, precautions must be taken to limit the potential for exposure to high-temperature gases and surfaces while inserting or removing the sample probe. Additionally, precautions must be taken to limit exposure to high-temperature surfaces in the mobile laboratory, such as heated sample lines, heated head pumps, and the heated FTIR cell.

5.2 Potential chemical hazards include the aldehydes and CO. Acetaldehyde and acrolein are respiratory irritants. Formaldehyde is also a respiratory irritant and a carcinogen, and should be handled accordingly. Internal combustion engines can potentially emit CO at toxic concentrations. Care should be taken to minimize exposure to the sample gas while inserting or removing the sample probe. Personal CO monitors must be used to insure that the concentration of CO in the work area is maintained at safe levels.

6.0 INSTRUMENTATION AND EQUIPMENT

6.1 <u>FTIR Spectrometer and Detector</u>. An instrument with a spectral resolution of at least 0.5 cm^{-1} and a nominal measurement cell pathlength of 10.8 meters is required. Alternative measurement cell pathlengths may be used if the method performance specifications are met. The system must include a personal computer with compatible software that provides realtime updates during data collection.

6.2 <u>Measurement Cell Temperature/Control</u>. A heating blanket and an active temperature controller capable of maintaining the measurement cell at 185°C (±2°C).

6.3 <u>Pressure Measurement Device</u>. A 0-1000 Torr electronic pressure measurement device to monitor the measurement cell pressure (±1 Torr). The device must also provide an electronic signal to the analyzer data system to continuously monitor and record the cell pressure.

6.4 <u>Analyzer Sample Pump</u>. A heated head pump capable of delivering a controlled flow rate that allows the cell volume to be exchanged at least once each minute.

6.5 <u>Sample Source Extraction Pump</u>. One or more heated head pumps capable of delivering a controlled extraction flow rate of 15-20 liters/minute.

6.6 <u>Heated Sample Transfer Line</u>. Heat traced sample lines, containing one to three individual Teflon gas lines, capable of maintaining a temperature in excess of 120°C.

6.7 Calibration/Analyte Spike Delivery System. A remotely activated 3-way solenoid that allows calibration, diagnostic standard, and analyte spike samples to be introduced through the heat traced line and sample conditioning system. The delivery system should include mass flow controllers or control valves with mass flow meters to facilitate injection of controlled amounts of gaseous spike standard(s). This system may also include a volatilization chamber for generation of formaldehyde vapors from formalin solution, if a gaseous formaldehyde standard is not available for analyte spiking.

6.8 Sample Probe. A glass or stainless steel probe. The sample probe should be heated or insulated to prevent moisture condensation.

6.9 Filter. Heated external filter to remove particulate matter from the extracted sample gas stream.

6.10 Distribution Manifold. A temperature controlled, glass or stainless steel sample gas distribution manifold.

6.11 Flow Meter. A heated rotameter or other flow measurement device to indicate excess sample flow.

6.12 Gas Regulators: Appropriate regulators for individual gas cylinders.

7.0 REAGENTS AND STANDARDS

7.1 Aldehyde Standards.

7.1.1 Formaldehyde, acetaldehyde, and acrolein are available as gas standards from commercial specialty gas suppliers. The formaldehyde gas standard is currently available at levels less than 25 ppmV. Higher level formaldehyde standards may be generated by thermal evolution from paraformaldehyde or by vaporizing formalin solutions of known concentrations. Formalin solution and paraformaldehyde are available from commercial chemical suppliers.

7.1.2 Acetaldehyde and acrolein are available as gas standards in concentrations greater than 50 ppmV in nitrogen. Since potential problems with the stability of these standards have been noted, the standards should be recertified on a regular basis (approximately every 6 months) to verify concentrations.

7.2 Criteria Pollutants. Certified gas standards of the target criteria pollutants are available from commercial specialty gas suppliers.

7.3 Diagnostic Standard. An NIST traceable or Protocol 1 CO gas standard at concentration levels appropriate for the emission source. Other compounds such as ethylene may be used; however, CO is recommended due to its sharp spectral features which are sensitive to system changes.

7.4 Absorbance Pathlength Standard. Obtain an NIST traceable or Protocol 1 chlorodifluoromethane ($CHClF_2$) gas standard at a concentration appropriate for the optical pathlength of the FTIR cell.

7.5 Nitrogen. Ultra high purity grade nitrogen gas for blanks and background checks.

7.6 Surrogate/Analyte Spike Gas with Tracer. A gas cylinder mixture of surrogate/analyte spike gas and silicon hexafluoride (SF_6) in nitrogen. Formaldehyde is recommended as the surrogate analyte since it represents the greatest sampling challenge due to its solubility in water. The SF_6 concentration in this gas mixture should be low (i.e., <10 ppmv). Note this gas mixture will be used for confirming the validity of the sampling system for the analytes of interest (see Section 9.0).

7.7 Reference Spectra. Obtain reference spectra for each of the target analytes at concentrations that bracket the emission source levels. Reference spectra must be recorded at the correct cell temperature, and at known pressure, pathlength, and concentration, in conjunction with a diagnostic (or calibration transfer) standard. The procedures for generation of reference spectra for this method are described in the addendum. Similar procedures developed by EPA are documented in Reference 2.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Pre-test.

8.1.1 Collect information about the site characteristics, such as exhaust pipe diameter, gas flow rates, port location, access to ports, access to power, and safety requirements during a pre-test site survey. If possible, collect samples of the exhaust gas under various operating conditions. Measure preliminary FTIR spectra to determine the concentration ranges of the target compounds and interferants (e.g., CO_2, H_2O) present in the emission source.

8.1.2 Set up the sampling train (see Figure 1).

8.1.3 Analyze blank samples by purging the sampling system and the FTIR cell with nitrogen gas to ensure there are no interferences due to outgassing.

8.1.4 Confirm integrity of the sampling system by running a humidified, surrogate/analyte spike sample from the probe inlet through the heat traced transfer line to the instrument.

8.1.5 Perform a sampling system leak check (from the probe tip to pump outlet). Connect a rotameter to the outlet of the pump. Close off the inlet to the probe and observe the leak rate. The leak rate must be less than 4 percent of sampling rate or 500 ml/min, whichever is less.

8.2 Analyzer Leak Check. Measure the leak rate of the FTIR measurement cell by evacuating the measurement cell to 20 percent (or less) of the normal operating pressure. After evacuation, isolate the measurement cell and monitor pressure with a cell pressure sensor. The leak rate must be less than 10 Torr per minute.

8.3 Background Spectrum. Continuously purge the measurement cell with N_2 gas at the same flow rate used to introduce sample gas into the analyzer. Purging ten to 20 minutes should be sufficient to thoroughly flush and condition all components. While purging, monitor the FTIR spectra until the concentrations of CO_2 and H_2O are reduced to normal steady-state background levels. After normal background levels are attained, record a background spectrum. The background spectrum must be comprised of a number of scans equal to or greater than the number of scans used to perform sample analysis. New background spectrum should be recorded when the interferometer is realigned, or when it is suspected that the optical system is being affected by components in the sample stream.

8.4 Pre-Test Calibration.

8.4.1 Prior to the first run of each day (or when the mobile laboratory is moved), calibrate the measurement cell pathlength with a standard gas containing $CHClF_2$ and perform calibration tests according to the procedures described in the protocol document (see addendum).

8.4.2 Introduce diagnostic standard (CO) into the FTIR instrument and record the spectrum (same number of scans as will be used during the field measurements). The measurements must agree within ±10 percent of the certified concentrations.

8.4.3 Introduce surrogate/analyte gas standard(s) at the inlet to the heated sample transfer line to assess sample recovery. The measurements must agree within ±10 percent of the certified concentrations.

8.5 Analyte Spiking. Use surrogate/analyte gas standard(s) with tracer gas to verify the validity of the sampling and analysis system (see Section 9.0).

8.6 Continuous Sampling. Extract sample gas from the source, through the sample collection system and FTIR measurement cell, until thoroughly flushed. Ten to 20 minutes should be sufficient to thoroughly flush and condition all components. While flushing the system, adjust the flow through the FTIR measurement cell to achieve a minimum of one complete cell volume exchange per minute. Begin recording sample spectra. Based on Reference 1, the spectra collected over a 5-minute period will consist typically of 185 scans. Monitor and record the FTIR cell pressure continuously. Ensure temperatures in the mobile laboratory remain steady during data collection.

8.7 Sampling Quality Assurance, Data Storage, and Reporting.

8.7.1 Record instrument conditions such as cell pathlength, cell temperature, cell pressure, ambient barometric pressure, instrument resolution, and the number of scans comprising each spectra in a signed and dated notebook. Record beginning and ending times for each sampling run in the notebook and correlate to the appropriate data file name and instrument conditions.

8.7.2 Assign individual, descriptive file names to all field-generated spectra and store on a magnetic media during sample collection. At the end of each day, backup all data files on separate magnetic media for raw data archival.

8.8 Baseline Stability Assessment. Monitor baseline absorbance continuously during the data collection. The baseline absorbance must not change more than 0.1 absorbance units or the analyzer interferometer must be realigned. After realignment, collect a new background spectrum.

8.9 Post-test Calibration. Repeat pre-test calibration procedures at the end of the test. The results from the pre- and post-test measurements must agree within ±10 percent of the certified concentrations.

8.10 Post-test Quality Assurance.

8.10.1 Examine the sample spectra immediately after a test run to ensure that the observed gas composition is similar to the expected gas matrix.

8.10.2 Confirm that the sampling and analysis system operating parameters were appropriate for the test conditions observed. Examine the CLS error bars to determine if any changes have occurred.

9.0 SYSTEM PERFORMANCE ASSESSMENT

A performance assessment is recommended prior to the first use of the sample collection and analysis system in the field and whenever a change is made in the optical system (e.g., replacement of any of the critical optical system components, such as the interferometer, detector, and the beam splitter).

The performance assessment is conducted in the field by spiking a slipstream of the exhaust gas with the target/surrogate analyte(s) at known concentrations to assess precision and accuracy. A direct-to-cell measurement of the spike gas should also be performed during the pre-test spiking. Results of the performance assessment are used to determine acceptability of the sampling and analytical system and to calculate the accuracy and precision for the specific hardware configuration and quantitation procedures considered.

9.1 **Reagents**. Use formaldehyde gas standard with SF_6 tracer gas for surrogate/analyte spiking. Alternatively, use formalin solution or paraformaldehyde to generate formaldehyde gas standards.

9.2 Spiking Procedures

9.2.1 Analyze the unspiked gas stream to establish concentrations of the target analyte(s) native to that source. Note that the operation of the engine being tested must be stable. Large variations in the source will be reflected in the accuracy and precision determined by this method.

9.2.2 Measure the flow rates of the spiked gas and the sample gas stream to calculate the concentrations of spiked compound(s) in the combined gas stream. Use calibrated mass flow meters/controllers for monitoring spike gas flow rates. Use calibrated orifice tubes or heated rotameters for exhaust flow rate measurements.

9.2.3 Using the spiking procedure specified in EPA Method 301 (see Reference 3), introduce the surrogate/analyte spike gas with the tracer into the sample collection and analysis system at flows which will approximately double the concentration native in the unspiked gas. The spiked gas stream flow should not comprise more than 25% of the total flow.

9.2.4 Record the analyzer responses for spiked and unspiked gas. Allow sufficient time between native and spiked concentration measurements to thoroughly flush the FTIR cell and avoid carryover between the two consecutive samples. Record concentrations from a minimum of four spiked/unspiked paired samples.

9.3 Calculations.

9.3.1 Calculate the dilution ratio using the tracer gas as follows:

$$DR = \frac{SF_{6(cyl)}}{SF_{6(spk)}} \qquad (5)$$

where

DR = dilution ratio;
$SF_{6(cyl)}$ = concentration of tracer gas in cylinder (undiluted); and
$SF_{6(spk)}$ = concentration of tracer gas in spiked gas (diluted).

9.3.2 Calculate concentration of spike added as follows:

$$CS = \frac{C_{(cyl)}}{DR} \tag{6}$$

where

CS = calculated concentration of spike added; and
$C_{(cyl)}$ = concentration of spike compound in gas cylinder (undiluted).

9.3.3 Calculate bias for the surrogate/analyte compound(s) as follows:

$$B = S_m - (M_m * D) - CS \tag{7}$$

where

B = bias at spike level;
S_m = measured mean concentration of spiked samples;
M_m = measured mean concentration of unspiked samples; and
D = $[1-(1/DR)]$; dilution factor for unspiked samples.

Calculate the percent bias as follows:

$$\% B = \frac{B}{(M_m * D) + CS} * 100 \tag{8}$$

9.3.4 Determine standard deviation of spiked sample measurements (SD_s) for the surrogate/analyte compound(s):

$$SD_s = \left[\frac{\sum (S_i - S_m)^2}{n - 1}\right]^{0.5} \tag{9}$$

where

SD_s = standard deviation of spiked sample measurements;
S_i = measured concentration of spiked sample i;
n = number of spiked sample measurements.

9.3.5 Calculate precision of the spiked samples for each surrogate/analyte compound(s) in terms of relative standard deviation (RSD):

$$RSD = \frac{SD_s}{(M_m * D) + CS} * 100 \qquad (10)$$

The bias and precision results must meet the method performance specifications presented in Section 1.0. The bias determined during the performance assessment can be used to calculate correction factors to obtain corrected concentration values.

10.0 ANALYTICAL PROCEDURE

A description of the analytical and quantitation procedures is included in the addendum to this method.

11.0 METHOD PERFORMANCE

Method performance for the target compounds is presented as performance specifications in Section 1.0. These specifications were determined as part of the Method 301 validation testing and other testing conducted for GRI, and should be representative of method performance under similar conditions.

12.0 POLLUTION PREVENTION

Sample gas from the engine exhaust is vented to the atmosphere after analysis.

13.0 WASTE MANAGEMENT

Standards of the aldehydes, particularly if formalin solution is used, should be handled according to the material safety data sheets.

14.0 REFERENCES

1. Radian Corporation. Fourier Transform Infrared (FTIR) Method Validation at a Natural Gas-Fired Internal Combustion Engine, prepared for Gas Research Institute, Chicago, Illinois, May 1995.

2. U.S. EPA. EPA Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions from Stationary Industrial Sources, Draft Version S9, 9/30/94.

3. Method 301 - Field Validation of Pollutant Measurement Methods from Various Waste Media, 40 CFR Part 63, Appendix A, December 1992.

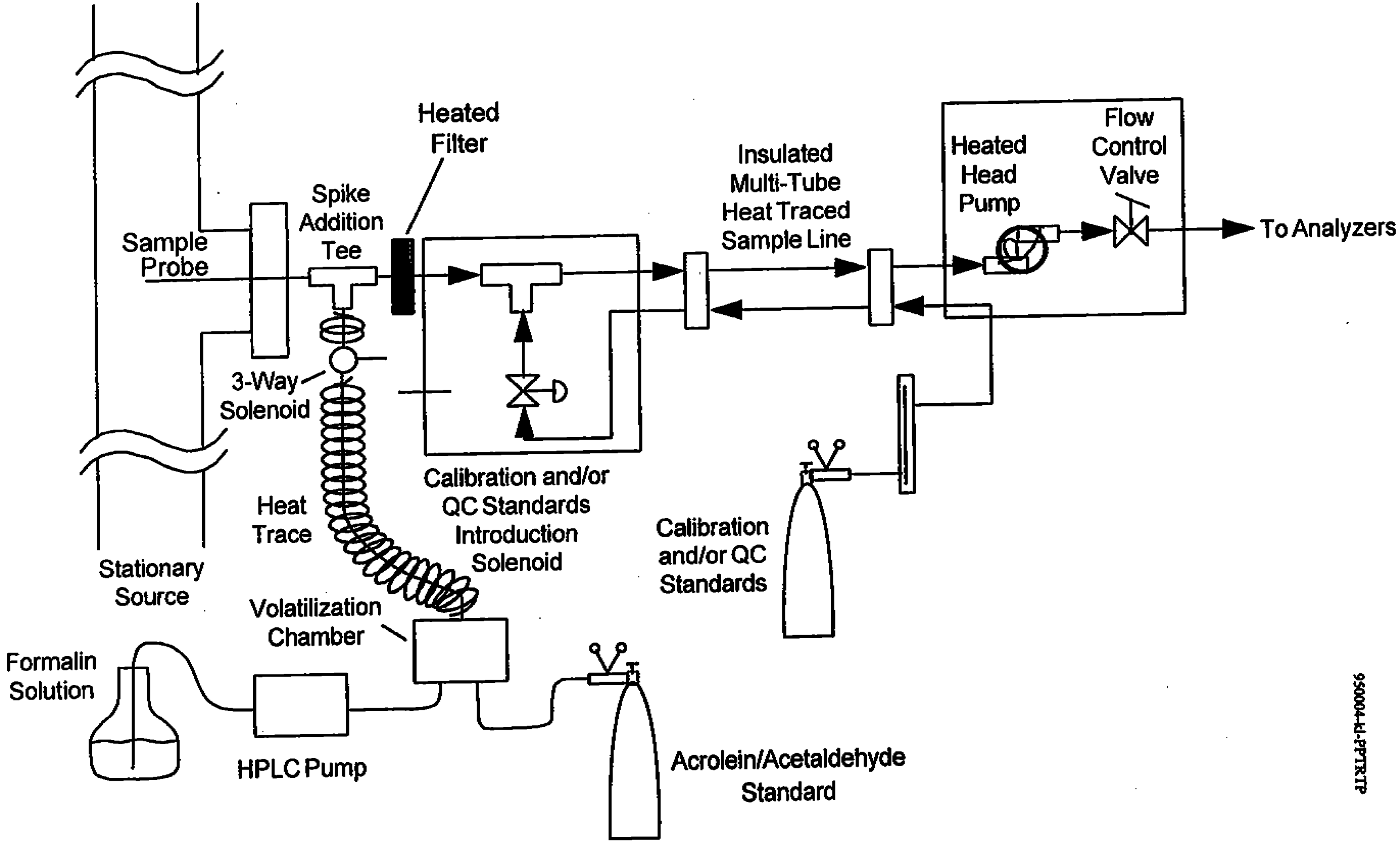

Figure 1. Sample Collection and Analysis System Configuration

APPENDIX A - DEFINITIONS OF TERMS

absorbance: the logarithm to the base 10 of the reciprocal of the transmittance, (T).

$$A = \log_{10}(1/T) = -\log_{10}T$$

absorption band: a wavenumber region of a spectrum containing a single or multiple spectral features.

analysis region: a wavenumber region used in the quantitation process for one or more target compounds. The quantitative result for a single target compound may be based on data from more than one analytical region.

background spectrum: the analyzer single beam spectrum obtained with all system components but no sample present.

Beer's law: the absorbance of a homogeneous sample containing an absorbing compound is directly proportional to the concentration of the absorbing compound.

interferogram: record of the interference signal.

line width: the full width at half maximum of an absorption feature.

measurement cell pathlength: the distance that the optical beam travels through the measurement cell.

reference spectrum: absorption spectrum of compound(s) recorded at a known measurement cell pathlength that are used as part of the quantitative analysis procedure.

scaling: application of a multiplicative factor to the absorbance values in a spectrum.

scan: digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

wavenumber: the number of waves per unit length (cm-1).

ADDENDUM

Protocol for Performing
Extractive FTIR Measurements
to Characterize Various
Gas Industry Sources for Air Toxics

PROTOCOL FOR PERFORMING EXTRACTIVE FTIR MEASUREMENTS TO CHARACTERIZE VARIOUS GAS INDUSTRY SOURCES FOR AIR TOXICS

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Table of Contents

1.0 INTRODUCTION

This protocol describes the procedures which will be used in performing the extractive Fourier Transform Infrared (FTIR) spectroscopic measurements on the various gas industry sources which will be investigated during the Gas Research Institute (GRI) Air Toxics program. Its purpose is to document the overall approach and provide guidance during execution of the work to ensure that the data collected meets the program's needs.

The protocol is divided into three sections. Section 2.0 includes a brief discussion of key issues related to emission source characterization. Section 3.0 describes the laboratory procedures including analytical method development and refinement, and data verification. Section 4.0 describes the field measurement procedures, with supporting information provided in Appendices A and B.

2.0 SOURCE CHARACTERIZATION

2.1 Determining Sample Composition

The information available from literature and previous source testing (e.g., data collected during the Phase I effort, gas canister sampling and analysis) will be used to determine emission stream composition for a particular emission source type. In some cases, canister samples will be obtained from the emission source as part of the pretest site surveys prior to the field effort. These samples will be analyzed by FTIR and other methods such as gas chromatography/mass spectrometry (GC/MS). Based on this information, potential interferants will be identified and incorporated into the analysis method development.

2.2 Emission Stream Characteristics

As part of the pretest site survey, the following emission stream information critical to FTIR measurements will be obtained:

- Temperature;
- Pressure;
- Flow rate; and
- Relative humidity.

Location of sampling ports relative to possible sampling vehicle locations will also be determined. This is especially important since the extractive FTIR procedure uses a heated sample line which should be as short as possible.

3.0 LABORATORY PROCEDURES

The objective of the laboratory study is to optimize the performance of the FTIR measurement system for a given measurement scenario. The key steps in the laboratory effort are described below for a given emission source type:

- Measurement objectives definition;
- Preliminary methods development;
- Reference spectra development;
- Final methods development; and
- Laboratory method verification.

3.1 Measurement Objectives

Once the emission source has been characterized, the following parameters must be defined:

- Accuracy;
- Precision;
- Detection range for each compound (i.e., minimum/maximum detectable concentrations); and
- Measurement (or signal averaging) period.

Accuracy is defined as:

$$A = 100 \left[\frac{C_m - C_s}{C_s} \right] \tag{3-1}$$

where

A = accuracy;
C_m = measured compound concentration; and
C_s = standard compound concentration.

Precision is defined as:

$$P = 100 \left[\frac{CI_{0.95}}{C_s}\right] \tag{3-2}$$

where

P = precision;
$CI_{0.95}$ = the 95 percent confidence interval of the measurement; and
C_s = standard compound concentration.

These data quality objectives will help establish the preliminary configuration of the FTIR system.

3.2 Preliminary Method Development

To define the operating parameters for the FTIR system, the following steps must be performed:

- Define spectral resolution;
- Determine reference spectrum requirements;
- Define spectral analysis technique;
- Establish spectral analysis regions; and
- Determine optical pathlength.

It is expected that these steps will be conducted in an iterative manner.

3.2.1 Define Spectral Resolution

Choice of spectral resolution is based on the following factors:

- Signal-to-noise ratio; and
- Interferences.

For a given source category, the lowest resolution which provides adequate discrimination should be used. The preliminary method development will be based on a resolution of 0.5 cm^{-1}, due to the following factors:

- The 0.5 cm^{-1} resolution provides a good balance between signal-to-noise ratio and compound discrimination; and

- A large number of reference spectra at this resolution are available.

3.2.2 Reference Spectrum Requirements

Reference spectra available in the FTIR library will be determined based on the sample matrix, and a list of those spectra not available in the FTIR library will be compiled. Reference spectra that are not available or do not meet concentration-pathlength product (CPLP, i.e., optical depth) or resolution requirements determined in the laboratory phase will need to be generated (see Section 3.3). If reference spectra were measured at a higher resolution than required, they can be used at lower resolution by de-resolving the spectrum. At least one reference spectrum per sample matrix component is required before proceeding further in the preliminary method development.

3.2.3 Establish Initial Analysis Regions

Given the list of compounds anticipated to be present in the source, a preliminary measurement matrix showing the spectral regions required to analyze for the compounds of interest will be constructed. In this matrix, all bands of other compounds which could possibly interfere will be included. Using the developed matrix, all compounds which will be required in setting up a valid data analysis method will be identified. The primary and secondary spectral regions which could be used for analysis will be noted.

3.2.4 Define Spectral Analysis Technique

Choice of spectral analysis technique is primarily based on experience. Classical Least Squares (CLS) has been shown to be successful in cases where interferences are significant. CLS also provides a confidence interval estimate for each compound. Other methods, such as band area or height techniques are useful when interferences are minimal, or where degradation of spectral resolution occurs due to drift in interferometer alignment, etc. CLS will be used in all phases of this program due to its extensive applications on many sources containing interfering compounds. Appendix B provides details on the CLS analysis technique.

Next, a computer-based data analysis method is constructed. Using this method, the regions and sub-regions (windows) will need to be modified to optimize all compound detections by simultaneously minimizing error and detection level. For the regions and windows chosen, the quality of all reference spectra will need to be verified by examining the signal-to-noise ratio, concentrations of foreign compounds present (if any), and the absorbance level for the given concentration-pathlength product.

A list of any spectra which are not adequate for use in the method will then be compiled. The measurement cell pathlength that will be required to achieve the desired detection levels will be determined, and the necessary spectral resolution to preserve speciation, detection, and signal-to-noise ratio under anticipated measurement conditions will be assessed.

3.2.5 Determine Optical Pathlength

Before conducting this procedure, insure all appropriate reference spectra have a signal-to-noise ratio of at least 10 in the quantitation regions to be used for analysis. An initial choice of optical pathlength is made according to the following procedure:

1. Measure a series of at least 10 spectra of zero air or nitrogen at the specified measurement time period. Use an instrumental configuration which is expected to be used in the field.

2. Quantitate the spectra collected in Step 1 using the computer-based data analysis method after applying a unit pathlength in the quantitation software.

3. For each spectrum, determine the peak-to-peak noise-equivalent absorbance (NEA) in each analysis region. For each analysis region, average all the NEA values obtained from each spectrum. Usually, the NEA values will be close in magnitude between regions. These average NEA values will be the maximum allowed for the lower detection limits specified in the data quality objectives.

4. Determine the peak-to-peak scatter in the results for each component using the following equation:

$$N_{p-p} = C_{max} - C_{min} \tag{3-3}$$

where

N_{p-p} = peak to peak scatter;
C_{max} = maximum quantitation results for the indicated compound; and
C_{min} = minimum quantitation results for the indicated compound.

5. Calculate the noise-limited CPLP ($CPLP_{nl}$) as follows:

$$CPLP_{nl} = 2 * N_{p-p} \tag{3-4}$$

6. Identify the component with the most critical detection requirements. The required minimum detectable concentration and $CPLP_{nl}$ for this component are used in the next step.

7. Compute the pathlength from the following equation:

$$PL = \frac{CPLP_{nl\,(crit)}}{MDC_{(crit)}} \tag{3-5}$$

where

PL = pathlength;
$CPLP_{nl\,(crit)}$ = critical component noise-limited CPLP; and
$MDC_{(crit)}$ = minimum detectable concentration for critical component identified in Step 6.

8. Use the computed pathlength to calculate noise-limited minimum detectable concentrations for the remaining compounds using the following equation:

$$MDC(i) = \frac{CPLP_{nl}\ (i)}{PL} \tag{3-6}$$

Use the $CPLP_{nl}$ derived for each component "i" in Step 5. Insure all noise-limited minimum detection limits meet the data quality objectives.

3.3 Reference Spectra Development

Reference spectra for those compounds not available in the current FTIR library will be generated and verified as described below.

3.3.1 Determine CPLP

Using the results of the preliminary methods development, the optimum CPLP for each of the reference spectra to be generated will be determined. These CPLP should closely match the conditions and maximum spread of conditions expected for the field measurements. The measurement cell total pressure and temperature must be matched to within 15 percent. Also, the CPLP produced in the laboratory with the measurement cell length anticipated for use should encompass the maximum, mean, and minimum concentrations anticipated. This process is important for compounds with a high degree of spectral structure but is less critical for broad-band absorbers which will scale linearly in CPLP. Compounds with a high degree of spectral structure (i.e., compounds such as CO with actual line widths which are less than or of the same magnitude as the instrumental resolution) will require multiple reference spectra in order to generate non-linear correction curves. The minimum CPLP required is 50 times the $CPLP_{nl}$ in the appropriate analysis region.

All compressed gases used should conform with EPA Protocol 1 requirements unless the physical characteristics of the components preclude meeting the accuracy specified in Protocol 1. For those compounds which cannot be produced and maintained in a stable state for extended periods of time, methods for accurate generation of these gases in the laboratory will need to be determined. Typically, a gas standard containing 100 ppmV used in conjunction with a 3- to 30-meter variable pathlength measurement cell will encompass most required CPLP levels.

3.3.2 Measure Reference Spectrum

The measurement cell will be heated and evacuated to eliminate all outgassing and then backfilled with the appropriate gas mixture at the temperature necessary to match field measurement conditions. Both static and dynamic fills should be considered depending on the adsorption characteristics of the compound on the measurement cell walls. Dynamic flows are used for adsorbing compounds and static fills for stable non-adsorbing compounds. For static fills, rapid (15- to 20-seconds) and measurements are taken with the FTIR immediately after completing a fill to look for trends in the data that would be indicative of concentration losses in the measurement cell. If any losses are observed, the fill is repeated after the measurement cell has been passivated to assure stable measurement cell conditions. If stable fills cannot be achieved, a dynamic flowing measurement should be attempted.

For dynamic flows, FTIR measurements are taken at 20- to 40-second intervals using as short a measurement time as possible commensurate with an acceptable signal-to-noise ratio. Two conditions are to be confirmed. The absorbance spectrum is constant within system error, and the spectrum is constant at both higher and lower flow rates indicative of insignificant loss to the measurement cell walls. During flow rate changes, however, the pressure in the measurement cell must be maintained constant to within 15 percent to assure that broadening effects on the spectral lines are not significantly altered. If variations in the spectra are observed, measurement cell passivation followed by a dynamic flow may be required to achieve stable conditions.

A spectrum of a diagnostic standard will be measured before and after recording the reference spectrum. The diagnostic standard is used primarily for wavelength shift, non-linear response, and resolution diagnostics. An appropriate level CO gas standard is recommended as a diagnostic check, due to its numerous sharp spectral features. The diagnostic standard will be measured under identical conditions as the reference spectrum.

Spectra are collected by coadding a sufficient number of interferograms and/or spectra to ensure noise equivalent absorbances of less than 0.01 times the minimum absorbance of concern for quantitation (i.e., signal-to-noise ratio of 100 or greater). Two replicate measurement cell fills and data acquisition sequences are taken to ensure reproducibility of the data. If discrepancies greater than 2 percent are observed between the absorbance spectra of the two tests, the process is repeated until a precision of at least 2 percent is achieved.

All spectra are stored as original interferograms as well as absorbance spectra, and the appropriate background spectrum is stored with the interferogram. The diagnostic spectra will be stored as inteferograms with the reference spectrum. The header of each file must specify the date, the gas concentration, the total pressure, the temperature, and the pathlength used.

3.3.3 Non-Linear Spectral Response Tests

For compounds with a high degree of spectral structure, tests of linearity will also be undertaken. These tests are necessary to determine the range over which the reference spectra can be legitimately scaled during quantitation. This procedure should be accomplished by collecting spectra spanning the full range of optical depths (i.e., CPLP) expected in the field, at a minimum spanning the minimum, maximum and mean optical depths. Using the mean as a reference, quantitation of the maximum and minimum spectra determines the errors incurred in scaling over these ranges. If unacceptable (i.e., greater than 5 percent) errors are observed, spectra at intermediate levels must be generated. These spectra should be used in conjunction with the non-linearity correction algorithm given in Appendix B to correct for any residual error, and the process should be carried out to guarantee a quantitation accuracy of at least 5 percent over the total range.

3.4 Final Methods Development

3.4.1 Final Analysis Method Optimization

Using the full set of reference spectra, development of the data analysis method will be completed by choosing final analysis regions and windows within these regions. Optimization of the method will be carried out in conjunction with the bias test described in Section 3.4.2. This test will constitute the worst case calculation of interference and the minimum concentration possible for the compound(s). Using the bias test, a data analysis method is constructed that produces minimum concentrations for the compound(s), minimum residuals, and minimum data scatter across multiple spectra. Such a method would be optimum for detection of the desired compound(s) in the presence of the other interferences.

This process may have to be repeated for cross interferences between compounds if there are multiple compounds in a given region/window which affect one another. If such a cross interference exists, a compromise method may be necessary which produces the best overall detection for all compounds in the presence of one another.

3.4.2 Bias Measurements

Bias testing requires several gas matrix standards in which a different target compound is missing in each standard, and the remaining components are at their expected concentrations. Bias tests will be conducted if suitable standards are available.

The test is conducted by measuring at least five spectra for each synthetic sample mixture. Each spectrum will be measured under identical conditions (i.e., measurement period) as expected in the field test. The five repetitions serve as a measure of scatter in quantitation bias. At a minimum, a test using a synthetic sample stream containing the major interfering species (e.g., H_2O, CO_2, and possibly CH_4 for internal combustion engines) will be conducted. The spectra obtained in the bias tests will be used in the procedure described above to optimize the analysis method.

3.4.3 Instrument Detection Limit Determination

Once the method has been optimized, instrument detection limits (IDLs) will be established for each compound of interest. The IDL for each target component is determined in the same way as in the methods refinement procedure, using spectra with all interferences present (at one or several concentrations) but void of the compound being tested.

Several spectra of this type are analyzed successively and the residuals as well as total scatter in the reported concentrations observed. The minimum detectable concentration should then be specified as twice the peak-to-peak scatter observed in the quantitated concentrations for the compound. This calculation is repeated for each compound of concern.

The IDL determination approach described here is similar to that described in the Code of Federal Regulations, Title 40, Part 136.1, Appendix B. The key differences are as follows:

- Peak-to-peak method measures quantitation scatter with zero compound present, while the Part 136.1, Appendix B procedure is a determination with a compound concentration of one to five times the estimated IDL; and
- IDL in the FTIR determination is twice the peak-to-peak scatter, while the Part 136.1, Appendix B method uses a t-distribution statistic at the 99 percent confidence interval.

Given the IDLs, the signal-to-noise ratio required to achieve interference-limited (non-signal-to-noise limited) data can be assessed. This is given to first order by determining the smallest of the compound absorbances at its minimum detectable concentration. This absorbance level should be at least a factor of two above the inherent noise level of the spectrum. This noise level, in turn, dictates the minimum integration time and the most rapid measurement frequency.

3.5 Laboratory Method Verification

3.5.1 Line Loss Test

In extractive sample collection, there is a possibility that the sample may be altered due to long heated sample transfer lines and low sample collection flow rates. Before performing a test in the field, it is imperative that an assessment of all possible line losses be performed. This task is best accomplished using reference gases in a "sampling mixture" representative of the actual mix of compounds to be encountered in the field. Ideally, the diluent should also be as close as possible to the actual exhaust stream to be sampled in order to simulate all possible reactive and loss effects.

In performing the line loss test, the "sampling mixture" will be admitted directly to the analyzer initially to quantify its concentrations under flowing conditions. The flow will then be diverted to the extraction line. The mathematical difference between the two spectra will then be indicative of the change in gas concentrations arising from the extraction system. This procedure will be repeated to ensure consistency of results.

In some cases, drying or other preparations of the sample may be desirable before admitting it to the FTIR to decrease interferences and improve detection limits. If drying of any kind is performed, it is important to ensure that the conditioning process does not influence the gas mixture as a whole.

3.5.2 Sample Residence Time

The final test which needs to be performed is a verification of the gas fill/flow times for the measurement cell and the gas sampling system. This testing can be accomplished by introducing the diluent into the system and then introducing a known step function concentration of an easily detectable and unreactive compound into the system. The FTIR instrument should be set up to sample as rapidly as possible consistent with an acceptable signal-to-noise ratio (perhaps 10- to 30-second measurements) and the gas concentrations recorded until an obvious stationary state is achieved. The resulting change in concentration can then be used to determine the time at which 95 percent of the target concentration level is measured. This value will then dictate the minimum transfer time required for sample set independence.

4.0 FIELD PROCEDURES

The following guidelines and procedures will be used in FTIR field operations.

4.1 Initial Instrument Checkout

The FTIR hardware and software will be checked according to the following procedures:

1. Fill measurement cell with zero air or dry nitrogen.

2. Check for proper interferogram signal using alignment software.

3. Collect a single beam spectrum and inspect for irregularities.

4. Check the single-beam spectrum for detector non-linearity and correct if necessary.

5. Collect two successive single-beam spectra (store first as a background), ratio, convert to absorbance, and examine resultant spectrum for irregularities and determine peak-to-peak (p-p) and/or root-mean-square (RMS) noise equivalent absorbance (NEA) in appropriate spectral regions. The NEA shall not exceed limits determined in the laboratory phase for the compounds in each analysis region. See Section 3.2.5, Step 3 for NEA criteria.

6. Analyze a zero gas (or dry nitrogen) sample. All quantitation results should be zero at the 95 percent confidence interval. The 95 percent confidence intervals for each compound measured shall be no greater than 3 times the MDL determined in the laboratory.

7. If the instrument passes these tests, measure the background spectrum.

All spectral data collection parameters used in the checkout will be identical to those used in the actual field data collection. If any failures are detected in the initial checkout, corrective action will be taken to restore instrumental performance to acceptable standards.

4.2 Pre-sampling Calibration

Prior to actual sampling, the FTIR system is subjected to calibration tests which will assess instrument performance. The indicator compounds will be selected before arrival on site, and will duplicate that sample matrix as closely as possible. A standard gas mixture(s) containing the set of indicator compounds will be used. In addition to the indicator compounds, chlorodifluoromethane ($CHClF_2$) will be used for measurement cell pathlength calibration. A carbon monoxide gas standard at an appropriate level will be used as an analyzer diagnostic. The diagnostic gas will provide information on instrument resolution, wavelength calibration, and non-linear response.

Procedure:

1. Pathlength Determination. Determine measurement cell pathlength using the $CHClF_2$ standard. Introduce the standard directly into the measurement cell. Compute the pathlength from the following formula:

$$PL = 37.6 \left[\frac{A_b \ T_c}{C_s \ P_c} \right] \tag{4-1}$$

where

PL = pathlength in meters;
37.6 = constant representing $CHClF_2$ intrinsic band strength and conversion factors;
A_b = area of $CHClF_2$ absorption band between 1040-1220 cm^{-1};
T_c = measured cell temperature (Kelvin);
C_s = concentration of the $CHClF_2$ standard in ppm;
P_c = measured cell pressure (Torr).

This constant is subject to slight changes due to anticipated improvements in the precision of $CHClF_2$ intrinsic band strength. The value obtained for the measurement cell pathlength will be used in all subsequent quantitations.

1a. Alternative Pathlength Calibration. Use CLS to analyze the $CHClF_2$ spectrum. Setup the CLS software in the following manner:

   i) Use an acceptable $CHClF_2$ reference spectrum (i.e., 1040-1220 cm^{-1} band strength is within ±3 percent of strength given in Equation 4-1) that was measured at same temperature and pressure as the test spectrum.

   ii) Use a CLS analysis region which includes the 1040-1220 cm^{-1} absorption band.

   iii) Use a "pathlength" equal to the $CHClF_2$ concentration in the CLS software to directly obtain the pathlength. Alternatively, one can use a unit "pathlength" to directly obtain the CPLP. Divide the CPLP by the $CHClF_2$ standard concentration to obtain the pathlength.

2. Analyzer Diagnostic. Analyze the diagnostic standard. Introduce the standard directly into the measurement cell. If the result meets Table 4-1 criteria, proceed to the next step. Otherwise, perform corrective actions in Appendix A.

3. Indicator Check. Analyze the indicator standard gas mixture(s). Introduce the indicator gas directly into the measurement cell. If the result meets Table 4-1 criteria, proceed to the next step. Otherwise, perform corrective actions in Appendix A.

4. Line Loss Test. Determine potential sample line losses by analyzing an indicator compound known to be susceptible to line losses. The indicator gas must be introduced directly into the cell and into the complete

measurement system (i.e., where sample gas is extracted from the source). Compute recovery using the following formula:

$$R = 100 \left[\frac{C_m - C_d}{C_d} \right] \tag{4-2}$$

where

R = recovery;
C_m = concentration based on the complete measurement system; and
C_d = concentration based on the complete direct measurement system.

The result must meet the recovery criteria in Table 4-1 before data collection can proceed.

5. Table 4-1 presents the pass/fail criteria for the calibration procedures:

Table 4-1

Calibration Pass/Fail Criteria

Category	Pass/Fail Criteria
Accuracy	± 10 percent
Precision	± 10 percent
Recovery	± 10 percent

Accuracy and precision are computed from Equations 3-1 and 3-2. Use the $CI_{0.95}$ reported from the CLS software in Equation 3-2. The line loss test (Step 4) is only required when a key component (i.e., heat-traced sample line) of the sample delivery system has been replaced since the last line loss test. The test should be carried out with a humidified sample, if possible.

4.3 Error Corrections

Corrections to unacceptable error can be classified as recoverable and non-recoverable. Unacceptable errors which occur after permanently recording the true infrared spectrum of the process stream under measurement are defined as recoverable.

Recoverable errors can be corrected on site as well as after the measurements are completed because the actual spectral data recorded are permanently preserved; thus subsequent manipulations (e.g. quantitation) can be adjusted to correct for the error.

Non-recoverable errors are only correctable on site. Any error which affects the collection of the true infrared spectrum of the process stream under investigation can be classified as non-recoverable. The most important of these errors is the possibility of sample line losses.

Procedure:

1. Determine whether the error is recoverable or non-recoverable.
2. If the error is recoverable and time permits, determine possible source(s) of error and attempt to correct. If time is critical, proceed with measurement. If correction is achieved, re-conduct calibration checks in Section 4.2.
3. If the error is non-recoverable, identify source(s) of error and correct before proceeding with any data collection.

4.4 Measurement Procedures

Before field measurements are attempted, the following parameters will be defined:

- Measurement frequency;
- Measurement cell flow rate, temperature, and pressure;
- Integration time;
- Number of measurement repetitions; and
- Measurements required under alternate test conditions.

Measurement frequency, repetition, measurement cell temperature, integration time, and alternate measurements will be defined before preliminary methods development. Measurement cell pressure will be kept to within 10 percent of ambient air pressure. Measurement cell flow rate must be sufficient to insure that at least five measurement cell volumes pass through the measurement cell within one integration period. Measurement cell temperature will be maintained to within 5 percent of the target.

4.5 Post-sampling Calibration

The procedures for post-sampling calibration are identical to those given in Steps 2-5, Section 4.2. If the diagnostic test fails, perform Steps 1 and 2, Section 4.2. If the diagnostic test still fails, proceed to the procedures in Appendix A.

4.6 Data Verification

To confirm data validity, the following procedures will be implemented:

4.6.1 Post-test Procedure

1. Examine the concentration vs. time series plots for each compound of interest, and determine initial regions for further examination. These regions may include: 1) sudden changes in concentration; 2) unrealistic concentration values; 3) significant changes in 95 percent confidence limits; and 4) increasing noise in data.
2. Select representative spectra from the time periods indicated in Step 1.
3. Subtract from the spectra chosen in Step 2 a spectrum which was taken immediately prior in time to the indicated time region.
4. Manually quantitate for the species in question and compare that result to the difference in software-computed concentrations for respective spectra.
5. If concentration values do not compare, then attempt to determine whether the difference is due to a recoverable or non-recoverable error.
6. If the error is non-recoverable, the spectra in the time region are declared invalid.
7. Determine the peak-to-peak scatter and/or the RMS NEA for the representative spectra.
8. If the NEA exceeds the limits imposed in the laboratory phase, the spectra in the time region are declared invalid (non-recoverable error).
9. Data found invalid are subject to the corrective actions in the test plan (re-measurement may be required).

4.6.2 Final Test

The procedures for final data validation include the above procedures; however, if a non-recoverable error is found during this phase, the data are considered invalid. In addition, the following procedures are carried out to perform a final data validation:

1. If any recoverable data errors are detected from the procedure, determine the cause and perform any necessary corrections.

2. Estimate MDL values from validated data (see Section 3.0).

3. Check data for linearity and bias (see Section 3.0).

4.7 Data Handling

To ensure data integrity throughout the sampling and subsequent archival of field data, the following procedures will be used:

1. All pertinent FTIR data collection parameters will be stored in the file header of each spectral data file.

2. A project notebook containing all sampling parameters for each spectral data file set collected will be maintained throughout the project.

3. Listings of all calibrations and data validations performed on the data will be entered in the project notebook, along with appropriate data file names.

4. Spectral data (with companion background spectrum) will be stored as interferograms or single-beam spectra and logged so that all data can be regenerated and re-quantitated as required.

APPENDIX A

CORRECTIVE ACTIONS

CORRECTIVE ACTIONS

The following procedures will be used if the diagnostic test in Section 4.2 fails.

A.1 Non-linear Correction Check

1. Ensure that the non-linear correction feature is enabled in the software and re-quantitate the diagnostic spectrum.

2. If the result is not within acceptable limits (Table 4-1), disable the non-linear correction feature and re-quantitate.

3. Manually compute the corrected concentration using the non-linear response algorithm derived in the laboratory phase and the quantitation result derived in Step 2.

4. If the result is not within acceptable limits, determine the validity of the correction curve.

    a. If the optical depth range is not within prescribed limits of the correction curve, regenerate non-linear response coefficients for optical depth used in the diagnostic test. Re-quantitate and correct for non-linearity with the new set of coefficients. Go to Step 5.

    b. If the optical depth is within range, proceed to A.2.

5. If the result is still not within limits, proceed to A.2.

A.2 Spectral Line Position and Width Diagnostic

1. Compare the diagnostic standard spectrum with the present diagnostic reference spectrum by subtraction.

2. Look for significant line shifts or changes in line width in the diagnostic analysis region.

3. If neither line shifts nor line width differences are present, continue to Section A.3.

4. i) If line shifting is present, invoke the line shifting algorithm, re-quantitate the spectrum, and go to Step 5.

ii) If line shifts are not present, but line width differences are significant, proceed to Step 6.

5. i) If the accuracy falls within the specifications stated in Table 4-1, the procedure is completed. Enable the line shifting algorithm in the data collection software and continue regular testing.

   ii) If the accuracy fails specification, proceed to Step 6.

6. If line width differences are significant, determine whether the appropriate reference spectrum is being used. If so, determine the cause of the line width difference and attempt to correct it.

A.3 Background Spectrum Quality Check

1. Fill the cell with dry nitrogen and measure a single-beam spectrum. Check the single-beam spectrum for detector linearity. Readjust the detector linearity if necessary. Detector gain may need slight adjustment if linearity is adjusted.

2. Calculate the ratio of the single-beam spectrum measured in Step 1 with the current background spectrum.

3. Optionally, convert the ratio to absorbance and examine the spectrum for abnormalities, such as baseline distortions in the quantitation regions or unexpected spectral features.

   a. If baseline percent transmittance (T) is flat (i.e., slope less than 0.01 absorbance units/1000cm^{-1}) and below 80 percent (or absorbance greater than 0.1), determine the source of signal reduction.

   b. If baseline is sloped, re-align the interferometer and check for stability.

   c. If baseline anomalies are present, repeat the diagnostic standard test with the original single-beam spectrum collected in Step 1 as a background. If quantitation is within limits stated in Table 4-1, corrective action is completed. If quantitation fails, proceed to Section A.4.

   d. If no abnormalities are found, proceed to Section A.4.

A.4 Sample Integrity Check

1. Check sample flow into the cell. Insure measurement cell flush time is within desired specifications. If flush time is not within specifications, take corrective action and repeat the diagnostic test. If the test fails again, proceed to Section A.1.

2. If sample flow is adequate, check the cell for leaks. Pump the cell to a pressure less than 20 percent of normal operating pressure. Isolate the cell, and measure the leak rate. Leak rate must be less than 10 Torr/minute. If the leak test passes, proceed to Section A.1.

APPENDIX B

CLASSICAL LEAST SQUARES TECHNIQUE

CLASSICAL LEAST SQUARES TECHNIQUE

B.1 Summary of CLS Equations

For each analysis region, the following matrix equation is used to determine the concentrations:

$$C = A^{-1}B \tag{B-1}$$

where

C = N-dimensional vector (or column matrix) representing the concentrations of the N-2 compounds analyzed in the region (two elements are used for linear baseline correction in the analysis region);
A = N-dimensional square matrix; and
B = N-dimensional vector.

A is defined as:

$$A = DD^{T} \tag{B-2}$$

where **D** is the reference spectrum matrix. Or in terms of matrix elements:

$$A(k,m) = \sum_{j=1}^{M} D(k,j)D(j,m) \tag{B-3}$$

The reference spectrum matrix is constructed in the following manner:

$$\mathbf{D} = \begin{pmatrix} D(1,1) & . & . & . & D(1,M) \\ . & . & . & . & . \\ . & . & D(k,j) & . & . \\ . & . & . & . & . \\ D(N,1) & . & . & . & D(N,M) \end{pmatrix} \tag{B-4}$$

where

k,m = compound identifiers;
j = spectral data point in the region; and
M = number of spectral data points in the analysis region.

The elements of **D** for a given compound are normalized by dividing by the CPLP of the reference spectrum. **B** is defined as:

$$B = DE \tag{B-5}$$

or for the elements:

$$B(k)=\sum_{j=1}^{M} D(k,j)E(j) \qquad \text{(B-6)}$$

where $E(j)$ equal the jth spectral data point in the region for the sample spectrum. In order to fit a linear baseline to the data, the following "reference" spectra are used for "compounds" N-1 and N:

$$\text{For } j=1,M$$

$$D(N\text{-}1,j)=1 \qquad \text{(B-7)}$$

$$D(N,j) = j \qquad \text{(B-8)}$$

B.2 Confidence Interval Estimation

The 95 percent confidence intervals derived for each compound are found from the following equation:

$$\text{For } l=1 \text{ to } N$$

$$CI(l)=1.96\sqrt{A(l,l)^{-1}\left(\frac{\sum_{j=1}^{M} E(j)^2-\sum_{k=1}^{N} C(k)B(k)}{(M-N)}\right)} \qquad \text{(B-9)}$$

where CI(l) = 95% confidence interval for compound l.

B.3 Incorporation of Sub-Regions

In cases where a strong absorption feature(s) is(are) present in the sample spectrum, the region may be broken up into sub-regions. This is achieved by removing the spectral data points in both sample and reference spectra which correspond to the interfering feature(s). This reduces the M dimension in all appropriate matrices.

B.4 Non-linear Response Corrections

Corrections for non-linear response are handled by quantitation of a series of reference spectra with increasing optical depth by the reference spectrum which will be used in the actual quantitation. The optical depths found by CLS are fitted using standard multivariate linear least-squares to the polynomial equation:

$$OD_{actual}=\sum_{i=0}^{O}(OD_{cls})^{i}C(i) \tag{B-10}$$

where

OD_{actual} = Actual optical depth;
OD_{cls} = CLS derived optical depth;
$C(i)$ = polynomial fit coefficients; and
O = highest order of the polynomial.

The lowest order polynomial which gives less than 3 percent error in optical depth is used. The derived polynomial is valid only over the range of optical depths used in the fit.

Cross-corrections due to molecular interactions or interferences may be required. If cross-corrections are necessary, then the following equation is used in a multivariate linear squares fit to the appropriate spectra:

$$OD_{actual}=\sum_{i=0}^{O_1}\sum_{j=0}^{O_2}C_n(i,j)(OD_{cls})^{i}(OD_{cls,i})^{j} \tag{B-11}$$

where $OD_{cls,i}$ represents the level of the major interfering compound(s). If more that one major interferant is present, then terms representing each interferant should be added in the expansion. Appropriate spectra containing the interference(s) or interactions are required for the fitting process.

An alternative approach is to use orthogonal polynomials as the fitting functions instead of monic polynomials. Orthogonal polynomials should be used when fit parameter stability is a concern.

B.5 Reference

1. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures", Applied Spectroscopy, 39(10), 73-84, 1985.

APPENDIX C

METHOD 301

U.S. EPA METHOD 301

"Field Validation of Pollutant Measurement
Methods for Various Media"

Appendix A to Part 63—Test Methods Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media

1. Applicability and principle

1.1 *Applicability.* This method, as specified in the applicable subpart, is to be used whenever a source owner or operator (hereafter referred to as an "analyst") proposes a test method to meet a U.S. Environmental Protection Agency (EPA) requirement in the absence of a validated method. This Method includes procedures for determining and documenting the quality, i.e., systematic error (bias) and random error (precision), of the measured concentrations from an effected source. This method is applicable to various waste media (i.e., exhaust gas, wastewater, sludge, etc.).

1.1.1 If EPA currently recognizes an appropriate test method or considers the analyst's test method to be satisfactory for a particular source, the Administrator may waive the use of this protocol or may specify a less rigorous validation procedure. A list of validated methods may be obtained by contacting the Emission Measurement Technical Information Center (EMTIC), Mail Drop 19, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, (919) 541–0200. Procedures for obtaining a waiver are in Section 12.0.

1.1.2 This method includes optional procedures that may be used to expand the applicability of the proposed method. Section 7.0 involves ruggedness testing (Laboratory Evaluation), which demonstrates the sensitivity of the method to various parameters. Section 8.0 involves a procedure for including sample stability in bias and precision for assessing sample recovery and analysis times; Section 9.0 involves a procedure for the determination of the practical limit of quantitation for determining the lower limit of the method. These optional procedures are required for the waiver consideration outlined in Section 12.0.

1.2 *Principle.* The purpose of these procedures is to determine bias and precision of a test method at the level of the applicable standard. The procedures involve (a) introducing known concentrations of an analyte or comparing the test method against a validated test method to determine the method's bias and (b) collecting multiple or collocated simultaneous samples to determine the method's precision.

1.2.1 *Bias.* Bias is established by comparing the method's results against a reference value and may be eliminated by employing a correction factor established from the data obtained during the validation test. An offset bias may be handled accordingly. Methods that have bias correction factors outside 0.7 to 1.3 are unacceptable. Validated method to proposed method comparisons, section 6.2, requires a more restrictive test of central tendency and a lower correction factor allowance of 0.90 to 1.10.

1.2.2 *Precision.* At the minimum, paired sampling systems shall be used to establish precision. The precision of the method at the level of the standard shall not be greater than 50 percent relative standard deviation. For a validated method to proposed method equivalency comparisons, section 6.2, the analyst must demonstrate that the precision of the proposed test method is as precise as the validated method for acceptance.

2. Definitions

2.1 *Negative bias.* Bias resulting when the measured result is less than the "true" value.

2.2 *Paired sampling system.* A sampling system capable of obtaining two replicate samples that were collected as closely as possible in sampling time and sampling location.

2.3 *Positive bias.* Bias resulting when the measured result is greater than the "true" value.

2.4 *Proposed method.* The sampling and analytical methodology selected for field validation using the method described herein.

2.5 *Quadruplet sampling system.* A sampling system capable of obtaining four replicate samples that were collected as closely as possible in sampling time and sampling location.

2.6 *Surrogate compound.* A compound that serves as a model for the types of compounds being analyzed (i.e., similar chemical structure, properties, behavior). The model can be distinguished by the method from the compounds being analyzed.

3. Reference Material

The reference materials shall be obtained or prepared at the level of the standard. Additional runs with higher and lower reference material concentrations may be made to expand the applicable range of the method, in accordance with the ruggedness test procedures.

3.1 *Exhaust Gas Tests.* The analyst shall obtain a known concentration of the reference material (i.e., analyte of concern) from an independent source such as a specialty gas manufacturer, specialty chemical company, or commercial laboratory. A list of vendors may be obtained from EMTIC (see Section 1.1.1). The analyst should obtain the manufacturer's stability data of the analyte concentration and recommendations for recertification.

3.2 *Other Waste Media Tests.* The analyst shall obtain pure liquid components of the reference materials (i.e., analytes of concern) from an independent manufacturer and dilute them in the same type matrix as the source waste. The pure reference materials shall be certified by the manufacturer as to purity and shelf life. The accuracy of all diluted reference material concentrations shall be verified by comparing their response to independently-prepared materials (independently prepared in this case means prepared from pure components by a different analyst).

3.3 *Surrogate Reference Materials.* The analyst may use surrogate compounds, e.g., for highly toxic or reactive organic compounds, provided the analyst can demonstrate to the Administrator's satisfaction that the surrogate compound behaves as the analyte. A surrogate may be an isotope or one that contains a unique element (e.g., chlorine) that is not present in the source or a derivation of the toxic or reactive compound, if the derivative formation is part of the method's procedure.

Laboratory experiments or literature data may be used to show behavioral acceptability.

3.4 *Isotopically Labeled Materials.* Isotope mixtures may contain the isotope and the natural analyte. For best results, the isotope labeled analyte concentration should be more than five times the natural concentration of the analyte.

4. EPA Performance Audit Material

4.1 To assess the method bias independently, the analyst shall use (in addition to the reference material) an EPA performance audit material, if it is available. The analyst may contact EMTIC (see section 1.1.1) to receive a list of currently available EPA audit materials. If the analyte is listed, the analyst should request the audit material at least 30 days before the validation test. If an EPA audit material is not available, request documentation from the validation report reviewing authority that the audit material is currently not available from EPA. Include this documentation with the field validation report.

4.2 The analyst shall sample and analyze the performance audit sample three times according to the instructions provided with the audit sample. The analyst shall submit the three results with the field validation report. Although no acceptance criteria are set for these performance audit results, the analyst and reviewing authority may use them to assess the relative error of sample recovery, sample preparation, and analytical procedures and then consider the relative error in evaluating the measured emissions.

5. Procedure for Determination of Bias and Precision in the Field

The analyst shall select one of the sampling approaches below to determine the bias and precision of the data. After analyzing the samples, the analyst shall calculate the bias and precision according to the procedure described in section 6.0. When sampling a stationary source, follow the probe placement procedures in section 5.4.

5.1 *Isotopic Spiking.* This approach shall be used only for methods that require mass spectrometry (MS) analysis. Bias and precision are calculated by procedures described in section 6.1.

5.1.1 *Number of Samples and Sampling Runs.* Collect a total of 12 replicate samples by either obtaining six sets of paired samples or three sets of quadruplet samples.

5.1.2 *Spiking Procedure.* Spike all 12 samples with the reference material at the level of the standard. Follow the appropriate spiking procedures listed below for the applicable waste medium.

5.1.2.1 *Exhaust Gas Testing.* The spike shall be introduced as close to the tip of the sampling probe as possible.

5.1.2.1.1 *Gaseous Reference Material with Sorbent or Impinger Sampling Trains.* Sample the reference material (in the laboratory or in the field) at a concentration which is close to the allowable concentration standard for the time required by the method, and then sample the gas stream for an equal amount of time. The time for sampling both the reference material and gas stream should be equal; however, the time should be adjusted to avoid sorbent breakthrough.

5.1.2.1.2 *Gaseous Reference Material with Sample Container (Bag or Canister).* Spike the sample containers after completion of each test run with an amount equal to the allowable concentration standard of the emission point. The final concentration of the reference material shall approximate the level of the emission concentration in the stack. The volume amount of reference material shall be less than 10 percent of the sample volume.

5.1.2.1.3 *Liquid and Solid Reference Material with Sorbent or Impinger Trains.* Spike the trains with an amount equal to the allowable concentration standard before sampling the stack gas. The spiking should be done in the field; however, it may be done in the laboratory.

5.1.2.1.4 *Liquid and Solid Reference Material with Sample Container (Bag or Canister).* Spike the containers at the completion of each test run with an amount equal to the level of the emission standard.

5.1.2.2 *Other Waste Media.* Spike the 12 replicate samples with the reference material either before or directly after sampling in the field.

5.2 *Comparison Against a Validated Test Method.* Bias and precision are calculated using the procedures described in section 6.2. This approach shall be used when a validated method is available and an alternative method is being proposed.

5.2.1 *Number of Samples and Sampling Runs.* Collect nine sets of replicate samples using a paired sampling system (a total of 18 samples) or four sets of replicate samples using a quadruplet sampling system (a total of 16 samples). In each sample set, the validated test method shall be used to collect and analyze half of the samples.

5.2.2 *Performance Audit Exception.* Conduct the performance audit as required in section 4.0 for the validated test method. Conducting a performance audit on the test method being evaluated is recommended.

5.3 *Analyte Spiking.* This approach shall be used when sections 5.1 and 5.2 are not applicable. Bias and precision are calculated using the procedures described in Section 6.3.

5.3.1 *Number of Samples and Sampling Runs.* Collect a total of 24 samples using the quadruplet sampling system (a total of 6 sets of replicate samples).

5.3.2 In each quadruplet set, spike half of the samples (two out of the four) with the reference material according to the applicable procedure in section 5.1.2.1 or 5.1.2.2.

5.4 *Probe Placement and Arrangement for Stationary Source Stack or Duct Sampling.* The probes shall be placed in the same horizontal plane. For paired sample probes the arrangement should be that the probe tip is 2.5 cm from the outside edge of the other with a pitot tube on the outside of each probe. Other paired arrangements for the pitot tube may be acceptable. For quadruplet sampling probes, the tips should be in a 6.0 cm × 6.0 cm square area measured from the center line of the opening of the probe tip with a single pitot tube in the center or two pitot tubes with their location on either side of the probe tip configuration. An alternative arrangement should be proposed whenever the cross-sectional area of the probe tip configuration is approximately 5 percent of the stack or duct cross-sectional area.

6 Calculations

Data resulting from the procedures specified in section 5.0 shall be treated as follows to determine bias, correction factors, relative standard deviations, precision, and data acceptance.

6.1 *Isotopic Spiking.* Analyze the data for isotopic spiking tests as outlined in sections 6.1.1 through 6.1.6.

6.1.1 Calculate the numerical value of the bias using the results from the analysis of the isotopically spiked field samples and the calculated value of the isotopically labeled spike:

$B = CS - S_m$ Eq. 301=1

where:

B=Bias at the spike level.
S_m=Mean of the measured values of the isotopically spiked samples.
CS=Calculated value of the isotopically labeled spike.

6.1.2 Calculate the standard deviation of the S_i values as follows:

$$SD = \sqrt{\frac{\sum (S_i - S_m)^2}{(n-1)}}$$

Eq. 301–2

where:

S_i=Measured value of the isotopically labeled analyte in the ith field sample,
n=Number of isotopically spiked samples, 12.

6.1.3. Calculate the standard deviation of the mean (SDM) as follows:

$$SDM = \frac{SD}{\sqrt{n}}$$

Eq. 301–3

$$t = \frac{|B|}{SDM}$$

6.1.4 Test the bias for statistical significance by calculating the t-statistic, Eq. 301–4 and compare it with the critical value of the two-sided t-distribution at the 95-percent confidence level and n−1 degrees of freedom. This critical value is 2.201 for the eleven degrees of freedom when the procedure specified in section 5.1.2 is followed. If the calculated t-value is greater than the critical value the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.1.5 *Calculation of a Correction Factor.* If the t-test does not show that the bias is statistically significant, use all analytical results without correction and proceed to the precision evaluation. If the method's bias is statistically significant, calculate the correction factor, CF, using the following equation:

$$CF = \frac{1}{1 + \frac{B}{CS}}$$

Eq. 301–5

If the CF is outside the range of 0.70 to 1.30, the data and method are considered unacceptable. For correction factors within the range, multiply all analytical results by the CF to obtain the final values.

6.1.6 *Calculation of the Relative Standard Deviation (Precision).* Calculate the relative standard deviation as follows:

$$RSD = \left(\frac{SD}{S_m}\right) \times 100$$

Eq. 301–6

where S_m is the measured mean of the isotopically labeled spiked samples.

6.2 *Comparison with Validated Method.* Analyze the data for comparison with a validated method as outlined in sections 6.2.1 or 6.2.2, as appropriate. Conduct these procedures in order to determine if a proposed method produces results equivalent to a validated method. Make all necessary bias corrections for the validated method, as appropriate. If the proposed method fails either test, the method results are unacceptable, and conclude that the proposed method is not as precise or accurate as the validated method. For highly variable sources, additional precision checks may be necessary. The analyst should consult with the Administrator if a highly variable source is suspected.

6.2.1 *Paired Sampling Systems.*

6.2.1.1. *Precision.* Determine the acceptance of the proposed method's variance with respect to the variability of the validated method results. If a significant difference is determined, the proposed method and the results are rejected. Proposed methods demonstrating F-values equal to or less than the critical value have acceptable precision.

6.2.1.2 Calculate the variance of the proposed method, S_p^2, and the variance of the validated method, S_v^2, using the following equation:

$S_{(p\ or\ v)}^2 = SD^2$ Eq. 301–7

where:

SD_v=Standard deviation provided with the validated method.

SD_p=Standard deviation of the proposed method calculated using Equation 301–9a.

6.2.1.3 *The F-test.* Determine if the variance of the proposed method is significantly different from that of the validated method by calculating the F-value using the following equation:

$$F = \frac{S_p^2}{S_v^2}$$

Eq. 301–8

Compare the experimental F value with the critical value of F. The critical value is 1.0 when the procedure specified in section 5.2.1 for paired trains is followed. If the calculated F is greater than the critical value, the difference in precision is significant and the data and proposed method are unacceptable.

6.2.1.4 *Bias Analysis.* Test the bias for statistical significance by calculating the t-statistic and determine if the mean of the differences between the proposed method and the validated method is significant at the 80-percent confidence level. This procedure requires the standard deviation of the validated method, SD_v, to be known. Employ the value furnished with the method. If the standard deviation of the validated method is not available, the paired replicate sampling procedure may not be used. Determine the mean of the paired sample differences, d_m, and the standard deviation, SD_d, of the differences, d_i's, using Equation 301–2 where: d_i replaces S_i, d_m replaces S_m. Calculate the standard deviation of the proposed method, SD_p, as follows:

$SD_p = SD_d - SD_v$ Eq. 301–9a

(If $SD_v > SD_d$, let $SD = SD_d/1.414$).

Calculate the value of the t-statistic using the following equation:

$$t = \frac{d_m}{\left(\frac{SD_p}{\sqrt{n}}\right)}$$

Eq. 301–9

where n is the total number of paired samples. For the procedure in section 5.2.1, n equals nine. Compare the calculated t-statistic with the corresponding value from the table of the t-statistic. When nine runs are conducted, as specified in section 5.2.1, the critical value of the t-statistic is 1.397 for eight degrees of freedom. If the calculated t-value is greater than the critical value the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.2.1.5 *Calculation of a Correction Factor.* If the statistical test cited above does not show a significant bias with respect to the reference method, assume that the proposed method is unbiased and use all analytical results without correction. If the method's bias is statistically significant, calculate the correction factor, CF, as follows:

$$CF = \frac{1}{1 + \frac{d_m}{V_m}}$$

Eq. 301–10

where V_m is the mean of the validated method's values.

Multiply all analytical results by CF to obtain the final values. The method results, and the method, are unacceptable if the correction factor is outside the range of 0.9 to 1.10.

6.2.2 *Quadruplet Replicate Sampling Systems.*

6.2.2.1 *Precision.* Determine the acceptance of the proposed method's variance with respect to the variability of the validated method results. If a significant difference is determined the proposed method and the results are rejected.

6.2.2.2 Calculate the variance of the proposed method, S_p^2, using the following equation:

$$S^2 = \frac{\sum d_i^2}{2n}$$

Eq. 301–11

where the d_i's are the differences between the validated method values and the proposed method values.

6.2.2.3 *The F-test.* Determine if the variance of the proposed method is more variable than that of the validated method by calculating the F-value using Equation 301–8. Compare the experimental F value with the critical value of F. The critical value is 1.0 when the procedure specified in section 5.2.2 for quadruplet trains is followed. The calculated F should be less than or equal to the critical value. If the difference in precision is significant the results and the proposed method are unacceptable.

6.2.2.4 *Bias Analysis.* Test the bias for statistical significance at the 80 percent confidence level by calculating the t-statistic. Determine the bias (mean of the differences between the proposed method and the validated method, d_m) and the standard deviation, SD_d, of the differences. Calculate the standard deviation of the differences, SD_d, using Equation 301–2 and substituting d_i for S_i. The following equation is used to calculate d_i:

$$d_i = \frac{(V_{1_i} + V_{2_i})}{2} - \frac{(P_{1_i} + P_{2_i})}{2}$$

Eq. 301–12

and: V_{1i}=First measured value of the validated method in the ith test sample.

P_{1i}=First measured value of the proposed method in the ith test sample.

Calculate the t-statistic using Equation 301–9 where n is the total number of test sample differences (d_i). For the procedure in section 5.2.2, n equals four. Compare the calculated t-statistic with the corresponding value from the table of the t-statistic and determine if the mean is significant at the 80-percent confidence level. When four runs are conducted, as specified in section 5.2.2, the critical value of the t-statistic is 1.638 for three degrees of freedom. If the calculated t-value is greater than the critical value the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.2.2.5 *Correction Factor Calculation.* If the method's bias is statistically significant, calculate the correction factor, CF, using Equation 301–10. Multiply all analytical results by CF to obtain the final values. The method results, and the method, are unacceptable if the correction factor is outside the range of 0.9 to 1.10.

6.3 *Analyte Spiking.* Analyze the data for analyte spike testing as outlined in Sections 6.3.1 through 6.3.3.

6.3.1 *Precision.*

6.3.1.1 *Spiked Samples.* Calculate the difference, d_i, between the pairs of the spiked proposed method measurements for each replicate sample set. Determine the standard deviation (SD_s) of the spiked values using the following equation:

$$SD_s = \sqrt{\frac{\sum d_i^2}{2n}}$$

Eq. 301–13

where: n = Number of runs.

Calculate the relative standard deviation of the proposed spiked method using Equation 301–6 where S_m is the measured mean of the analyte spiked samples. The proposed method is unacceptable if the RSD is greater than 50 percent.

6.3.1.2 *Unspiked Samples.* Calculate the standard deviation of the unspiked values using Equation 301–13 and the relative standard deviation of the proposed unspiked method using Equation 301–6 where S_m is the measured mean of the analyte spiked samples. The RSD must be less than 50 percent.

6.3.2 *Bias.* Calculate the numerical value of the bias using the results from the analysis of the spiked field samples, the unspiked field samples, and the calculated value of the spike:

$B=S_m-M_m-CS$

Eq. 301–14

where: B = Bias at the spike level.

S_m = Mean of the spiked samples.

M_m = Mean of the unspiked samples.

CS = Calculated value of the spiked level.

6.3.2.1 Calculate the standard deviation of the mean using the following equation where SD_s and SD_u are the standard deviations of the spiked and unspiked sample values respectively as calculated using Equation 301–13.

$$SD = \sqrt{SD_s^2 + SD_u^2}$$

Eq. 301–15

6.3.2.2 Test the bias for statistical significance by calculating the t-statistic using Equation 301–4 and comparing it with the critical value of the two-sided t-distribution at the 95-percent confidence level and n-1 degrees of freedom. This critical value is 2.201 for the eleven degrees of freedom.

6.3.3 *Calculation of a Correction Factor.* If the t-test shows that the bias is not statistically significant, use all analytical results without correction. If the method's bias is statistically significant, calculate the correction factor using Equation 301–5. Multiply all analytical results by CF to obtain the final values.

7. Ruggedness Testing (Optional)

7.1 *Laboratory Evaluation.*

7.1.1 Ruggedness testing is a useful and cost-effective laboratory study to determine the sensitivity of a method to certain parameters such as sample collection rate, interferant concentration, collecting medium temperature, or sample recovery temperature. This Section generally discusses the principle of the ruggedness test. A more detailed description is presented in citation 10 of Section 13.0.

7.1.2 In a ruggedness test, several variables are changed simultaneously rather than one variable at a time. This reduces the number of experiments required to evaluate the effect of a variable. For example, the effect of seven variables can be determined in eight experiments rather than 128 (W.J. Youden, Statistical Manual of the Association of Official Analytical Chemists, Association of Official Analytical Chemists, Washington, DC, 1975, pp. 33–36).

7.1.3 Data from ruggedness tests are helpful in extending the applicability of a test method to different source concentrations or source categories.

8. Procedure for Including Sample Stability in Bias and Precision Evaluations

8.1 *Sample Stability.*

8.1.1 The test method being evaluated must include procedures for sample storage and the time within which the collected samples shall be analyzed.

8.1.2 This section identifies the procedures for including the effect of storage time in bias and precision evaluations. The evaluation may be deleted if the test method specifies a time for sample storage.

8.2 *Stability Test Design.* The following procedures shall be conducted to identify the effect of storage times on analyte samples. Store the samples according to the procedure specified in the test method. When using the analyte spiking procedures (section 5.3), the study should include equal numbers of spiked and unspiked samples.

8.2.1 Stack Emission Testing.

8.2.1.1 For sample container (bag or canister) and impinger sampling systems, sections 5.1 and 5.3, analyze six of the samples at the minimum storage time. Then analyze the same six samples at the maximum storage time.

8.2.1.2 For sorbent and impinger sampling systems, sections 5.1 and 5.3, that require extraction or digestion, extract or digest six of the samples at the minimum storage time and extract or digest six other samples at the maximum storage time. Analyze an aliquot of the first six extracts (digestates) at both the minimum and maximum storage times. This will provide some freedom to analyze extract storage impacts.

8.2.1.3 For sorbent sampling systems, sections 5.1 and 5.3, that require thermal desorption, analyze six samples at the minimum storage time. Analyze another set of six samples at the maximum storage time.

8.2.1.4 For systems set up in accordance with section 5.2, the number of samples analyzed at the minimum and maximum storage times shall be half those collected (8 or 9). The procedures for samples requiring extraction or digestion should parallel those in section 8.2.1.

8.2.2 *Other Waste Media Testing.* Analyze half of the replicate samples at the minimum storage time and the other half at the maximum storage time in order to identify the effect of storage times on analyte samples.

9. Procedure for Determination of Practical Limit of Quantitation (Optional)

9.1 *Practical Limit of Quantitation.*

9.1.1 The practical limit of quantitation (PLQ) is the lowest level above which quantitative results may be obtained with an acceptable degree of confidence. For this protocol, the PLQ is defined as 10 times the standard deviation, s_o, at the blank level. This PLQ corresponds to an uncertainty of ±30 percent at the 99-percent confidence level.

9.1.2 The PLQ will be used to establish the lower limit of the test method.

9.2 *Procedure I for Estimating s_o.* This procedure is acceptable if the estimated PLQ is no more than twice the calculated PLQ. If the PLQ is greater than twice the calculated PLQ use Procedure II.

9.2.1 Estimate the PLQ and prepare a test standard at this level. The test standard could consist of a dilution of the reference material described in section 3.0.

9.2.2 Using the normal sampling and analytical procedures for the method, sample and analyze this standard at least seven times in the laboratory.

9.2.3 Calculate the standard deviation, s_o, of the measured values.

9.2.4 Calculate the PLQ as 10 times s_o.

9.3 *Procedure II for Estimating s_o.* This procedure is to be used if the estimated PLQ is more than twice the calculated PLQ.

9.3.1 Prepare two additional standards at concentration levels lower than the standard used in Procedure I.

9.3.2 Sample and analyze each of these standards at least seven times.

9.3.3 Calculate the standard deviation for each concentration level.

9.3.4 Plot the standard deviations of the three test standards as a function of the standard concentrations.

9.3.5 Draw a best-fit straight line through the data points and extrapolate to zero concentration. The standard deviation at zero concentration is S_o.

9.3.6 Calculate the PLQ as 10 times S_o.

10.0 Field Validation Report Requirements

The field validation report shall include a discussion of the regulatory objectives for the testing which describe the reasons for the test, applicable emission limits, and a description of the source. In addition, validation results shall include:

10.1 Summary of the results and calculations shown in section 6.0.

10.2 Reference material certification and value(s).

10.3 Performance audit results or letter from the reviewing authority stating the audit material is currently not available.

10.4 Laboratory demonstration of the quality of the spiking system.

10.5 Discussion of laboratory evaluations.

10.6 Discussion of field sampling.

10.7 Discussion of sample preparations and analysis.

10.8 Storage times of samples (and extracts, if applicable).

10.9 Reasons for eliminating any results.

11. Followup Testing

The correction factor calculated in section 6.0 shall be used to adjust the sample concentrations in all followup tests conducted at the same source. These tests shall consist of at least three replicate samples, and the average shall be used to determine the pollutant concentration. The number of samples to be collected and analyzed shall be as follows, depending on the validated method precision level:

11.1 Validated relative standard deviation (RSD) ≤±15 Percent. Three replicate samples.

11.2 Validated RSD ≤±30 Percent. Six replicate samples.

11.3 Validated RSD ≤±50 Percent. Nine replicate samples.

11.4 Equivalent method. Three replicate samples.

12. Procedure for Obtaining a Waiver

12.1 *Waivers.* These procedures may be waived or a less rigorous protocol may be granted for site-specific applications. The following are three example situations for which a waiver may be considered.

12.1.1 *"Similar" Sources.* If the test method has been validated previously at a "similar" source, the procedures may be waived provided the requester can demonstrate to the satisfaction of the Administrator that the sources are "similar." The methods's applicability to the "similar" source may be demonstrated by conducting a ruggedness test as described in section 6.0.

12.1.2 *"Documented" Methods.* In some cases, bias and precision may have been documented through laboratory tests or protocols different from this method. If the analyst can demonstrate to the satisfaction of the Administrator that the bias and precision apply to a particular application, the Administrator may waive these procedures or parts of the procedures.

12.1.3 *"Conditional" Test Methods.* When the method has been demonstrated to be valid at several sources, the analyst may seek a "conditional" method designation from the Administrator. "Conditional" method status provides an automatic waiver from the procedures provided the test method is used within the stated applicability.

12.2 *Application for Waiver.* In general, the requester shall provide a thorough description of the test method, the intended application, and results of any validation or other supporting documents. Because of the many potential situations in which the Administrator may grant a waiver, it is neither possible nor desirable to prescribe the exact criteria for a waiver. At a minimum, the requester is responsible for providing the following.

12.2.1 A clearly written test method, preferably in the format of 40 CFR part 60, appendix A Test Methods. The method must include an applicability statement, concentration range, precision, bias (accuracy), and time in which samples must be analyzed.

12.2.2.2 Summaries (see section 10.0) of previous validation tests or other supporting documents. If a different procedure from that described in this method was used, the requester shall provide appropriate documents substantiating (to the satisfaction of the Administrator) the bias and precision values.

12.2.2.3 Results of testing conducted with respect to sections 7.0, 8.0, and 9.0.

12.2.3 Discussion of the applicability statement and arguments for approval of the waiver. This discussion should address as applicable the following: Applicable regulation, emission standards, effluent characteristics, and process operations.

12.3 *Requests for Waiver.* Each request shall be in writing and signed by the analyst. Submit requests to the Director, OAQPS, Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

13. Bibliography

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12. Youdon, W.J. Statistical techniques for collaborative tests. In: Statistical Manual of the Association of Official Analytical Chemists, Association of Official Analytical Chemists, Washington, DC, 1975, pp. 33–36.

APPENDIX B TO PART 63—SOURCES DEFINED FOR EARLY REDUCTION PROVISIONS

Source	Location of definition
1. Organic Process Equipment in Volatile Hazardous Air Pollutant Service at Chemical Plants and Other Designated Facilities.	56 FR 9315, March 6, 1991, Announcement of Negotiated Rulemaking
a. All valves in gas or light liquid service within a process unit	
b. All pumps in light liquid service within a process unit	
c. All connectors in gas or light liquid service within a process unit	
d. Each compressor	
e. Each product accumulator vessel	
f. Each agitator	
g. Each pressure relief device	
Each open-ended valve or line	
i. Each sampling connection system	
j. Each instrumentation system	
k. Each pump, valve, or connector in heavy liquid service	
l. Each closed vent system and control device	

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METHOD 301 ERRATA

1. Section 6.1.1, Eq 301-1, the terms to the right of the equals sign should be reversed:

   $B = S_m - CS$

2. Section 6.2.1.4, Eq 301-9, SD_p should be SD_u.

3. Section 6.2.1.5, Eq 301-10, remove the numerator to the right of the equals sign.

   $CF = 1 + d_m/V_m$

4. Section 6.3.1.2, should read: "...the measured mean of the unspiked samples."; <u>not</u> "...the measured mean of the analyte spiked samples."

5. Section 6.3.2.1 should read: "Calculate the standard deviation of the mean using Equation 301-3. The standard deviation shall be calculated by using the following equation where..."

APPENDIX D

ENGINE PROCESS DATA

GRI FTIR Validation Program - Engine #2 Process Data
Formaldehyde Spiking Test Period - July 13, 1994

Time (HHMM):	1135	1150	1200	1215	1230	1245	1335	1345	1400	1515	1530
Engine Speed (RPM):	301	301	300	300	300	300	300	298	301	301	300
Suction Pressure (psi):	81.5	77.6	91.7	68.7	66.4	66.6	78.9	78	77.8	75.4	75.8
Intermediate Pressure (psi):	215.7	198.5	212.7	180.3	177.8	180.4	203.5	200.9	200.7	196.2	196.1
Discharge Pressure (psi):	419.8	329.4	306.1	306.6	305.2	303.1	344.8	344.5	343.6	342.7	342.9
Scavenger Inlet Pressure (" H20):	-3.75	-3.75	-3.75	-3.8	-3.8	-3.75	-3.75	-3.75	-3.8	-3.75	-3.75
Crank Case Pressure (" H20):	1	1	1	1	1	1	1	1	1	1	1
Scavanger Outlet Pressure (" H2O):	-3.75	-3.75	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.6	-3.6	-3.6
Cylinder #1 Temperature (F):	693	668	672	654	653	655	670	671	670	670	669
Cylinder #2 Temperature (F):	744	714	721	703	700	701	719	719	717	719	719
Cylinder #3 Temperature (F):	700	678	684	668	666	664	683	680	682	680	681
Cylinder #4 Temperature (F):	706	683	687	674	674	677	684	684	684	685	684
Cylinder #5 Temperature (F):	698	674	679	661	662	659	675	675	674	675	675
Cylinder #6 Temperture (F):	750	726	736	714	712	715	732	731	731	731	730
Cylinder #7 Temperature (F):	691	669	674	654	644	649	672	671	671	668	668
Cylinder #8 Temperature (F):	745	725	730	715	713	714	728	729	728	728	731
Cylinder #9 Temperature (F):	699	674	682	661	688	658	678	679	677	678	677
Cylinder #10 Temperature (F):	746	723	729	712	711	710	729	728	726	725	724
Low P:ressure Suction Temp. (F):	193	190	184	192	194	194	190	190	190	193	192
High Pressure Suction Temp. (F):	207	189	175	187	186	185	185	186	187	189	189
Break Horse Power:	1201	1069	1059	985.8	968.3	986.2	1099	1101	1092	1079	1077
Torgue (%):	104			83.7	82.9	84.2	94.9	94.5	94.02	93.3	92.6
Pumping Capacity (MMSCFD):	13.72	13.64	13.66	12.32	11.95	12.05	13.89	13.81	13.65	13.28	13.39
Fuel Flow (SCFM):	143.9	148	130.2	128.0	129.0	130.4	137.8	137.8	138.0	135.4	135.8
Oxygen (%):	11.01	13.22	11.89	11.99	14.19	12.34	11.49	13.62	11.51	13.64	11.56
Rotometer Flow (LPM):	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
Dry Bulb Temperature (F):	77		76		77					81	
Wet Bulb Temperature (F):	73		74		75					77	
Relative Humidity (%):	82		90		91					83	

Formaldehyde Spiking Test Period - July 13, 1994

Time (HHMM):	1545	1600	1625	1645	1700	1715	1730	Mean	Standard Deviation
Engine Speed (RPM):	301	300	301	298	300	300	300	300.1	0.9
Suction Pressure (psi):	75.5	75.4	74.7	75.1	75.9	75.1	74.3	75.8	.5.6
Intermediate Pressure (psi):	196.5	196.5	195.6	196.9	197.4	196.3	196.4	196.6	9.7
Discharge Pressure (psi):	343	342.6	342.9	343.3	338.6	342.7	342.6	338.0	25.9
Scavenger Inlet Pressure (" H20):	-3.75	-3.75	-3.75	-3.75	-3.75	-3.75	-3.75	-3.76	0.02
Crank Case Pressure (" H20):	1	1	1	1	1	1	1	1.0	0.0
Scavanger Outlet Pressure (" H2O):	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	0.04
Cylinder #1 Temperature (F):	671	669	669	668	669	667	668	668.1	8.6
Cylinder #2 Temperature (F):	720	719	719	720	718	718	715	716.9	9.5
Cylinder #3 Temperature (F):	680	681	682	682	682	679	681	679.6	7.8
Cylinder #4 Temperature (F):	686	684	684	684	683	684	683	683.9	6.6
Cylinder #5 Temperature (F):	676	675	675	675	675	675	676	674.1	8.2
Cylinder #6 Temperture (F):	729	729	729	729	729	729	730	728.4	8.5
Cylinder #7 Temperature (F):	670	671	668	670	668	670	668	667.6	10.1
Cylinder #8 Temperature (F):	731	729	727	727	727	726	728	726.7	7.2
Cylinder #9 Temperature (F):	675	677	676	676	676	676	672	676.6	8.7
Cylinder #10 Temperature (F):	724	724	724	723	724	723	724	723.8	7.9
Low P:ressure Suction Temp. (F):	193	193	192	192	192	193	193	191.7	2.3
High Pressure Suction Temp. (F):	189	189	189	188	189	189	189	188.2	5.8
Break Horse Power:	1079	1069	1059	1062	1071	1058	1071	1066	51
Torgue (%):	92.7	92.4	92.4	92.5	92.6	92.5	92.5	92.0	5.0
Pumping Capacity (MMSCFD):	13.24	13.33	13.14	13.18	13.12	13.22	13.21	13.2	0.6
Fuel Flow (SCFM):	135.8	135.3	135.0	136.2	135.7	136.6	135.6	135.8	4.8
Oxygen (%):	11.55	11.55	11.57	11.57	11.54	13.66	13.66	12.3	1.0
Rotometer Flow (LPM):	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	0.0
Dry Bulb Temperature (F):	80		79			79		78.4	1.8
Wet Bulb Temperature (F):	76		75			77		75.3	1.5
Relative Humidity (%):	80		83			91		85.7	4.8

GRI FTIR Validation Program - Engine #2 Process Data
Criteria Pollutants Test Period - July 14, 1994

Time (HHMM):	1000	1115	1305	1440	1603	1745	1930	2050	2215	Mean	Standard Deviation
Engine Speed (RPM):	300	300	300	300	300	300	300	300	299	299.9	0.3
Suction Pressure (psi):	73.5	73.6	73.3	73.9	74.2	75.5	75.5	74.9	75	74.4	0.9
Intermediate Pressure (psi):	199.7	197.5	196.9	197.8	197.3	204	203.5	203	203.4	200.3	3.1
Discharge Pressure (psi):	360.9	360.6	358.6	358.2	360.1	387.6	381.7	381.8	379.4	369.9	12.3
Scavenger Inlet Pressure (" H20):	-3.75	-3.75	-3.75	-3.75	-3.75	-3.75	-3.75	-3.75	-3.75	-3.75	0.00
Crank Case Pressure (" H20):	1	1	1	1	1	1	1	1	1	1.0	0.0
Scavanger Outlet Pressure (" H2O):	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	-3.7	0.0
Cylinder #1 Temperature (F):	665	668	672	673	671	679	679	676	672	672.8	4.7
Cylinder #2 Temperature (F):	719	729	730	733	728	739	739	734	726	730.8	6.4
Cylinder #3 Temperature (F):	679	684	687	688	684	691	693	690	686	686.9	4.3
Cylinder #4 Temperature (F):	685	688	691	693	689	699	698	694	689	691.8	4.7
Cylinder #5 Temperature (F):	674	677	682	683	679	689	690	685	682	682.3	5.2
Cylinder #6 Temperture (F):	729	733	739	740	735	743	744	740	737	737.8	4.8
Cylinder #7 Temperature (F):	661	668	669	668	665	672	673	672	668	668.4	3.8
Cylinder #8 Temperature (F):	726	729	731	734	728	738	740	737	731	732.7	4.8
Cylinder #9 Temperature (F):	674	673	678	682	673	683	687.	683	678	679.0	5.0
Cylinder #10 Temperature (F):	724	725	731	731	727	736	739	736	731	731.1	5.2
Low P:ressure Suction Temp. (F):	195	195	197	197	195	198	198	196	195	196.2	1.3
High Pressure Suction Temp. (F):	193	195	196	197	192	202	202	197	195	196.6	3.5
Break Horse Power:	1081	1081	1081	1083	1079	1117	1109	1113	1112	1095	17
Torgue (%):	93.5	93.7	93.2	93.3	93.3	96.6	96.2	96.6	96.2	94.7	1.6
Pumping Capacity (MMSCFD):	12.78	12.77	12.8	12.8	12.88	12.75	12.81	12.94	12.76	12.8	0.1
Fuel Flow (SCFM):	137.3	136.2	135.7	136.1	136.2	139.7	139.3	139.7	141.1	137.9	2.0
Oxygen (%):	13.72	13.68	13.62	13.61	13.67	13.45	13.47	13.54	13.59	13.6	0.1
Rotometer Flow (LPM):	>22	>22	>22	>22	>22	>22	>22	>22	>22	0.0	0.0
Dry Bulb Temperature (F):	75	80	86	87	80	84	83	79	75	81.0	4.4
Wet Bulb Temperature (F):	74	75	75	77	77	77	76	76	73	75.6	1.4
Relative Humidity (%):	95	80	60	66	87	68	72	86	88	78.0	11.9

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI Method 301 Validation Page 1 of 1
TRAIN Velocity Profile
SAMPLING LOCATION Engine 2 Exhaust RUN NO. 1 COND. NO. Full Load
DATE 071394 TIME START 1946 TIME FINISH 1950 TEST DURATION 4 min.
DUCT DIMENSIONS ___ X ___ DIAMETER 10 ft INITIAL LEAK RATE — cfm
PTCF 0.84 DGMCF — NOZZLE DIA. — inches FINAL LEAK RATE — cfm
BAR PRESS 29.45 Hg
STATIC PRESS +8.25 " H2O OPERATOR LDO / WG

Travers Point	Clock Time	Dry gas meter reading ft3	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	___
H6	1946	—	4.2	—	640	—	—	—	—	—	—	
H5	↓	—	4.1	—	640	—	—	—	—	—	—	
H4		—	4.0	—	642	—	—	—	—	—	—	
H3		—	3.9	—	643	—	—	—	—	—	—	
H2		—	3.8	—	644	—	—	—	—	—	—	
A1	1950	—	3.6	—	644	—	—	—	—	—	—	
Avg.	---											
Check'd												

CONSOLE # A161361
FILTER #
AMBIENT TEMP.
PROBE LENGTH
LINER MATERIAL

Velocity
% Moisture
Flowrate (DSCFM)
Isokinetic (%)

13.7% O_2
4.1% CO_2
CEM data

REMARKS Assumed 10.3% Moisture

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams			
1				Final		Weight	
				Initial		Gain	
2				Final		Weight	
				Initial		Gain	
3				Final		Weight	
				Initial		Gain	
4				Final		Weight	
				Initial		Gain	
5				Final		Weight	
				Initial		Gain	
6				Final		Weight	
				Initial		Gain	

Total Impinger Weight Gain (Wc)__________grms

Analyst__________

Vf = Final Meter Volume = ____________ft3

Vi = Initial Meter Volume= _________ ft3

DGMCF = Dry Gas Meter Correction Factor = _________

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = _________ ft3

Tm = Average Meter Temp. = F+460 = ________ R

Pm = Meter Pressure (Barometric Pressure) = _______ in. Hg

%CO __________

%CO2 _________

%O2 _________

%N2 _________

%H2 _________

%CH _________

CONDENSED WATER ___________gms

FILTER WT. GAIN ___________gms

PROBE WASH WT. GAIN ___________gms

$$Vm\ (std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(\_\_\_\_\ ft3)(\_\_\_\_\ "Hg)}{(\_\_\_\_\ R)} = \_\_\_\_\ ft3$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(_____g) = _______ft3

$$Bws = \text{Moisture Fraction} = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{\_\_\_\_\ ft3}{\_\_\_\_\ ft3 + \_\_\_\_\ ft3} = \_\_\_\_$$

Revision Date 4/93

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI Method 301 Validation
Page 1 of 1
TRAIN Velocity
SAMPLING LOCATION Engine 2 Exhaust
RUN NO. 2 COND. NO. Full Load
DATE 071494 TIME START 1905 TIME FINISH 1908 TEST DURATION ____ min.
DUCT DIMENSIONS ____ X ____ DIAMETER 1.0 ft INITIAL LEAK RATE Good cfm
PTCF 0.84 DGMCF — NOZZLE DIA. — inches FINAL LEAK RATE — cfm
BAR PRESS 29.41 " Hg
STATIC PRESS +8.5 " H2O OPERATOR LAR

Travers Point	Clock Time	Dry gas meter reading ft3	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	____
H6	1905	—	4.5	—	652	—	—	—	—	—	—	
H5		—	4.3	—	657	—	—	—	—	—	—	
H4		—	4.2	—	657	—	—	—	—	—	—	
H3		—	4.2	—	658	—	—	—	—	—	—	
H2		—	3.8	—	653	—	—	—	—	—	—	
H1	1908	—	3.5	—	640	—	—	—	—	—	—	
Avg.	---											
Check'd												

CONSOLE # Alt 1341
FILTER # ____
AMBIENT TEMP. ____
PROBE LENGTH ____
LINER MATERIAL ____

Velocity ____
% Moisture ____
Flowrate (DSCFM) ____
Isokinetic (%) ____

13.5% O2
4.3% CO2
CEM data

REMARKS Assumed 10.3% Moisture

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams	
1	________	______	______	Final ______ Initial ______	Weight Gain ______
2	________	______	______	Final ______ Initial ______	Weight Gain ______
3	________	______	______	Final ______ Initial ______	Weight Gain ______
4	________	______	______	Final ______ Initial ______	Weight Gain ______
5	________	______	______	Final ______ Initial ______	Weight Gain ______
6	________	______	______	Final ______ Initial ______	Weight Gain ______

Total Impinger Weight Gain (Wc)__________grms

Analyst__________

Vf = Final Meter Volume = ____________ft3

Vi = Initial Meter Volume= _________ ft3

DGMCF = Dry Gas Meter Correction Factor = _________

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = _________ ft3

Tm = Average Meter Temp. = F+460 = _______ R

Pm = Meter Pressure (Barometric Pressure) = ______ in. Hg

%CO	________	%N2	________
%CO2	________	%H2	________
%O2	________	%CH	________

CONDENSED WATER __________gms

FILTER WT. GAIN __________gms

PROBE WASH WT. GAIN __________gms

$$\text{Vm (std)} = \frac{(17.64)(\text{Vm})(\text{Pm})}{\text{Tm}} = \frac{(17.64)(\_\_\_\_\ \text{ft3})(\_\_\_\_\ \text{"Hg})}{(\_\_\_\_\ \text{R})} = \_\_\_\_\ \text{ft3}$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(____g) = ______ft3

$$\text{Bws} = \text{Moisture Fraction} = \frac{\text{Vw(std)}}{\text{Vw(std)} + \text{Vm(std)}} = \frac{\_\_\_\_\ \text{ft3}}{\_\_\_\_\ \text{ft3} + \_\_\_\_\ \text{ft3}} = \_\_\_\_$$

Revision Date 4/93

Plant Name: **GRI FTIR Method 301 Validation**
Location: **Engine 2 Exhaust**
Type of Sample: **Velocity - Full Load**

Run No.	One
Date	07/13/94
Time Start	1946
Time Finish	1950
Operator	LDO/WG
Initial Leak Rate	N/A
Final Leak Rate	N/A
Duct Dimensions (ft)	0
Stack Diameter (ft)	1.00
Pitot Tube Correction Factor (Cp)	0.84
Dry Gas Meter Calibration (Yd)	N/A
Nozzle Diameter (inches)	N/A
Barometric Pressure ("Hg)	29.45
Static Pressure ("H2O)	8.25
Meter Volume (acf)	N/A
Average square root of delta p	1.9826
Average delta H (" H2O)	N/A
Average Stack Temperature (F)	642
Average DGM Temp (F)	N/A
Test Duration (minutes)	N/A
Condensed Water (g)	N/A
Filter Weight Gain (g)	N/A
PNR Weight Gain (g)	N/A
Impinger Residue (g)	N/A
% CO2	4.1
% O2	13.7
% N2	82.2
Meter Volume (dscf)	0.000
Flue Gas Moisture (%)	10.3
Gas Molecular Weight (Wet) (g/g-m	28.05
Absolute Stack Pressure (" Hg)	30.06
Absolute Stack Temperature (R)	1102
Average Gas Velocity (f/sec)	162.77
Avg Flow Rate (acfm)	7,671
Avg Flow Rate (dscfm)	3,310
Isokinetic Sampling Rate (%)	N/A

Run No.	Two
Date	07/14/94
Time Start	1905
Time Finish	1908
Operator	LDO/WG
Initial Leak Rate	N/A
Final Leak Rate	N/A
Duct Dimensions (ft)	0
Stack Diameter (ft)	1.00
Pitot Tube Correction Factor (Cp)	0.84
Dry Gas Meter Calibration (Yd)	N/A
Nozzle Diameter (inches)	N/A
Barometric Pressure ("Hg)	29.41
Static Pressure ("H2O)	8.5
Meter Volume (acf)	N/A
Average square root of delta p	2.0190
Average delta H (" H2O)	N/A
Average Stack Temperature (F)	653
Average DGM Temp (F)	N/A
Test Duration (minutes)	N/A
Condensed Water (g)	N/A
Filter Weight Gain (g)	N/A
PNR Weight Gain (g)	N/A
Impinger Residue (g)	N/A
% CO2	4.3
% O2	13.5
% N2	82.2
Meter Volume (dscf)	0.000
Flue Gas Moisture (%)	10.3
Gas Molecular Weight (Wet) (g/g-m	28.07
Absolute Stack Pressure (" Hg)	30.04
Absolute Stack Temperature (R)	1113
Average Gas Velocity (f/sec)	166.58
Avg Flow Rate (acfm)	7,850
Avg Flow Rate (dscfm)	3,352
Isokinetic Sampling Rate (%)	N/A

Note: The moisture data was assumed. Horizontal traverse only.

APPENDIX E

FIELD/CALIBRATION DATA

- **E.1 Spiking Data**
- **E.2 Moisture Measurements**
- **E.3 Calibration Data**
- **E.4 Field Log**
- **E.5 Certification Sheets**

APPENDIX E.1

Spiking Data

GRI FTIR Method 301 Validation Tests

Formalin Solution Spiking Rate Data

Test No.	Initial Mass (grams)	Final Mass (grams)	Elapsed Time (min.)	Feed Rate (grams/min)
1	35.4	25.5	10	0.99
2	13.8	4.4	10	0.94
3	94.7	84.9	10	0.98
4	75.4	65.4	10	1.00
5	56	46.2	10	0.98
6	36.5	31.6	5	0.98
7	10.3	5.3	5	1.00
8	98.4	88.6	10	0.98
9	82.1	77.2	5	0.98
10	98	88.1	10	0.99
11	80.2	70.6	10	0.96
12	61.5	51.7	10	0.98
13	41.9	31.9	10	1.00
14	22.7	12.9	10	0.98
15	703.1	693.5	10	0.96
16	83.7	74	10	0.97

Pg 1 of 3

GRI Method 301 Validation

Formaldehyde Spiking Solution
Flow Rate Documentation Data Sheet

Date: 071394 Recorded By: LAR

Pump ID No. : A108717 Balance ID No. : A164430

	Start Time of Day	Pump Setting	Spiking Solution Weight Change Data Start (grams)	Stop (grams)	Delta Change	Elapsed Time (min)	Flow Rate (grams/min)	ΔH
Test 1	11:16	1.0	35.4	30.3	5.1	5.0	1.02	1.83
	11:21	1.0	30.3	25.5	4.8	5.0	0.96	1.83
Test 2	11:38	1.0	1013.8	1008.8	5.0	5.0	1.0	1.82
	11:43	1.0	1008.8	1004.4	4.4	5.0	0.88	1.82
st3	11:58	1.0	994.7	989.8	4.9	5.0	0.98	1.88
	12:03	1.0	989.8	984.9	4.9	5.0	0.98	1.91
est 4	12:18	1.0	975.4	970.4	5.0	5.0	1.00	1.76
	12:23	1.0	970.4	965.4	5.0	5.0	1.00	1.79
est 5	12:38	1.0	956.0	951.1	4.9	5.0	0.98	1.83
	12:43	1.0	951.1	946.2	4.9	5.0	0.98	1.82
est 6	12:58	1.0	936.5	931.6	4.9	5.0	0.98	1.77
*	13:03	1.0	931.6	9	Could not	measure water	because of on balance	1.82

Comments: ΔH does not include spiking solution Flow.
ΔH with Total Exhaust flow ~ 2.18"

*(Raining)

Pg 2 of 3

GRI Method 301 Validation

Formaldehyde Spiking Solution
Flow Rate Documentation Data Sheet

Date: 071394 Recorded By: LAR

Pump ID No. : A108717 Balance ID No. : A164430

Start

	Time of Day	Pump Setting	Spiking Solution Weight Change Data Start (grams)	Stop (grams)	Delta Change	Elapsed Time (min)	Flow Rate (grams/min)	ΔH
st7	1326	1.0	910.3	905.3	5.0	5.0	1.0	Not measured
	~~1331~~	Only	One Sample	Because	of Rain on	Balance	Pan	
st8	1338	1.0	898.4	893.4	5.0	5.0	1.0	1.79
	1343	1.0	893.4	888.6	4.8	5.0	0.96	1.73
st9	1354	1.0	882.1	877.2	4.9	5.0	0.98	
	Stopped	testing	to Conduct	FTIR	QC's			
st10	1521	1.0	798.0	793.0	5.0	5.0	1.0	1.73
	1526	1.0	793.0	788.1	4.9	5.0	0.98	1.74
st11	1541	1.0	780.2	775.7	4.5	5.0	0.90	1.82
	1546	1.0	775.7	770.6	5.1	5.0	1.02	1.83
			~~771.5~~					
st12	1601	1.0	761.5	756.7	4.8	5.0	0.96	1.83
	1606	1.0	756.7	751.7	5.0	5.0	1.00	1.80

Comments: Spent time between 1300 - 1330 trying to Weather proof Balance because of Rain. Only one flowrate check measurement made during tests 6 and 7

Average feed rate from 1354 - 1521 = 0.967 grams/min

Pg 3 of 3

GRI Method 301 Validation

Formaldehyde Spiking Solution
Flow Rate Documentation Data Sheet

Date: 071394 Recorded By: LAR

Pump ID No. : A108717 Balance ID No. : A 164430

Start

	Time of Day	Pump Setting	Spiking Solution Weight Change Data Start (grams)	Stop (grams)	Delta Change	Elapsed Time (min)	Flow Rate (grams/min)	ΔH
st13	1621	1.0	741.9	736.9	5.0	5.0	1.0	1.88
	1626	1.0	736.9	731.9	5.0	5.0	1.0	1.81
st14	1641	1.0	722.7	717.8	4.9	5.0	0.98	1.77
	1646	1.0	717.8	712.9	4.9	5.0	0.98	1.78
st15	1701	1.0	703.1	698.2	4.9	5.0	0.98	1.91
	1706	1.0	698.2	693.5	4.7	5.0	0.94	1.92
st16	1721	1.0	683.7	678.1	5.6	5.0	1.12	1.82
	1726	1.0	678.1	674.0	4.1	5.0	0.82	1.75
~~st17~~	~~1741~~	~~1.0~~						

Comments:

GRI Method 301 Validation

Aldehyde(s) Spiking Gas
Flow Rate Documentation Data Sheet

Date: 7/13/94 Recorded By: L D Ogle

Test Sequence No. : 1 Room Temperature (° F): 70

Barometric Pressure (~~in.~~ mm Hg.): 748 mm Hg

Time of Day (hhmm)	Mass Flow Rate Meters - Indicated Flow Rate Data (ml/min)			
	Reading) Meter 1 (LPM)	Meter 2	Meter 3	Meter 4
11:10	1.74 (204)			
11:25	1.73			
11:43	1.74			
11:55	1.74			
12:07	1.74			
12:27	1.74			
12:48	1.75			
12:58	1.74			
~1:15	1.74			
1:28	1.74			
2:03	1.74			
stopped for	QCs			
Average Indicated Flow (ml/min)				
Average Adjusted Flow (ml/min)				

Comments:

GRI Method 301 Validation

Aldehyde(s) Spiking Gas
Flow Rate Documentation Data Sheet

Date: 7/13/94 Recorded By: L.D. Ogle

Test Sequence No. : 2 Room Temperature (° F): 70

Barometric Pressure (in. Hg.): 748

Time of Day (hhmm)	Mass Flow Rate Meters - Indicated Flow Rate Data (ml/min)			
	Meter 1	Meter 2	Meter 3	Meter 4
15:22	1.74			
15:50	1.73			
16:10	1.74			
17:10	1.73			
17:25	1.74			
Average Indicated Flow (ml/min)				
Average Adjusted Flow (ml/min)				

Comments:

APPENDIX E.2

Moisture Measurements

Run #1

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI 301 Validation

Page 1 of 9

TRAIN Moisture

SAMPLING LOCATION Manifold

RUN NO. 1 COND. NO. 1

DATE 071494 TIME START ____ TIME FINISH ____ TEST DURATION ____ min.

DUCT DIMENSIONS ____ X ____ DIAMETER ____ ft INITIAL LEAK RATE OK cfm

PTCF — DGMCF 0.956 NOZZLE DIA. — inches FINAL LEAK RATE OK cfm

BAR PRESS 29.41 " Hg

STATIC PRESS — " H2O

OPERATOR LAR

~~Travers Point~~	Clock Time	Dry gas meter reading ~~ft3~~ Liters	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	
	0934	1247.59	—	—	—	69	—	—	—	—	4	
	0958	1290.5	—	—	—	72	—	—	—	—	4	
	1030	1346.20	—	—	—	74	—	—	—	—	4	
Total Vol		98.61 (liters)	X 0.956		=	94.27 /		28.04 40	=	~~3.362~~ 3.319	ft³	
Avg.	---					72						
Check'd												

CONSOLE # 20-02870

FILTER # —

AMBIENT TEMP. —

PROBE LENGTH —

LINER MATERIAL —

Velocity

% Moisture

Flowrate (DSCFM)

Isokinetic (%)

REMARKS Sample Collected at Manifold inside Lab Trailer

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		
1	H_2O	20 ~~100~~	Midget	Final Initial	60.6 54.9	Weight Gain 5.70
2	Silica Gel	20 ~~100~~	Midget	Final Initial	68.2 66.6	Weight Gain 1.60
3				Final Initial		Weight Gain
4				Final Initial		Weight Gain
5				Final Initial		Weight Gain
6				Final Initial		Weight Gain

Total Impinger Weight Gain (Wc) 7.30 grms

Analyst ________

Vf = Final Meter Volume = ________ ft3

Vi = Initial Meter Volume= ________ ft3

DGMCF = Dry Gas Meter Correction Factor = ________

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 3.3~~62~~ 19 ft3

Tm = Average Meter Temp. = F+460 = 532 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ________
%CO2 ________
%O2 ________

%N2 ________
%H2 ________
%CH ________

CONDENSED WATER ________ gms
FILTER WT. GAIN ________ gms
PROBE WASH WT. GAIN ________ gms

$$Vm\ (std) = \left[\frac{(17.64)(Vm)(Pm)}{Tm}\right] = \frac{(17.64)(\cancel{3.36}\ 3.319\ ft3)(29.41\ Hg)}{(532\ R)} = \cancel{3.28}\ 3.24\ ft3$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(7.30 g) = 0.345 ft3

$$Bws = Moisture\ Fraction = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{0.345\ ft3}{0.345\ ft3 + \cancel{3.28}\ 3.24\ ft3} = \cancel{0.1952}\ 0.0963$$

~~9.52~~ % H_2O

Revision Date 4/93

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI 301 Validation
Page 2 of 9
TRAIN Moisture
SAMPLING LOCATION Manifold
RUN NO. 2 COND. NO. 1
DATE 7/14/94 TIME START ______ TIME FINISH ______ TEST DURATION ______ min.
DUCT DIMENSIONS ______ X ______ DIAMETER ______ ft INITIAL LEAK RATE Good cfm
PTCF — DGMCF 0.956 NOZZLE DIA. — inches FINAL LEAK RATE Good cfm
BAR PRESS 29.41 " Hg
STATIC PRESS ______ " H2O OPERATOR LAR/LDO

Travers Point	Clock Time	Dry gas meter reading ~~ft3~~ (Liters)	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	______
~~—~~		~~1360.3~~		~~—~~	~~—~~	~~71~~	~~—~~		~~—~~			
—	1120	1363.2	—	—	—	71	—	—	—	—	6	
—	1210	1454.06	—	—	—		—	—	—	—		
Total Vol.		90.86	X	0.956	=	86.86 /	28.~~04~~ 40 LDO		=	3.06 ~~3.098~~ ft³ LDO		
Avg.	---					71						
Check'd												

CONSOLE # 20-02870
FILTER # —
AMBIENT TEMP. —
PROBE LENGTH —
LINER MATERIAL —

Velocity
% Moisture
Flowrate (DSCFM)
Isokinetic (%)

REMARKS Sample collected at Manifold inside trailer

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		Weight Gain
1	H2O	20	Midget	Final	64.1	1.60
				Initial	62.5	
2	Dry	—	" "	Final	53.8	2.30
				Initial	51.45	
3	Silica Gel	20	" "	Final	67.9 LDO	1.80
				Initial	~~66.0~~ 66.1 LDO	
4				Final		
				Initial		
5				Final		
				Initial		
6				Final		
				Initial		

Total Impinger Weight Gain (Wc) 5.70 grms +1.8 = 7.50

unit not originally weighed

Analyst________

Vf = Final Meter Volume = ________ ft3

Vi = Initial Meter Volume= ________ ft3

DGMCF = Dry Gas Meter Correction Factor = ________

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = ~~0.5.362~~ ft3 LDO LDO ~~3.098~~ 3.06

Tm = Average Meter Temp. = F+460 = 531 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ________

%CO2 ________

%O2 ________

%N2 ________

%H2 ________

%CH ________

CONDENSED WATER ________ gms

FILTER WT. GAIN ________ gms

PROBE WASH WT. GAIN ________ gms

$$Vm\,(std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(\overset{3.06}{\cancel{3.08}}\,ft3)(29.41\,"Hg)}{(531\,R)} = \overset{2.99}{\cancel{3.03}}\,ft3$$

LDO LDO

$$Vw(std) = \text{Volume of Water Vapor} = .0472(Wc) = .0472(\overset{7.5}{\cancel{5.70}}\,g) = 0.354\,ft3$$

LDO

$$Bws = \text{Moisture Fraction} = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{0.354\,ft3}{0.354\,ft3 + \underset{2.99}{\cancel{3.03}}\,ft3} = \overset{0.106}{\cancel{0.105}}$$

LDO LDO

Revision Date 4/93

LDO ~~10.5~~ % moisture

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI M301 Validation

TRAIN Moisture

Page 3 of 9

SAMPLING LOCATION Manifold

RUN NO. 3

COND. NO. ______

DATE 07-14-94

TIME START ______

TIME FINISH ______

TEST DURATION ______ min.

DUCT DIMENSIONS ______ x ______

DIAMETER ______ ft

INITIAL LEAK RATE Good cfm

PTCF —

DGMCF 0.956

NOZZLE DIA. N/A inches

FINAL LEAK RATE Good cfm

BAR PRESS 29.41 " Hg

STATIC PRESS ______ " H2O

OPERATOR LAR/LDO

Travers Point	Clock Time	Dry gas meter reading ~~ft3~~ Liters	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	______
—	1304	1483.07	—	—	—	73	—	—	—	—	7.0	
—		1588.95	—	—	—		—	—	—	—		
—			—	—	—		—	—	—	—		
—			—	—	—		—	—	—	—		
Total Volume		105.9 liters × 0.956 = 101.2/28.40 = 3.56 ft³										
Avg.	---											
Check'd												

CONSOLE # 20-02870

FILTER # —

AMBIENT TEMP. —

PROBE LENGTH —

LINER MATERIAL —

Velocity

% Moisture

Flowrate (DSCFM)

Isokinetic (%)

REMARKS Sample Collected at manifold inside of trailer

Moisture Run 3

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		Weight Gain
1	H2O	20	Midget	Final	61.7	6.20
				Initial	55.5	
2	Dry	—	" "	Final	53.8	0.10
				Initial	53.7	
3	Silica Gel	20	" "	Final	67.7	2.0
				Initial	65.7	
4				Final		
				Initial		
5				Final		
				Initial		
6				Final		
				Initial		

Total Impinger Weight Gain (Wc) 8.3 grms

Analyst ________

Vf = Final Meter Volume = ________ ft3

Vi = Initial Meter Volume= ________ ft3

DGMCF = Dry Gas Meter Correction Factor = 0.956

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 3.56 ft3

Tm = Average Meter Temp. = F+460 = 533 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ________

%CO2 ________

%O2 ________

%N2 ________

%H2 ________

%CH ________

CONDENSED WATER ________ gms

FILTER WT. GAIN ________ gms

PROBE WASH WT. GAIN ________ gms

$$Vm\ (std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(3.56\ ft3)(29.41\ "Hg)}{(533\ R)} = 3.43\ ft3$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(8.3 g) = 0.39 ft3

$$Bws = \text{Moisture Fraction} = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{0.39\ ft3}{0.39\ ft3 + 3.43\ ft3} = 0.102$$

Revision Date 4/93

10.2%

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI M301 Validation
Page ~~3~~ 4 of 9
TRAIN Moisture
SAMPLING LOCATION Manifold
RUN NO. 34
COND. NO.
DATE 7/14/94
TIME START
TIME FINISH
TEST DURATION min.
DUCT DIMENSIONS X
DIAMETER ft
INITIAL LEAK RATE Good cfm
PTCF NA
DGMCF 0.956
NOZZLE DIA. NA inches
FINAL LEAK RATE Good cfm
BAR PRESS 29.41 " Hg
STATIC PRESS " H2O
OPERATOR LAR/LDO

Travers Point	Clock Time	Dry gas meter reading ft3	^ P in H2O	^ H in H2O	Stack Temp. F	Dry gas meter temp		Hot box Temp.	Probe Temp	Last Impinger	Vacuum In. Hg	
						Inlet	Outlet					
—	1437	1591.73	—	—	—	75	—	—	—	—	6	
~~—~~	~~1537~~	~~170~~	—	—	—	—	—	—	—	—		
—	1537	1695.60	—	—	—	77	—	—	—	—	6	
Avg.	---					76						
Check'd												

Total Volume 103.9 liters X 0.956 = $\frac{99.3 l}{28.4}$ = 3.497 scf

CONSOLE # 20-02870
FILTER # —
AMBIENT TEMP. —
PROBE LENGTH —
LINER MATERIAL —

Velocity
% Moisture
Flowrate (DSCFM)
Isokinetic (%)

REMARKS Sample collected at manifold inside trailer

#4

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		Weight Gain
1	H2O	20	Midget	Final Initial	64.1 61.7	2.40
2	Dry	—	" "	Final Initial	57.6 53.8	3.8
3	Silica Gel	20	" "	Final Initial	66.5 64.7	1.8
4				Final Initial		
5				Final Initial		
6				Final Initial		

Total Impinger Weight Gain (We) 8.0 grms

Analyst ______

Vf = Final Meter Volume = ______ ft3

Vi = Initial Meter Volume = ______ ft3

DGMCF = Dry Gas Meter Correction Factor = 0.956

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 3.497 ft3

Tm = Average Meter Temp. = F+460 = 536 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ______
%CO2 ______
%O2 ______

%N2 ______
%H2 ______
%CH ______

CONDENSED WATER ______ gms
FILTER WT. GAIN ______ gms
PROBE WASH WT. GAIN ______ gms

$$Vm\ (std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(3.497\ ft3)(29.41\ "Hg)}{(536\ R)} = 3.38\ ft3$$

$$Vw(std) = \text{Volume of Water Vapor} = .0472(Wc) = .0472(8.0\ g) = 0.378\ ft3$$

$$Bws = \text{Moisture Fraction} = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{0.378\ ft3}{0.378\ ft3 + 3.38\ ft3} = 0.101$$

Revision Date 4/93

10.1% H_2O

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI Method 301 Validation

TRAIN Moisture

Page 5 of 9

SAMPLING LOCATION Manifold

RUN NO. 5

COND. NO. ____

DATE 071494

TIME START ____

TIME FINISH ____

TEST DURATION ____ min.

DUCT DIMENSIONS ____ X ____

DIAMETER ____ ft

INITIAL LEAK RATE Good cfm

PTCF –

DGMCF 0.956

NOZZLE DIA. NA inches

FINAL LEAK RATE Good cfm

BAR PRESS 29.41 " Hg

STATIC PRESS – " H2O

OPERATOR DAR/LDO

Travers Point	Clock Time	Dry gas meter reading ft3	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	____
–	1603	1700.62	–	–	–	76	–	–	–	–		
–	1703	1805.25										
–												
Avg.	---					76						
Check'd												

Total Flow 104.63 × 0.956 = 100.0 / 28.4 = 3.52 scf

CONSOLE # 20-02870

FILTER # –

AMBIENT TEMP. –

PROBE LENGTH –

LINER MATERIAL –

Velocity

% Moisture

Flowrate (DSCFM)

Isokinetic (%)

REMARKS ____

Moisture 5

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams	Weight Gain
1	H_2O	20	Midget	Final 62.1 Initial 55.5	6.6
2	Dry	—	" "	Final 57.8 Initial 57.6	0.2
3	Silica Gel	20	" "	Final 64.9 Initial 63.2	1.70
4				Final Initial	
5				Final Initial	
6				Final Initial	

Total Impinger Weight Gain (Wc) 8.5 grms

Analyst ________

Vf = Final Meter Volume = ________ ft3

Vi = Initial Meter Volume= ________ ft3

DGMCF = Dry Gas Meter Correction Factor = ________

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 3.52 ft3

Tm = Average Meter Temp. = F+460 = 536 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ________

%CO2 ________

%O2 ________

%N2 ________

%H2 ________

%CH ________

CONDENSED WATER ________ gms

FILTER WT. GAIN ________ gms

PROBE WASH WT. GAIN ________ gms

$$\text{Vm (std)} = \frac{(17.64)(\text{Vm})(\text{Pm})}{\text{Tm}} = \frac{(17.64)(3.52\ \text{ft3})(29.41\ \text{Hg})}{(536\ \text{R})} = 3.37\ \text{ft3}$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(8.5 g) = 0.401 ft3

$$\text{Bws} = \text{Moisture Fraction} = \frac{\text{Vw(std)}}{\text{Vw(std)} + \text{Vm(std)}} = \frac{0.401\ \text{ft3}}{0.401\ \text{ft3} + 3.37\ \text{ft3}} = 0.106$$

Revision Date 4/93

10.6%

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI Method 301 Validation Page 6 of 9

TRAIN Moisture

SAMPLING LOCATION Manifold RUN NO. 6 COND. NO.

DATE 071494 TIME START TIME FINISH TEST DURATION min.

DUCT DIMENSIONS x DIAMETER ft INITIAL LEAK RATE Good cfm

PTCF — DGMCF 0.956 NOZZLE DIA. NA inches FINAL LEAK RATE Good cfm

BAR PRESS 29.41 " Hg

STATIC PRESS " H2O OPERATOR LAR/LDO

Travers Point	Clock Time	Dry gas meter reading ft3	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	
—	1742	1806.95	—	—	—	76	—	—	—	—	8.0	—
—	1842	1911.05	—	—	—	78	—	—	—	—		
—												
Avg.	---											
Check'd												

Total Flow 104.10 X 0.956 = 99.52/28.4 ≅ 3.50 ft^3

CONSOLE # A20-02870

FILTER # —

AMBIENT TEMP. —

PROBE LENGTH —

LINER MATERIAL —

Velocity

% Moisture

Flowrate (DSCFM)

Isokinetic (%)

REMARKS

Moisture 6

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		Weight Gain
1	H_2O	20	Midget	Final Initial	64.4 62.1	2.3
2	Dry	—	" "	Final Initial	62.4 57.8	4.6
3	Silica Gel	20	" "	Final Initial	66.8 65.4	1.4
4				Final Initial		
5				Final Initial		
6				Final Initial		

Total Impinger Weight Gain (Wc) 8.3 grms

Analyst ____

Vf = Final Meter Volume = ____ ft3

Vi = Initial Meter Volume= ____ ft3

%CO ____
%CO2 ____
%O2 ____

%N2 ____
%H2 ____
%CH ____

DGMCF = Dry Gas Meter Correction Factor = ____

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 3.50 ft3

Tm = Average Meter Temp. = F+460 = 537 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

CONDENSED WATER ____ gms
FILTER WT. GAIN ____ gms
PROBE WASH WT. GAIN ____ gms

$$Vm\ (std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(3.5\ ft3)(29.41\ Hg)}{(537\ R)} = 3.38\ ft3$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(8.3 g) = 0.392 ft3

$$Bws = Moisture\ Fraction = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{0.39\ ft3}{0.39\ ft3 + 3.50\ ft3} = 0.101$$

Revision Date 4/93

10.1%

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI Method 301 Validation

Page 7 of 9

TRAIN Moisture

SAMPLING LOCATION Manifold

RUN NO. 7

COND. NO. ____

DATE 071494

TIME START ____

TIME FINISH ____

TEST DURATION ____ min.

DUCT DIMENSIONS ____ X ____

DIAMETER ____ ft

INITIAL LEAK RATE Good cfm

PTCF —

DGMCF 0.956

NOZZLE DIA. — inches

FINAL LEAK RATE Good cfm

BAR PRESS 29.41 " Hg

STATIC PRESS ____ " H2O

OPERATOR LAR/LDO

Travers Point	Clock Time	Dry gas meter reading ft3	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	____
—	1923	1913.51	—	—	—	76	—	—	—	—	6	
—	2023	2014.23	—	—	—	77	—	—	—	—		
—			—	—	—		—	—	—	—		
Avg.	---											
Check'd												

Total Flow 100.72 X 0.956 = 96.29 / 28.4 = 3.39 ft³

CONSOLE # 20-02870

FILTER # —

AMBIENT TEMP. ____

PROBE LENGTH —

LINER MATERIAL —

Velocity

% Moisture

Flowrate (DSCFM)

Isokinetic (%)

REMARKS ____

Moisture 7

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration		Weight in grams		
1	H_2O	20	Midget	Final	64.1	Weight	
				Initial	58.5	Gain	5.6
2	Dry	—	" "	Final	54.8	Weight	
				Initial	54.1	Gain	0.7
3	Silica Gel	20	" "	Final	66.3	Weight	
				Initial	64.5	Gain	1.8
4				Final		Weight	
				Initial		Gain	
5				Final		Weight	
				Initial		Gain	
6				Final		Weight	
				Initial		Gain	

Total Impinger Weight Gain (Wc) 8.1 grms

Analyst ______

Vf = Final Meter Volume = ______ ft3

Vi = Initial Meter Volume= ______ ft3

DGMCF = Dry Gas Meter Correction Factor = ______

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 3.39 ft3

Tm = Average Meter Temp. = F+460 = 537 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ______
%CO2 ______
%O2 ______

%N2 ______
%H2 ______
%CH ______

CONDENSED WATER ______ gms
FILTER WT. GAIN ______ gms
PROBE WASH WT. GAIN ______ gms

$$\text{Vm (std)} = \frac{(17.64)(\text{Vm})(\text{Pm})}{\text{Tm}} = \frac{(17.64)(3.39\ \text{ft3})(29.41\ \text{in. Hg})}{537\ \text{R})} = 3.28\ \text{ft3}$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(8.1 g) = 0.382 ft3

$$\text{Bws} = \text{Moisture Fraction} = \frac{\text{Vw(std)}}{\text{Vw(std)} + \text{Vm(std)}} = \frac{0.382\ \text{ft3}}{0.382\ \text{ft3} + 3.28\ \text{ft3}} = 0.104$$

Revision Date 4/93

10.4%

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI Method 301 Validation
Page 8 of 9
TRAIN Moisture
SAMPLING LOCATION Manifold
RUN NO. 8
COND. NO.
DATE 7-14-94
TIME START
TIME FINISH
TEST DURATION min.
DUCT DIMENSIONS x
DIAMETER ft
INITIAL LEAK RATE Good cfm
PTCF —
DGMCF 0.956
NOZZLE DIA. — inches
FINAL LEAK RATE Good cfm
BAR PRESS 29.41 " Hg
STATIC PRESS — " H2O
OPERATOR LAR/LDO

Travers Point	Clock Time	Dry gas meter reading ft3	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	
–	2048	2017.36	–	–	–	76	–	–	–	–	10.5	
–		2113.63	–	–	–		–	–	–	–		
–			–	–	–		–	–	–	–		
Avg.	---											
Check'd												

Total Flow 96.27 × 0.956 = $\frac{92.03}{28.4}$ = 3.24 ft^3

CONSOLE # 20-02870
FILTER # —
AMBIENT TEMP. —
PROBE LENGTH —
LINER MATERIAL —

Velocity
% Moisture
Flowrate (DSCFM)
Isokinetic (%)

REMARKS

Moisture 8

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		
1	H_2O	20	midget	Final 60.7 Initial 55.0	Weight Gain	5.7
2	Dry	—	" "	Final 54.9 Initial 54.8	Weight Gain	0.1
3	Silica Gel	20	" "	Final 65.8 Initial 64.3	Weight Gain	1.5
4				Final Initial	Weight Gain	
5				Final Initial	Weight Gain	
6				Final Initial	Weight Gain	

Total Impinger Weight Gain (Wc) 7.3 grms

Analyst ______

Vf = Final Meter Volume = ______ ft3

Vi = Initial Meter Volume = ______ ft3

DGMCF = Dry Gas Meter Correction Factor = ______

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 3.24 ft3

Tm = Average Meter Temp. = F+460 = 536 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ______
%CO2 ______
%O2 ______

%N2 ______
%H2 ______
%CH ______

CONDENSED WATER ______ gms
FILTER WT. GAIN ______ gms
PROBE WASH WT. GAIN ______ gms

$$\text{Vm (std)} = \frac{(17.64)(\text{Vm})(\text{Pm})}{\text{Tm}} = \frac{(17.64)(3.24\ \text{ft3})(29.41\ \text{Hg})}{(537\ \text{R})} = 3.13\ \text{ft3}$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(7.3 g) = 0.345 ft3

$$\text{Bws} = \text{Moisture Fraction} = \frac{\text{Vw(std)}}{\text{Vw(std)} + \text{Vm(std)}} = \frac{0.345\ \text{ft3}}{0.345\ \text{ft3} + 3.13\ \text{ft3}} = 0.0993$$

Revision Date 4/93

9.9% H_2O

SOURCE SAMPLING FIELD DATA

PLANT NAME Method 301 Validation
TRAIN Moisture
Page 9 of 9
SAMPLING LOCATION Manifold
RUN NO. 9
COND. NO. ____
DATE 7/14/94
TIME START ____
TIME FINISH ____
TEST DURATION ____ min.
DUCT DIMENSIONS ____ x ____
DIAMETER ____ ft
INITIAL LEAK RATE Good cfm
PTCF –
DGMCF 0.956
NOZZLE DIA. N A inches
FINAL LEAK RATE Good cfm
BAR PRESS 29.41 " Hg
STATIC PRESS ____ " H2O
OPERATOR LDO/LAR

Travers Point	Clock Time 2209	Dry gas meter reading ft3	^ P in H2O	^ H in H2O	Stack Temp. F	Dry gas meter temp		Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	
						Inlet	Outlet					
–	~~1009~~	2116.15	–	–	–	74	–	–	–	–	5	
–	~~1109~~	2216.04	–	–	–	74	–	–	–	–	–	
–	2309		–	–	–		–	–	–	–		
Total	Flow	99.84	x 0.956		=	95.5	/28.4		=	3.36		
Avg.	---											
Check'd												

CONSOLE # 20-02870
FILTER # –
AMBIENT TEMP. –
PROBE LENGTH –
LINER MATERIAL –

Velocity
% Moisture
Flowrate (DSCFM)
Isokinetic (%)

REMARKS ____

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		Weight Gain
1	H_2O	20	Midget	Final Initial	65.5 60.7	4.8
2	Dry	—	" "	Final Initial	57.0 54.8	2.2
3	Selica Gel	20	" "	Final Initial	66.5 65.1	1.4
4				Final Initial		
5				Final Initial		
6				Final Initial		

Total Impinger Weight Gain (Wc) 8.4 grms

Analyst________

Vf = Final Meter Volume = ________ ft3

Vi = Initial Meter Volume= ________ ft3

DGMCF = Dry Gas Meter Correction Factor = ________

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 3.36 ft3

Tm = Average Meter Temp. = F+460 = 534 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ________

%CO2 ________

%O2 ________

%N2 ________

%H2 ________

%CH ________

CONDENSED WATER ________ gms

FILTER WT. GAIN ________ gms

PROBE WASH WT. GAIN ________ gms

$$Vm\ (std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(3.36\ ft3)(29.41\ "Hg)}{(534\ R)} = 3.23\ ft3$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(8.4 g) = 0.397 ft3

$$Bws = Moisture\ Fraction = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{0.397\ ft3}{0.397\ ft3 + 3.23\ ft3} = 10.95\%$$

0.1095

Revision Date 4/93

APPENDIX E.3

APPENDIX E.3

Calibration Data

GRI FTIR Method 301 Validation Tests

CEM System Rotometer Calibration and Flow Rate Check

Date	Rotometer Setting (lpm)	Dry Gas Meter Volume (acf)	Elapsed Sampling Time (min.)	Average Meter Temp. (F)	Barometeric Pressure ("Hg)	Gas Flow Rate (slpm)
07-11-94	10	1.7	5	98	29.45	8.95
07-11-94	15	2.535	5	101	29.45	13.27
07-11-94	20	3.21	5	99	29.45	16.85
07-12-94	17.5	2.77	5	85	29.41	14.91
07-13-94	17.5	2.68	5	80	29.45	14.58

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI 301 Validation Page ____ of ____

TRAIN N/A

SAMPLING LOCATION ambient air RUN NO. N/A COND. NO. N/A

DATE 071194 TIME START ________ TIME FINISH ________ TEST DURATION ________ min.

DUCT DIMENSIONS ____ x ____ DIAMETER N/A ft INITIAL LEAK RATE 6000 cfm

PTCF NA DGMCF 0.998 NOZZLE DIA. N/A inches FINAL LEAK RATE ________ cfm

BAR PRESS 748 mm " Hg 29.45

STATIC PRESS N/A " H2O OPERATOR LAR

	~~Travers Point~~ Test	Clock Time	Dry gas meter reading ft3	^ P in H2O	^ H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	______
.69	10-1	1630	970.0	—	—	—	95	97	—	—	—	—	
	STOP	1635	971.69	—	—	—	96	99	—	—	—	—	
70	10-2	1636	971.90	—	—	—	96	99	—	—	—	—	
	STOP	1641	973.60	—	—	—	96	100	—	—	—	—	
71	10-3	1642	974.00	—	—	—	96	100	—	—	—	—	
	STOP	1647	975.71	—	—	—	98	102	—	—	—	—	
					8.95 liters/minute								
.54	15-1	1650	977.8	—	—	—	98	103	—	—	—	—	
	STOP	1655	980.34	—	—	—	96	104	—	—	—	—	
535	15-2	1656	980.80	—	—	—	96	104	—	—	—	—	
	STOP	1701	983.335	—	—	—	96	104	—	—	—	—	
	15-3	1702	983.80	—	—	—	96	104	—	—	—	—	
.53	STOP	1707	986.303	—	—	—	95	104	—	—	—	—	
					13.27 liters/minute								
21	20-1	1715	991.00	—	—	—	95	103	—	—	—	—	
	STOP	1720	994.21	—	—	—	96	104	—	—	—	—	
21	20-2	1721	995.00	—	—	—	96	104	—	—	—	—	
	STOP	1726	998.21	—	^	—	95	103	—	—	—	—	
21	20-3	1727	999.00	—	—	—	94	103	—	—	—	—	
	STOP	1732	1002.21	—	—	—	94	103	—	—	—	—	
					16.85 liters/minute								
	Avg.	---											
	Check'd												

DGM ~~CONSOLE~~ # 39040

FILTER # —

AMBIENT TEMP. ~100

PROBE LENGTH —

LINER MATERIAL —

Velocity

% Moisture

Flowrate (DSCFM)

Isokinetic (%)

REMARKS Orifice / Rotometer Calibration Data using Dry Gas Meter

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams	
1	______	______	______	Final ______ Initial ______	Weight Gain ______
2	______	______	______	Final ______ Initial ______	Weight Gain ______
3	______	______	______	Final ______ Initial ______	Weight Gain ______
4	______	______	______	Final ______ Initial ______	Weight Gain ______
5	______	______	______	Final ______ Initial ______	Weight Gain ______
6	______	______	______	Final ______ Initial ______	Weight Gain ______

Total Impinger Weight Gain (Wc)__________grms

Analyst__________

Vf = Final Meter Volume = ____________ft3

Vi = Initial Meter Volume= ________ ft3

DGMCF = Dry Gas Meter Correction Factor = ________

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = ________ ft3

Tm = Average Meter Temp. = F+460 = _______ R

Pm = Meter Pressure (Barometric Pressure) = ______ in. Hg

%CO __________
%CO2 ________
%O2 __________

%N2 __________
%H2 __________
%CH __________

CONDENSED WATER __________gms
FILTER WT. GAIN __________gms
PROBE WASH WT. GAIN __________gms

$$Vm\ (std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(\_\_\_\_\ \text{ft3})(\_\_\_\_\ \text{"Hg})}{(\_\_\_\_\ \text{R})} = \_\_\_\_\ \text{ft3}$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(____g) = ______ft3

$$Bws = \text{Moisture Fraction} = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{\_\_\_\_\ \text{ft3}}{\_\_\_\_\ \text{ft3} + \_\_\_\_\ \text{ft3}} = \_\_\_\_$$

Revision Date 4/93

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI 301 Validation

Page 1 of 1

TRAIN Calibration

SAMPLING LOCATION Ambient Air

RUN NO. ______ COND. NO. ______

DATE 071294 TIME START ______ TIME FINISH ______ TEST DURATION ______ min.

DUCT DIMENSIONS ______ X ______ DIAMETER N A ft INITIAL LEAK RATE ______ cfm

PTCF N A DGMCF 0.998 NOZZLE DIA. N A inches FINAL LEAK RATE ______ cfm

BAR PRESS 29.41 " Hg 747

STATIC PRESS N A " H2O

OPERATOR LAR

	Travers Point	Clock Time	Dry gas meter reading ft3	^ P in H2O	^ H* in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	______
7.5	17.5-1	0922	14.70	—	1.28	—	83	86	—	—	—	—	
	STOP	0927	17.45	—	1.28	—	82	86	—	—	—	—	
	17.5-2	0929	18.00	—	1.29	—	82	86	—	—	—	—	
77	STOP	0934	20.77	—	1.29	—	82	86	—	—	—	—	
.77	17.5-3	0935	21.40	—	1.31	—	82	86	—	—	—	—	
	STOP	0940	24.17	—	1.31	—	83	87	—	—	—	—	
.77	17.5-4	0941	25.00	—	1.29	—	83	88	—	—	—	—	
	STOP	0946	27.77	—	1.29	—	83	88	—	—	—	—	

$$\frac{2.77\ \text{ft}^3}{5\ \text{min}} \times 0.998 \times \frac{528}{545} \times \frac{29.41}{29.92} \times \frac{28.32\ \text{liters}}{\text{ft}^3} = 14.91\ \text{liters per minute at } 68^\circ\text{F and } 29.92$$

Avg.	---
Check'd	

~~CONSOLE~~ DGM # 39040

FILTER # N A

AMBIENT TEMP. ~85

PROBE LENGTH —

LINER MATERIAL —

Velocity

% Moisture

Flowrate (DSCFM)

Isokinetic (%)

REMARKS Calibration of System Rotometer set at 17.5 lpm

* [illegible] ΔH orifice with magnehelic NO. M-05-06

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams	
1	________	____	____	Final ____ Initial ____	Weight Gain ____
2	________	____	____	Final ____ Initial ____	Weight Gain ____
3	________	____	____	Final ____ Initial ____	Weight Gain ____
4	________	____	____	Final ____ Initial ____	Weight Gain ____
5	________	____	____	Final ____ Initial ____	Weight Gain ____
6	________	____	____	Final ____ Initial ____	Weight Gain ____

Total Impinger Weight Gain (Wc)________grms

Analyst________

Vf = Final Meter Volume = ________ft3

Vi = Initial Meter Volume= ______ ft3

DGMCF = Dry Gas Meter Correction Factor = ______

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = ______ ft3

Tm = Average Meter Temp. = F+460 = ______ R

Pm = Meter Pressure (Barometric Pressure) = ______ in. Hg

%CO ________
%CO2 ________
%O2 ________

%N2 ________
%H2 ________
%CH ________

CONDENSED WATER ________gms
FILTER WT. GAIN ________gms
PROBE WASH WT. GAIN ________gms

$$Vm\ (std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(\_\_\_\_ ft3)(\_\_\_\_ "Hg)}{(\_\_\_\_\ R)} = \_\_\_\_ ft3$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(____g) = ______ft3

$$Bws = \text{Moisture Fraction} = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{\_\_\_\_ ft3}{\_\_\_\_ ft3 + \_\_\_\_ ft3} = \_\_\_\_$$

Revision Date 4/93

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI 301 Validation
Page ____ of ____
TRAIN ________
SAMPLING LOCATION FTIR Exit
RUN NO. ______ COND. NO. ______
DATE 071294 TIME START ______ TIME FINISH ______ TEST DURATION ______ min.
DUCT DIMENSIONS ______ X ______ DIAMETER ______ ft INITIAL LEAK RATE ______ cfm
PTCF ______ DGMCF .998 NOZZLE DIA. N/A inches FINAL LEAK RATE ______ cfm
BAR PRESS 29.47 " Hg
STATIC PRESS ______ " H2O
OPERATOR WG/LAR

Avg FTIR = 9.85%

Travers Point	Clock Time	Dry gas meter reading ft3	^ P in H2O	^ H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	____
~~2119~~	2119	28.863	—	—	—	80	79	—	—	—	—	
		36.530				84	73					
		7.667										
Avg.	---											
Check'd												

DGM ~~CONSOLE~~ # 39040
FILTER # ______
AMBIENT TEMP. ______
PROBE LENGTH ______
LINER MATERIAL ______

Velocity
% Moisture
Flowrate (DSCFM)
Isokinetic (%)

REMARKS Check of the Moisture Content in Gas Exiting FTIR
HPLC Grade Water injected

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		Weight Gain
1	H2O	~100	MSG	Final	676.5	9.0
				Initial	667.5	
2	Silica Gel	~100	MSG	Final	660.5	2.3
				Initial	658.2	
3				Final		
				Initial		
4				Final		
				Initial		
5				Final		
				Initial		
6				Final		
				Initial		

Total Impinger Weight Gain (Wc) 11.3 grms

Analyst ______

Vf = Final Meter Volume = 36.530 ft3

Vi = Initial Meter Volume= 28.863 ft3

DGMCF = Dry Gas Meter Correction Factor = 0.998

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 7.652 ft3

Tm = Average Meter Temp. = F+460 = 539 R

Pm = Meter Pressure (Barometric Pressure) = 29.411 in. Hg

%CO ______

%CO2 ______

%O2 ______

%N2 ______

%H2 ______

%CH ______

CONDENSED WATER ______ gms

FILTER WT. GAIN ______ gms

PROBE WASH WT. GAIN ______ gms

$$\frac{6.75}{9.85} = 68.5$$

$$\text{Vm (std)} = \frac{(17.64)(\text{Vm})(\text{Pm})}{\text{Tm}} = \frac{(17.64)(7.652\ \text{ft3})(29.41\ "\text{Hg})}{(539\ \text{R})} = 7.365\ \text{ft3}$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(11.3 g) = 0.533 ft3

$$\text{Bws} = \text{Moisture Fraction} = \frac{\text{Vw(std)}}{\text{Vw(std)} + \text{Vm(std)}} = \frac{.533\ \text{ft3}}{.533\ \text{ft3} + 7.36\ \text{ft3}} = 6.75$$

Revision Date 4/93

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI 301 Validation

Page ____ of ____

TRAIN ____

SAMPLING LOCATION FTIR Exhaust

RUN NO. 2

COND. NO. ____

DATE 07/12/94

TIME START ____

TIME FINISH ____

TEST DURATION ____ min.

DUCT DIMENSIONS ____ X ____

DIAMETER ____ ft

INITIAL LEAK RATE ____ cfm

PTCF —

DGMCF 0.998

NOZZLE DIA. N/A inches

FINAL LEAK RATE ____ cfm

BAR PRESS 29.41 " Hg

STATIC PRESS — " H2O

OPERATOR LAR/WG

~~Travers Point~~	Clock Time	Dry gas meter reading ft3	^P in H2O	^H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	____
	2052	36.55	—	—	—	72	76	—	—	—	—	
	2149	48.29	—	—	—	86	72	—	—	—	—	
		11.74					76					
Avg.	---											
Check'd												

DGM ~~CONSOLE~~ # 39040

FILTER # ____

AMBIENT TEMP. ____

PROBE LENGTH ____

LINER MATERIAL ____

Velocity ____

% Moisture ____

Flowrate (DSCFM) ____

Isokinetic (%) ____

~1.1 ml/min H2O liquid

REMARKS Moisture Comparison Check

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams		Weight Gain
1	H2O	100	MSG	Final	703.7	27.2
				Initial	676.5	
2	Silica Gel	100	MSG	Final	662.8	2.3
				Initial	660.5	
3				Final		
				Initial		
4				Final		
				Initial		
5				Final		
				Initial		
6				Final		
				Initial		

Total Impinger Weight Gain (Wc) 29.50 grms

Analyst ______

Vf = Final Meter Volume = ______ ft3

Vi = Initial Meter Volume = ______ ft3

DGMCF = Dry Gas Meter Correction Factor = .998

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = 11.72 ft3

Tm = Average Meter Temp. = F+460 = 537 R

Pm = Meter Pressure (Barometric Pressure) = 29.41 in. Hg

%CO ______

%CO2 ______

%O2 ______

%N2 ______

%H2 ______

%CH ______

CONDENSED WATER ______ gms

FILTER WT. GAIN ______ gms

PROBE WASH WT. GAIN ______ gms

$$\frac{10.93}{16.0} \quad 68.3\%$$

$$\text{Vm (std)} = \frac{(17.64)(\text{Vm})(\text{Pm})}{\text{Tm}} = \frac{(17.64)(11.72\ \text{ft3})(29.41\ \text{"Hg})}{(537\ \text{R})} = 11.33\ \text{ft3}$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(29.5 g) = 1.39 ft3

$$\text{Bws} = \text{Moisture Fraction} = \frac{\text{Vw(std)}}{\text{Vw(std)} + \text{Vm(std)}} = \frac{1.39\ \text{ft3}}{1.39\ \text{ft3} + 11.33\ \text{ft3}} = \_\_\_\_$$

10.93%

Revision Date 4/93

SOURCE SAMPLING FIELD DATA

PLANT NAME GRI FTIR 301 Validation

Page 1 of 1

TRAIN

SAMPLING LOCATION Ambient Air

RUN NO.

COND. NO.

DATE 071394

TIME START

TIME FINISH

TEST DURATION min.

DUCT DIMENSIONS X

DIAMETER ft

INITIAL LEAK RATE cfm

PTCF —

DGMCF 0.998

NOZZLE DIA. NA inches

FINAL LEAK RATE cfm

BAR PRESS 29.45 " Hg

STATIC PRESS N/A " H2O

OPERATOR LAR

	Travers Point	Clock Time	Dry gas meter reading ft3	^ P in H2O	^ H in H2O	Stack Temp. F	Dry gas meter temp Inlet	Dry gas meter temp Outlet	Hot box Temp.	Probe Temp	Last Impinger	Vacuum in. Hg	
	17.5-1	0852	53.00	—	1.28	—	76	76	—	—	—	—	
.68	STOP	0857	55.68	—	1.28	—	77	78	—	—	—	—	
	17.5-2	0858	56.00	—	1.26	—	77	78	—	—	—	—	
67	STOP	0903	58.67	—	1.26	—	78	82	—	—	—	—	
	17.5-3	0904	59.00	—	1.24	—	78	82	—	—	—	—	
69	STOP	0909	61.69	—	1.24	—	79	84	—	—	—	—	
	Avg.	---											
	Check'd												

$$\frac{8.04\ \text{ft}^3}{15\ \text{min}} \times .998 \times \frac{528}{540} \times \frac{29.45}{29.92} \times \frac{28.32\ \text{liters}}{\text{ft}^3} = 14.58\ \text{lpm}$$

@ 68 °F and 29.92" Hg

DGM ~~CONSOLE~~ # 39040

FILTER # —

AMBIENT TEMP. —

PROBE LENGTH —

LINER MATERIAL —

Velocity

% Moisture

Flowrate (DSCFM)

Isokinetic (%)

REMARKS Rotometer/System Flow Check

MOISTURE AND IMPINGER CATCH DATA SHEET

Impinger Number	Solution	Approx. ml	Configuration	Weight in grams			
1	____________	______	______	Final	______	Weight	
				Initial	______	Gain	______
2	____________	______	______	Final	______	Weight	
				Initial	______	Gain	______
3	____________	______	______	Final	______	Weight	
				Initial	______	Gain	______
4	____________	______	______	Final	______	Weight	
				Initial	______	Gain	______
5	____________	______	______	Final	______	Weight	
				Initial	______	Gain	______
6	____________	______	______	Final	______	Weight	
				Initial	______	Gain	______

Total Impinger Weight Gain (Wc)__________grms

Analyst__________

Vf = Final Meter Volume = ____________ft3

Vi = Initial Meter Volume= ________ ft3

DGMCF = Dry Gas Meter Correction Factor = ________

Vm = Metered Gas Volume = (Vf-Vi)(DGMCF) = ________ ft3

Tm = Average Meter Temp. = F+460 = _______ R

Pm = Meter Pressure (Barometric Pressure) = ______ in. Hg

%CO __________

%CO2 ________

%O2 __________

%N2 __________

%H2 __________

%CH __________

CONDENSED WATER __________gms

FILTER WT. GAIN __________gms

PROBE WASH WT. GAIN __________gms

$$Vm\ (std) = \frac{(17.64)(Vm)(Pm)}{Tm} = \frac{(17.64)(\_\_\_\_\,\text{ft3})(\_\_\_\_\,\text{"Hg})}{(\_\_\_\_\ \text{R})} = \_\_\_\_\_\,\text{ft3}$$

Vw(std) = Volume of Water Vapor = .0472(Wc) = .0472(_____g) = _______ft3

$$Bws = \text{Moisture Fraction} = \frac{Vw(std)}{Vw(std) + Vm(std)} = \frac{\_\_\_\_\_\,\text{ft3}}{\_\_\_\_\_\,\text{ft3} + \_\_\_\_\_\,\text{ft3}} = \_\_\_\_\_$$

Revision Date 4/93

6/27/94

Dynamic Spiking System for Method 301 Validation

Mass Flow Meter Calibration

The dynamic spiking system contains four Tylan mass flow meters (MFM) for measuring the flow of the spiking gas. Three of the MFM's have a range of 0-5 liters per minute, one has a range of 0-10 liters per minute. The larger range MFM is for blending the other three MFM into one stream for delivery to the sampling probe.

All of the low range MFM's were calibrated, with nitrogen, throughout their ranges (0-6 Lpm) using a mini-Buck bubble flow meter (m-7337) that had been referenced to a primary standard. The larger range MFM was calibrated (also using nitrogen) using the mini-Buck up to 5 liters per minute and with a bubble flow meter from 5.5 to 10 liters per minute. All measurements were made at the measurement ports on the front panel of the spiking system, at half liter intervals. The flow was also checked at the outlet ports for all four channels at least once during calibrations to ensure that the flow from the measured port did equal the flow that would be delivered in a normal operating mode. In addition to measuring the actual flows at each flow setting, the output voltage for each channel was also recorded for each flow setting. The output voltages were measured using a Fluke 8020 multimeter at the end of the 100ft of signal line running from the back of the mass flow meter display.

Three calibration curves were generated for each channel; actual flow v. observed flow, actual flow v. output voltage, and observed flow v. output voltage. The results of linear regression analyses on all the curves showed R squared values ranging from 0.99916 to 1.00000. The graph of each curve along with the equation of its regression line is provided in the calibration notebook.

Actual Flow vs. Observed Flow

Channel ONE R squared = .99985

err of y = .02150

err of x = .00370

Channel TWO R squared = .99962

err of y = .03397

err of x = .00589

Channel THREE R squared = .99972

err of y = .02951

err of x = .00512

Channel FOUR R squared = .99916

err of y = .09214

err of x = .00610

Actual Flow vs. Output Voltage

Channel ONE R squared = .99985
err of y = .02475
err of x = .00426

Channel TWO R squared = .99959
err of y = .03513
err of x = .00609

Channel THREE R squared = .99967
err of y = .03166
err of x = .00549

Channel FOUR R squared = .99920
err of y = .04502
err of x = .00298

Observed Flow vs. Output Voltage

Channel ONE R squared = .99999
err of y = .00549
err of x = .00104

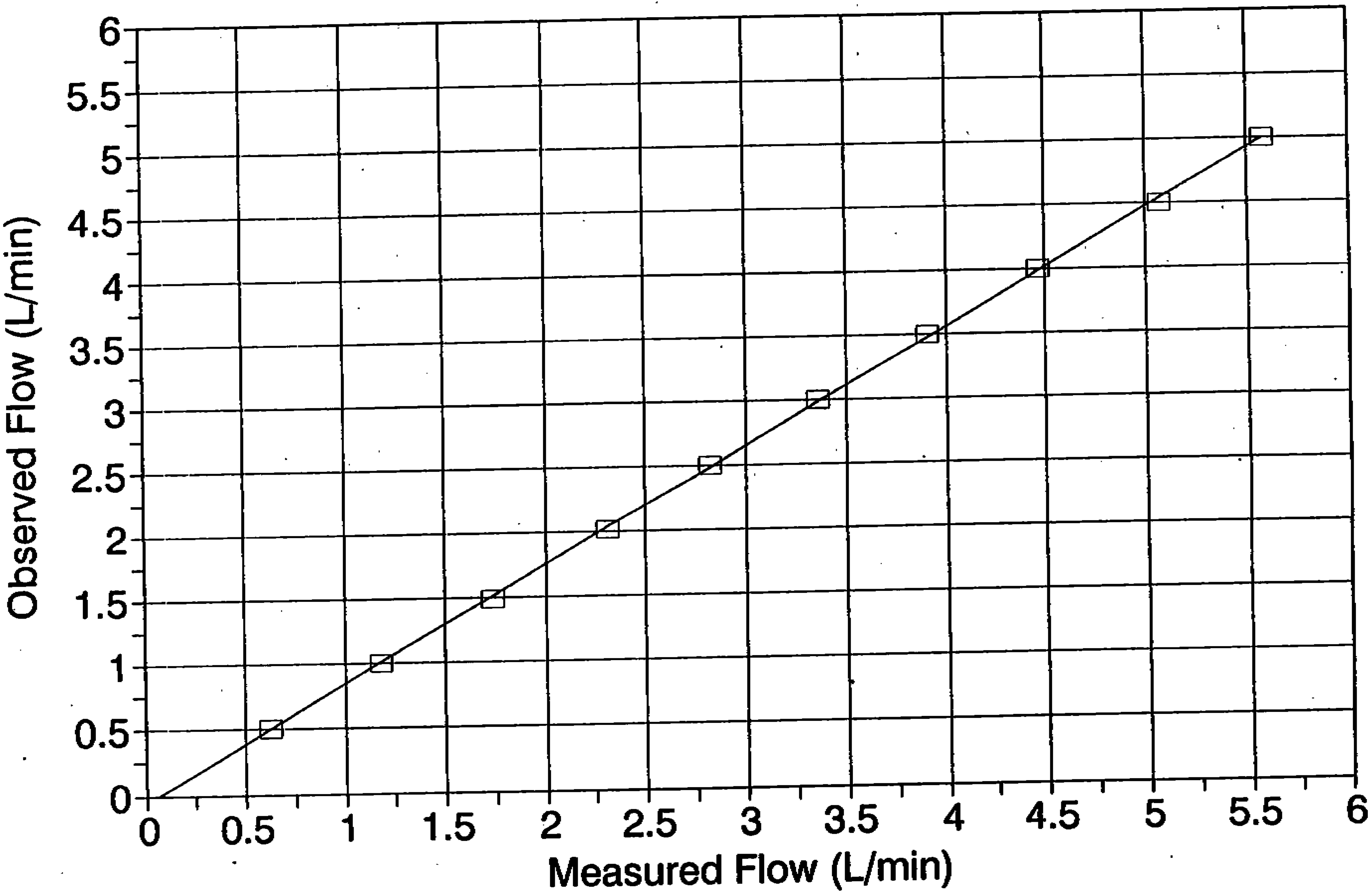
Channel TWO R squared = 1.00000
err of y = .00275
err of x = .00053

Channel THREE R squared = .99999
err of y = .00550
err of x = .00105

Channel FOUR R squared = 1.00000
err of y = .00263
err of x = .00019

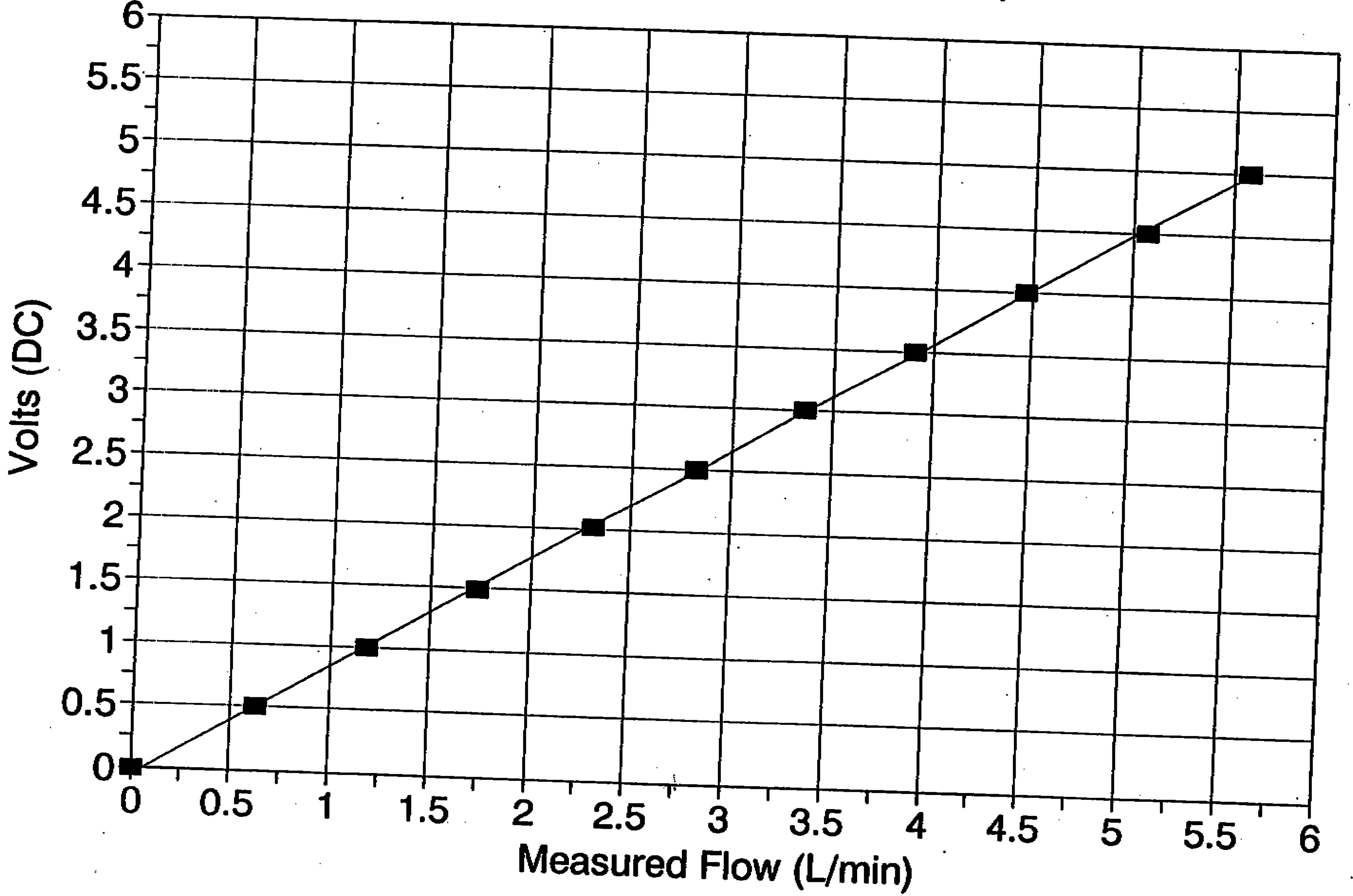
CHANNEL 1

Flow = (Observed Flow + .05692)/.90479



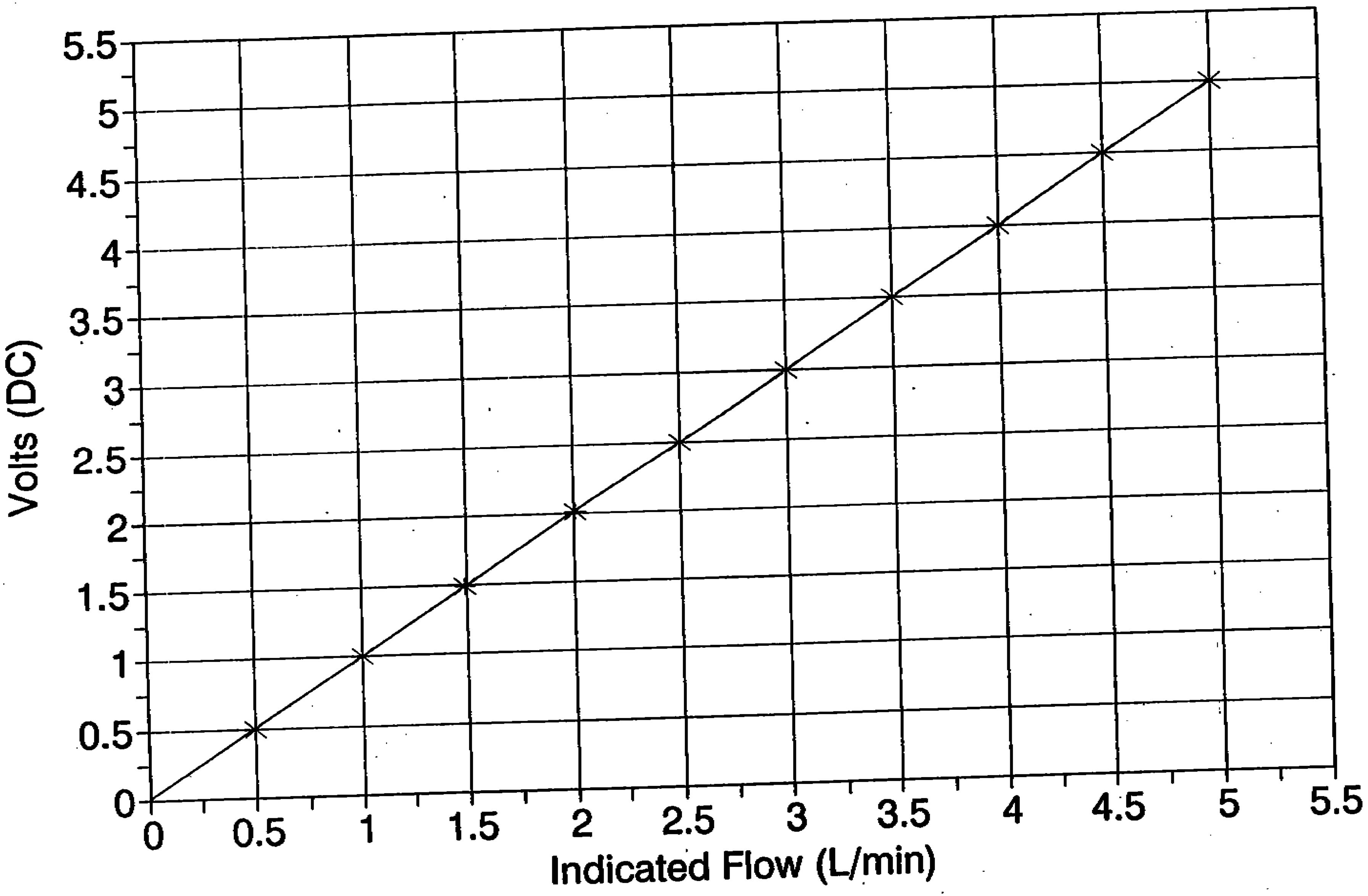
CHANNEL 1

Flow = (Output Voltage + .05038)/.90312



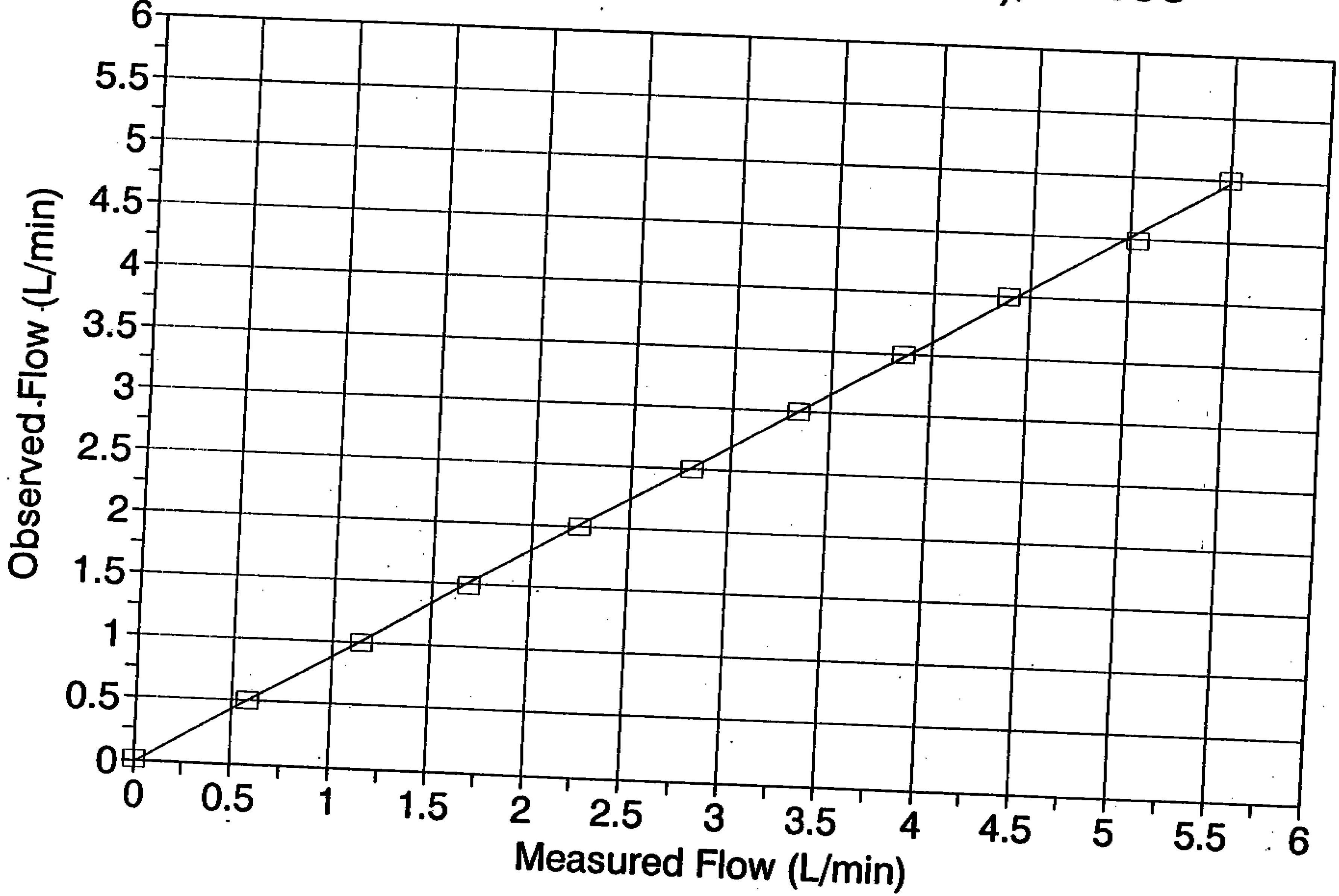
CHANNEL 1

Indctd Flow = (Volts - .00638)/.99817



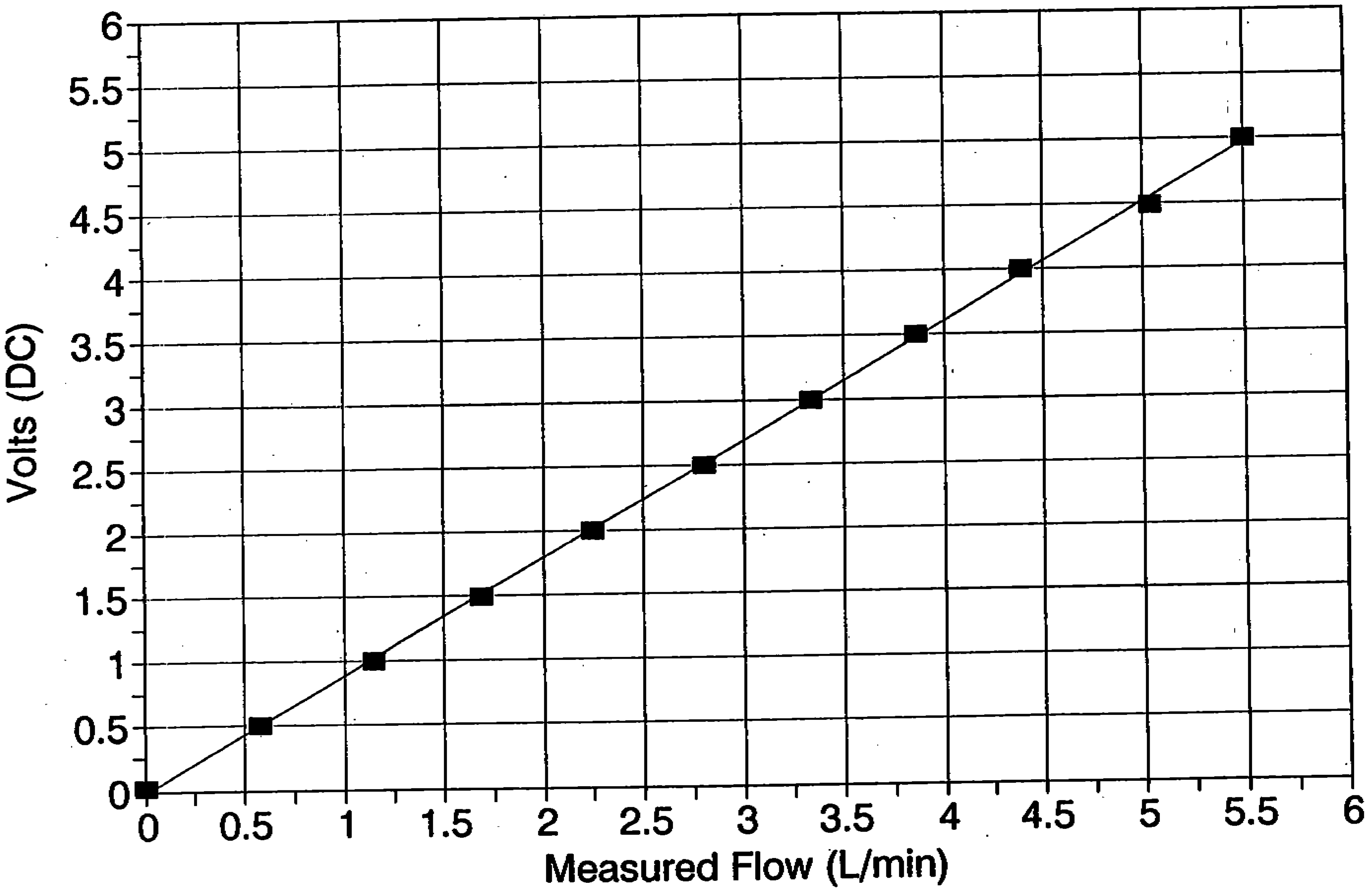
CHANNEL 2

Flow = (Observed Flow + .02280)/.90636



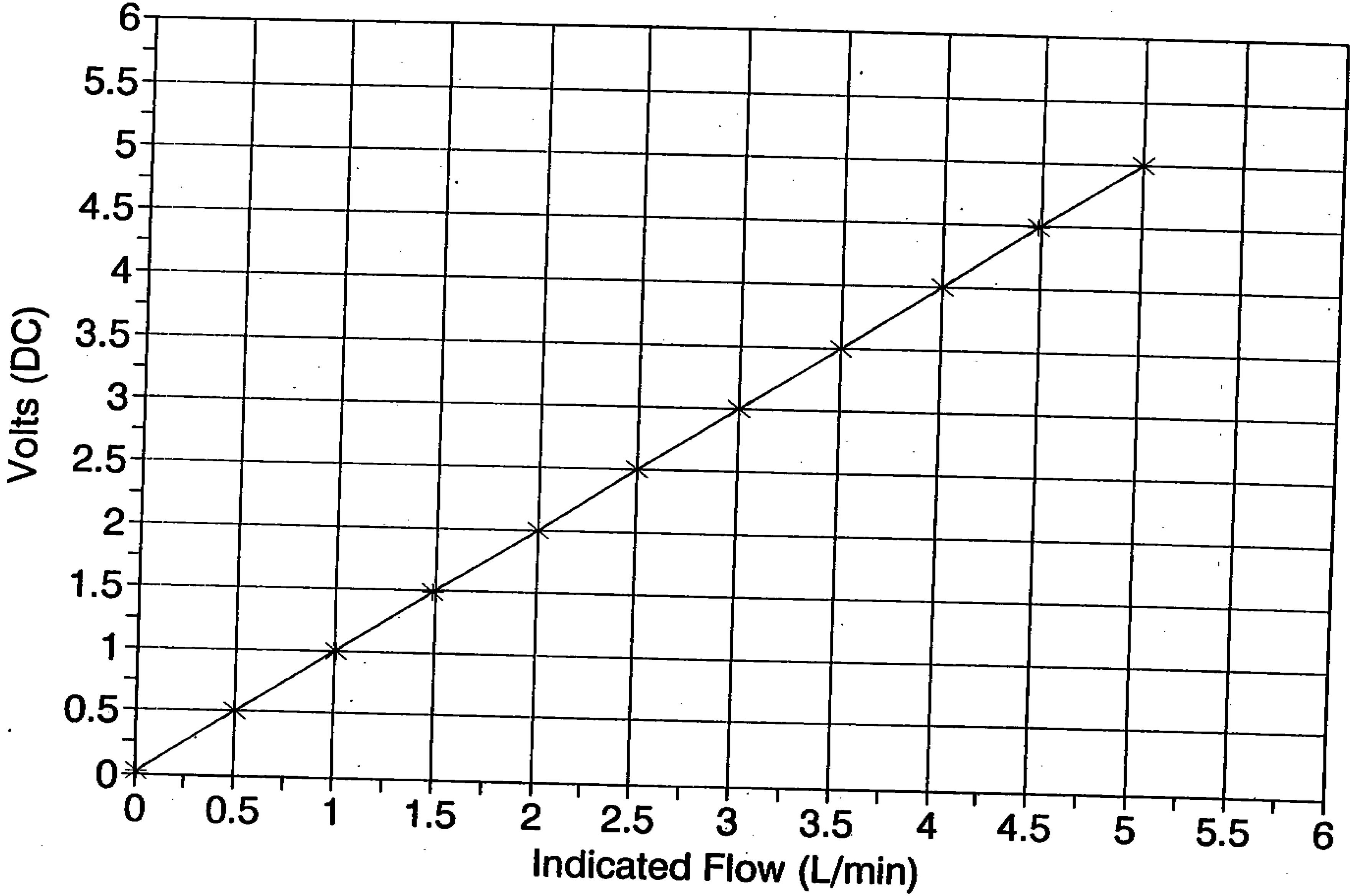
CHANNEL 2

Flow = (Output Voltage + .01957)/.90552



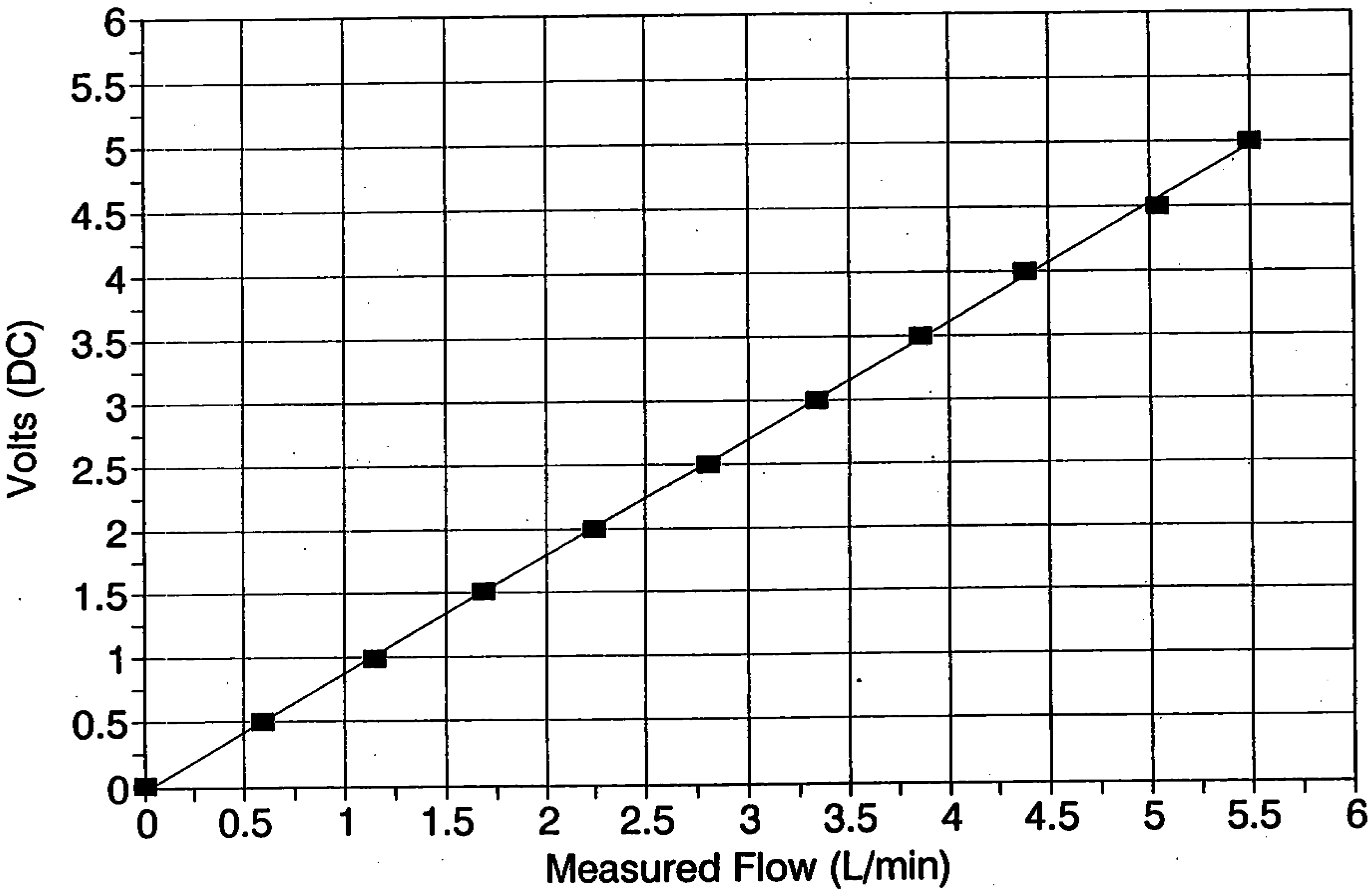
CHANNEL 2

Indctd Flow = (Volts -.00318)/.99909



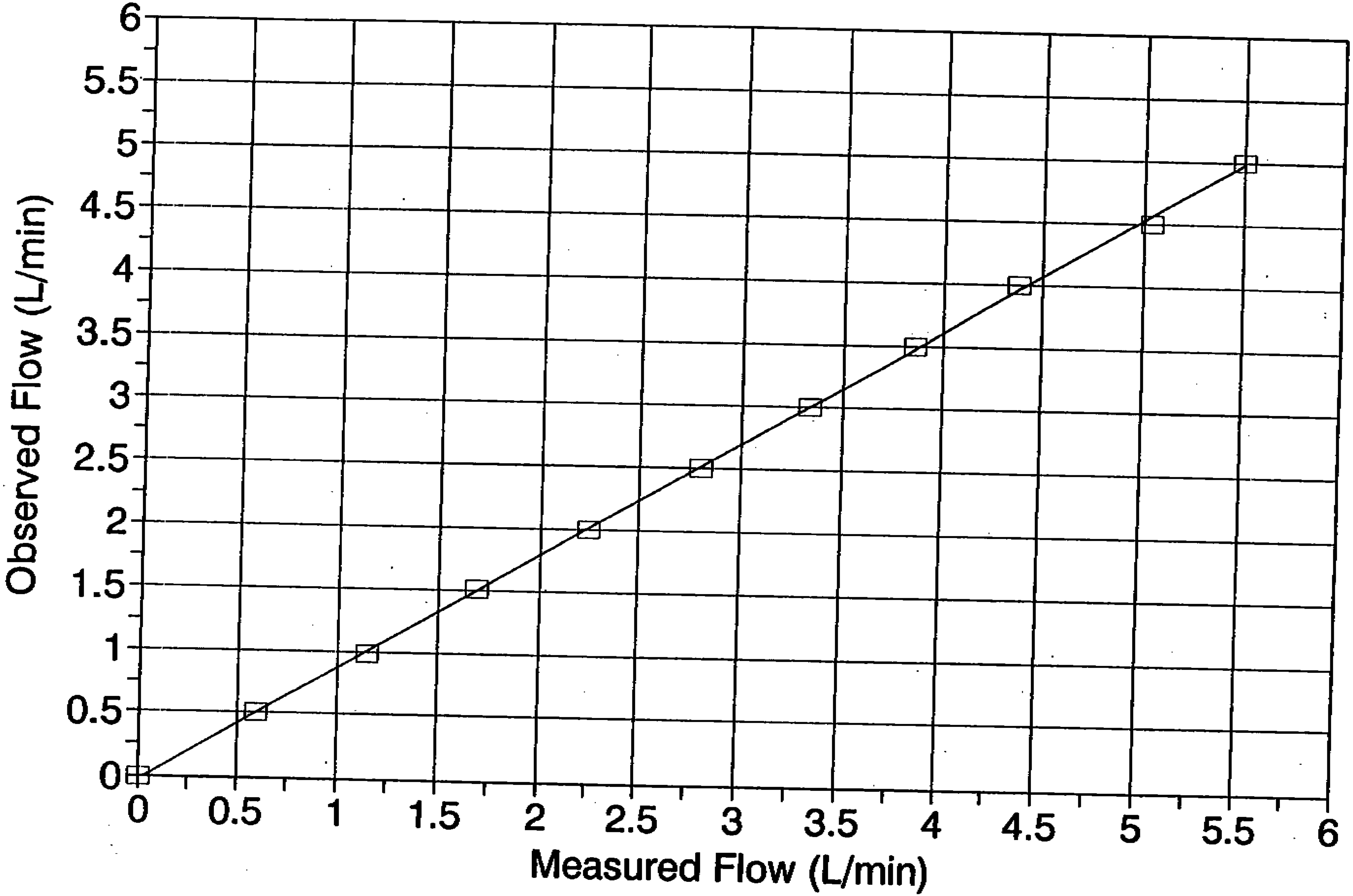
CHANNEL 3

Flow = (Output Voltage + .02636)/.90854



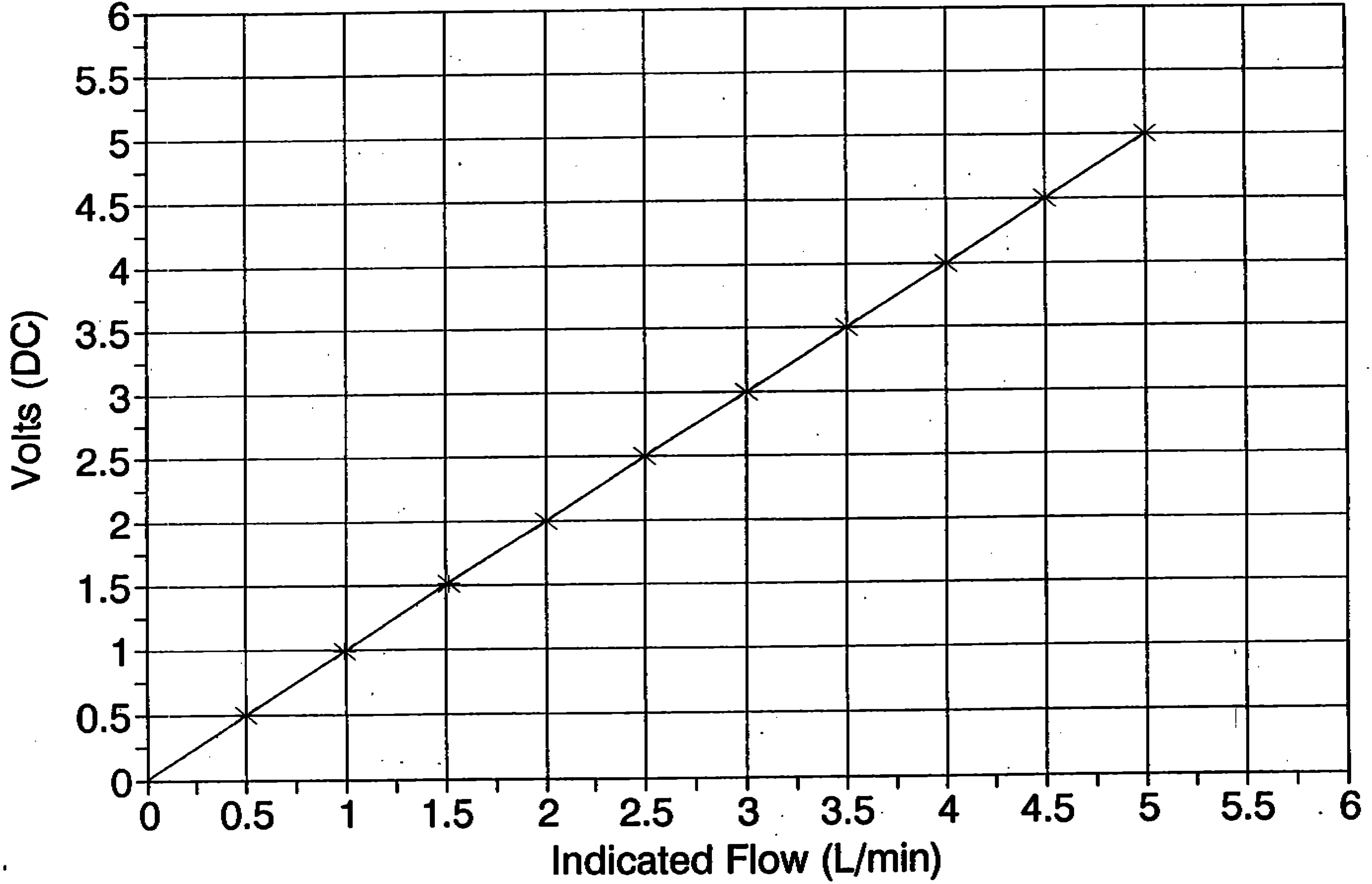
CHANNEL 3

Flow = (Observed Flow + .03284)/.91022



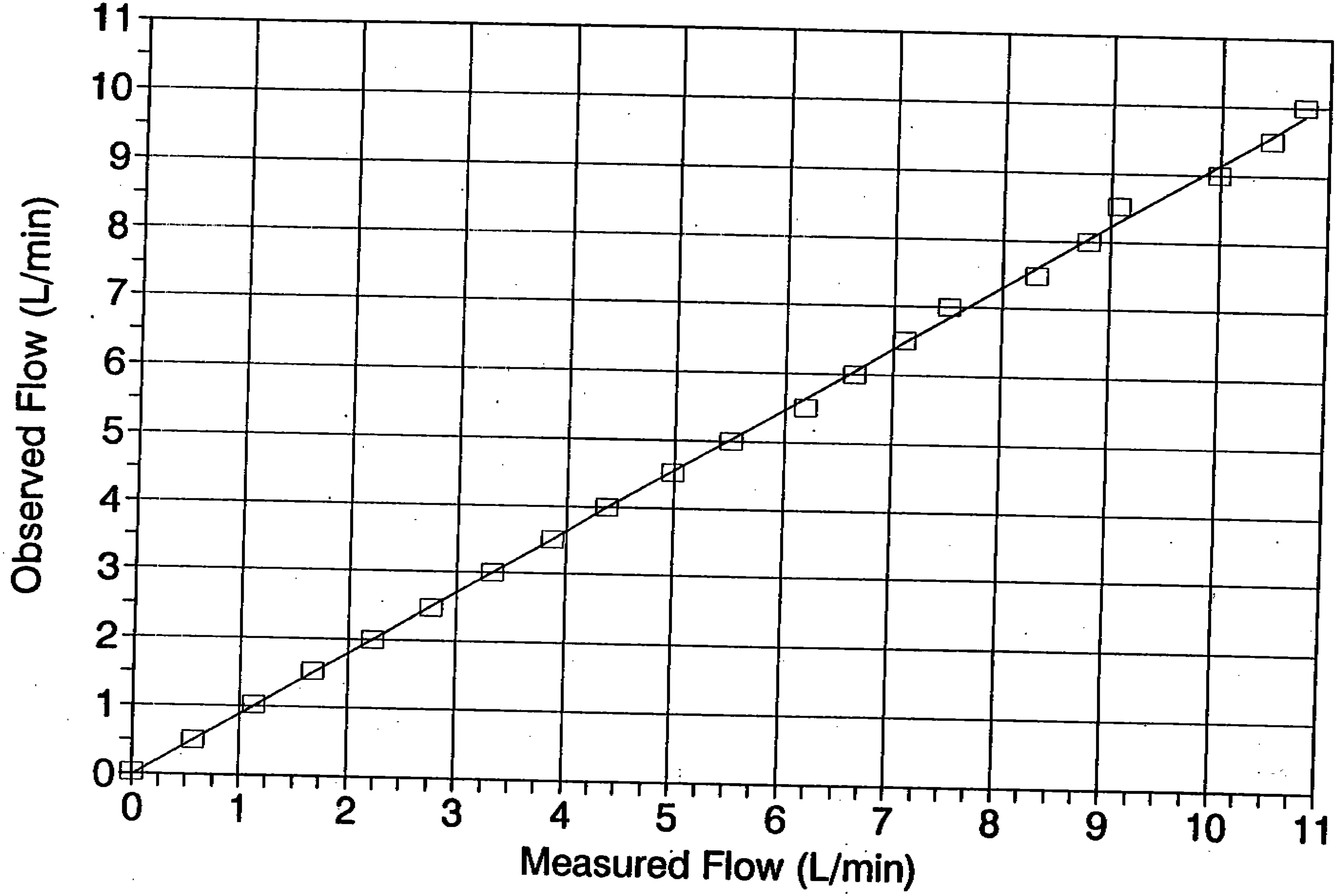
CHANNEL 3

Indctd Flow = (Volts - .00638)/.99818



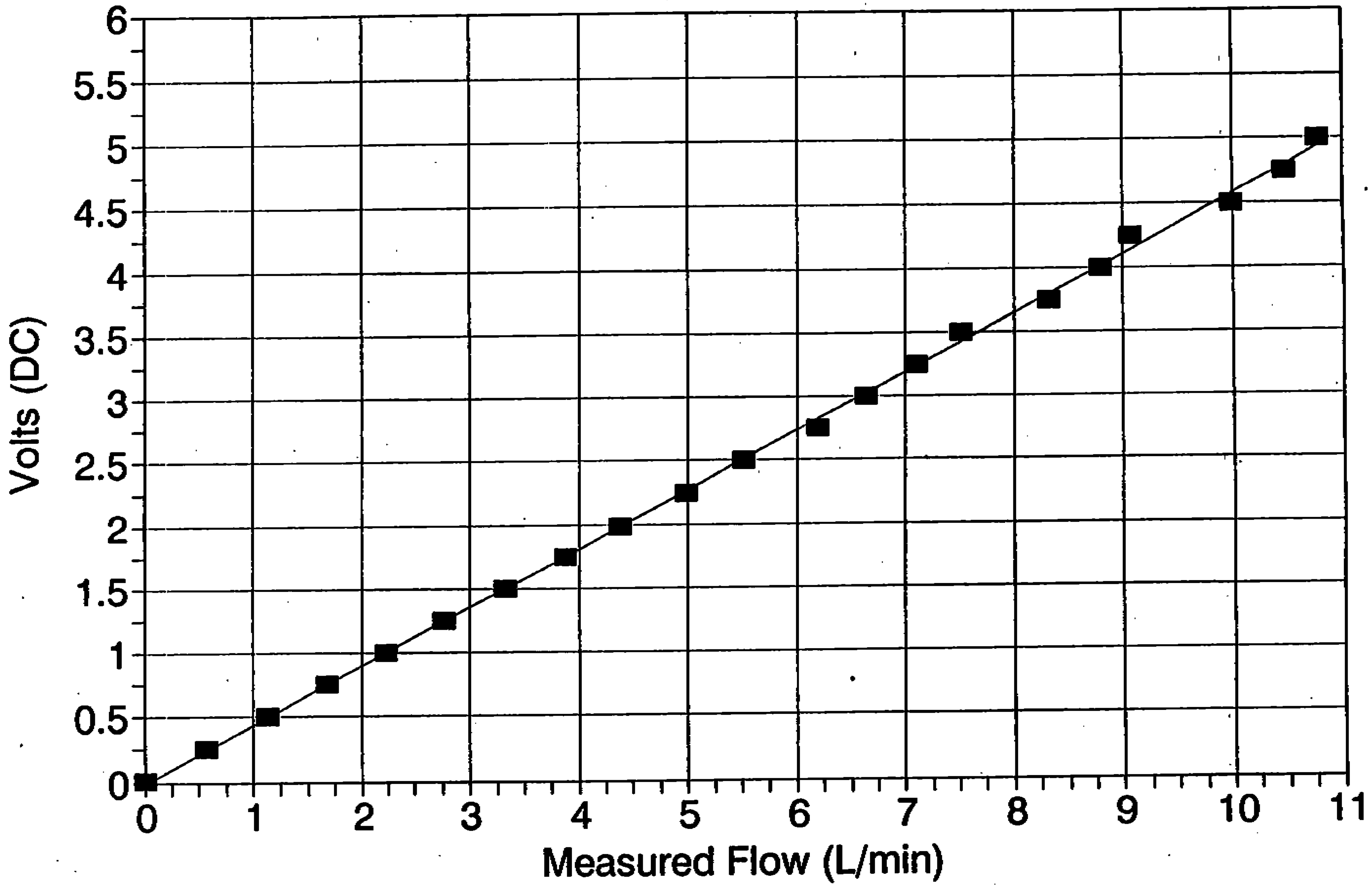
CHANNEL 4

Flow = (Observed Flow + .03793)/.91806



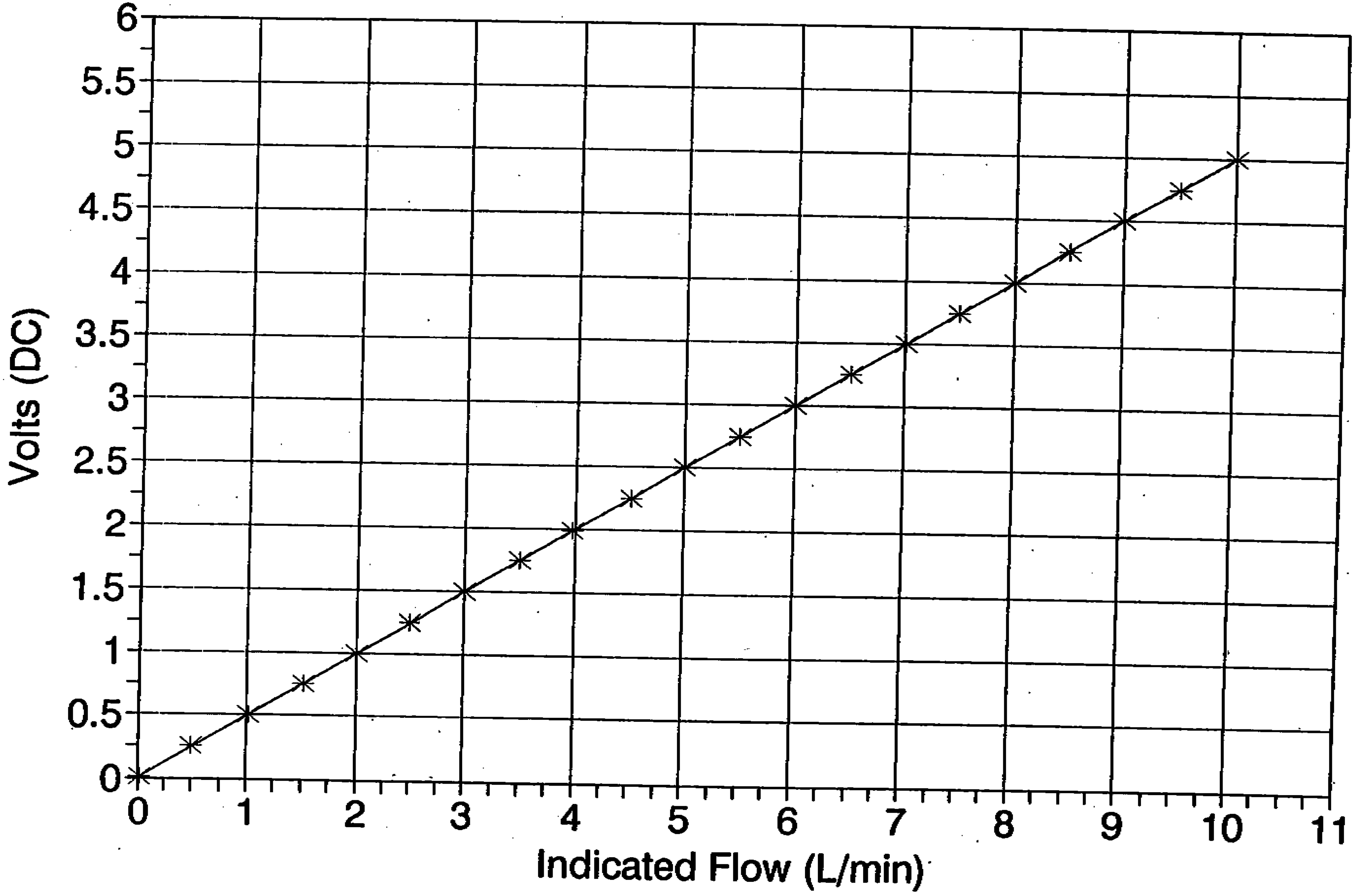
CHANNEL 4

Flow = (Output Voltage + .01996)/.45904



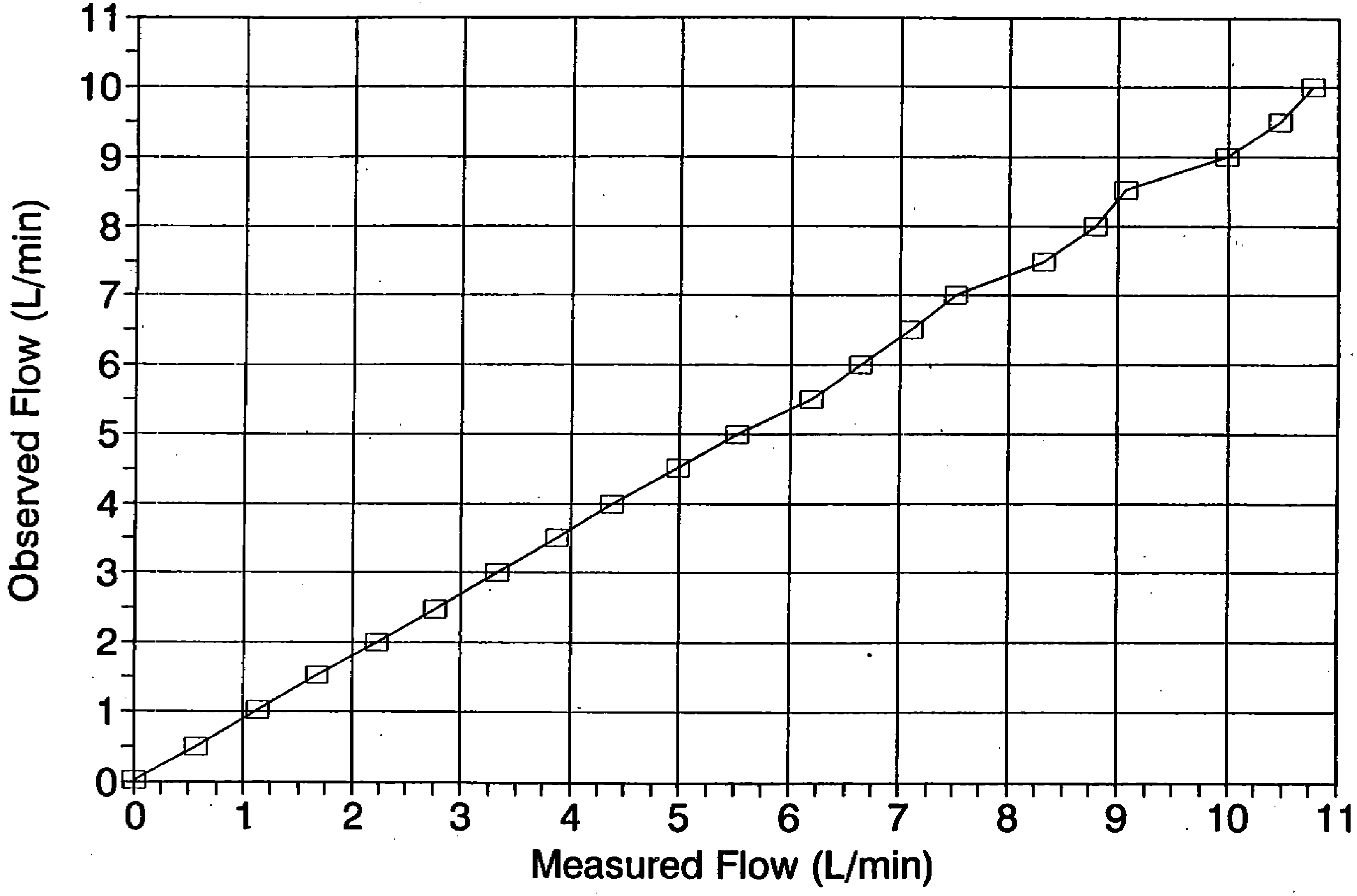
CHANNEL 4

Indctd Flow = (Volts + .00095)/.50000



CHANNEL 4

Flow = (Observed Flow + .03793)/.91806



APPENDIX E.4

Field Log

From Page No.__

7/11/94 Method 301 Validation $ml/sec \times \frac{60 sec}{min} = \frac{ml}{min} \cdot \frac{L}{1000 ml}$

Dynamic Spiking System Calibration: Gas Flowrates Calibrated against NBS Traceable Bubblemeter

Channel 1		Measured Bubblemeter (LPM)	Flowmeter Reading (LPM)	
	0.889	0.885	0.75	
		0.894	0.75	Correlation coef 0.99999
		0.887	0.75	
	1.727	1.726	1.49	slope = 0.88893
		1.724	1.49	
		1.731	1.49	int = -0.0417
	2.317	2.332	2.02	
		2.332	2.02	
		2.287	2.02	
Channel 2	0.855	0.848	0.75	
		0.858	0.75	Corr coeff = 0.99993
		0.858	0.75	
	1.608	1.609	1.41	slope = 0.8954
		1.622	1.41	
		1.594	1.41	int = -0.0204
	2.419	2.381	2.15	
		2.429	2.15	
		2.446	2.15	

$y = mx + b$ 1.32 on MFM = 1.497 Lpm actual

$y - b = mx$

$x = \frac{y-b}{m}$

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Witnessed & Understood by me.	Date	Invented by	Date
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Channel 4	Measured (Bubblemeter) LPM	Flowmeter Reading LPM	*added 4th point
	0.90 (not accurate)	0.81	
	0.873	0.81	
0.880	0.885	0.81	corr coef = ~~0.9997~~ 3pt
	0.883	0.81	0.9994 4th
	1.735	1.56	slope = ~~0.8674~~ 3pt
1.715	1.695	1.56	0.8669 4th
	1.711	1.56	int = ~~0.0544~~
	2.335	2.08	0.0551 4th
2.347	2.372	2.08	
	2.335	2.08	
	4.065	3.54	
4.020	4.005	3.54	
	3.968	3.54	
	4043	3.54	

set Channel 1 @ 1.29 on flowmeter calc 1.51 LPM
measured w/ 1.518
bubblemeter and 1.514

set Channel 2 @ 1.32 on flowmeter calc 1.497
measured 1.498

added acrolein/acetonitrile std to channel 1 set @ 1.30 = 1.51 LPM
standard 4
measured at 1.514 LPM
1.516

added propionaldehyde/Bnt/isoluol to channel 2 set @ 1.32 = 1.497 calc
measured @ 1.536 LPM
& 1.542

Combined should be 3.055 measured 3.083 LPM

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Barometric pressure 748 mm Hg
Flowrate through heat trace 17.5 L/min
Heat trace temp 280°F (740°R) ambient temp ~~79%~~ 7.00 F (539°R)
Formaldehyde conc ~23 ppm

$17.5\ L/min \times \frac{539}{740} \times \frac{748}{760} = 12.54\ Lpm$ @ STD

$\frac{23\ \mu L}{L} \times \frac{\mu mole}{24.1\ \mu L} \times \frac{30.03\ \mu g}{\mu mole} = \frac{28.66\ \mu g}{L} \times \frac{12.54\ L}{min} = 359.4\ \mu g/min$

~~3~~ Formaldehyde solution = 0.37 mg/mL = 370 µg/mL

@ 1.0 ml/min × 370 µg/mL = 370 µg/min

★ cylinder gases

$3.083\ L/min \times \frac{740}{539} \times \frac{748}{760} = 4.166\ L/min$

~~★~~ water vapor $1.0\ \frac{mL}{min} \times \frac{1\ gm}{mL} \times \frac{mole}{18\ g} \times \frac{24.1\ L}{mole} = 1.34\ L/min$ @ STD

$1.34 \times \frac{740}{539} \times \frac{748}{760} = 1.81\ LPm$

1.81 + 4.166 = 5.976 total flow added

17.5 LPm − 5.976 = 11.52 Lpm sample gas

$\frac{11.52}{17.5} = 0.658 \times 230$ ppm formaldehyde = 15.14 ppm native formaldehyde

adding 370 µg/min spike

~~$370\ \mu g/min \times \frac{1\ min}{1\ mL} \times \frac{1\ mL}{1\ g} \times \frac{1\ \mu mole}{30.03\ \mu g}$~~ LAO

$370\ \mu g/min \times \frac{\mu mole}{30.03\ \mu g} \times \frac{24.10\ \mu L}{1\ \mu mole} = 297\ \mu L/min \times \frac{1\ min}{17.5\ L} = 16.97$ ppm µL/L spiked

16.97 + 15.14 native = 32.11 LAO p. 29

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Note: All calculations on p. 28 are based on heated rotameter flow - this is not correct. Standard Lpm @ a setting of 17.5 L/min is ~ 15 Lpm. The rotometer is being calibrated w/ ambient air using a dry gas meter. We will use this calibration to determine actual flow used during experiments and base final calculations on that number. See data sheets

7/12/94

Opened formaldehyde Bottle 2 of 4 & collected duplicate samples for analyses These samples are:

Formaldehyde spike Dup 1 Begin Test M301-1B Bottle#Lot B0028020
Formaldehyde spike Dup. 2 Begin Test M301-2B Bottle Lot B0028020

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7/12/94 Pre-test setup

Calibrated HPLC pump using formaldehyde solution and balance
Set flow @ 7.1 mL/min – pumped 7 mL/min

Set flow @ 1.1 mL/min and monitored for 2 min – flow 1.0 mL/min

Decided to NOT use propionaldehyde, butanal and isobutanal due to the interferences with acetaldehyde. We will do these on Thursday with BTEX.

Decided to up flow of acetaldehyde & acrolein to ~2.0 LPM. This will give concs of ~6.7 ppm each.

Channel 1 set 1.7~~35~~4 ~~200~~ on FC calc @ ~~1.993~~ 2.004 ~~740~~ measured 1.996, 2.009, 1.993 } 1.999

Channel 4 ~~measures~~ flo reads 1.80 measured as 2.016, 2.002, 2.002, 1.988 } 2.002

Barometric pressure 747 mm Hg

Flowrate through gas sample line = 14.95 LPM @ STD
68°F 29.92" Hg

* Check on calibration sheets for cylinder gases w/ Carl Galloway in Austin

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		Recorded by L D Ogle	7/12/94

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Aldehyde spike cylinders

		cylinder conc.	FTIR
7/11/94	Acetaldehyde	55.4	49.5
	Acrolein	55.2	68.3
7/12/94	acetaldehyde	55.4	
	acrolein	55.2	

- Using 2.0 LPM spike Acetaldehyde & Acrolein standard (p. 29) we have a 0.1338 dilution factor

	cylinder dil	measured dilution
Acetaldehyde 55.4	7.41 ppm	6.62 ppm
acrolein 55.2	7.38 ppm	9.14 ppm

formaldehyde @ 1.0 mL/min of 0.337% Measured concentration was 0.37% 370 µg/mL

$$370\,\mu g/min \times \frac{mmole}{30.03} \times \frac{24.04\,\mu L}{mmole}\ (68°F) = 296.2\,\frac{\mu L}{min} \times \frac{min}{14.95\,L} = 19.81\,\frac{\mu L}{L}\ ppm$$

Acrolein Gas Flow - 2.0 LPM

water vapor (gas) flow = 1.34 LPM

3.34 total spike LPM

Stack gas flow while spiking = 11.61 LPM

77.66% native gas, so formaldehyde conc × 0.7766 gives native contribution

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7/12/94	10:56 (computer) 11:02 am	11:01 (computer) 11:05 am	11:06 comp 11:10
Formaldehyde	= 26.6 ppm	27.5	~~27~~ 27.5
O_2	= 14.12 %	14.11	
THC	= 8733 ppm	885	
CO	= 111.2	100.5	
CO_2	= 3.9 %	4.0	
spike gas	= 1.97 LPM	1.97	

Mean native formaldehyde = 27.2 ppm

Started spike which is 19.81 ppm + 27.2(0.7766) = 19.81 + 21.12 = 40.93 ppm in spiked stream

Measured - 49.29 ppm formaldehyde using old reference spectra.

spiked ambient air 32.3 ppm form }
31.2 ppm form } 32.9 avg for ½ hr

Calibration of balance A164428

	measure
100.0 g weight	100.2

VOA vial 25.5 g
after collect 36.1
10.6 for 10 min. 1.06 ml/min from HPLC pump

Ambient moisture measured by FTIR = 4.3%

1.34 LPM / 4.98 = 8.9% + 4.3% = 13.3% theo w/dil ~ 12.7
measuring ~ 18%

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Prepared fresh formaldehyde solution from 10% stock

Added 3.8 g 10% formaldehyde
diluted to ~~1000~~ ~~g~~ 996.2 g

$\frac{3.8g}{996.2g} = 0.0038 \times 10\% = 0.038\%$ 380 µg/mL

$10\% = \frac{10g\ form}{100g\ sol} \times 3.8g\ sol = \frac{0.38g\ formaldehyde}{996.2g\ sol} = 3.81 \times 10^{-4} g$

0.381 mg/mL 381 µg/mL

@ 1 mL/min $\frac{381 \mu g}{14.95 L} \times \frac{\mu mole}{3003 \mu g} \times \frac{2404 \mu l}{\mu mole} = 20.4 \frac{\mu l}{L}$

Measured @ 25.3, 25.4 ppm using old reference spectra

BTEX 1.73 on channel 1 = 2.03 LPM $\frac{14.95}{2.03} = 7.36$ dF

Benzene 97.6 ppm ÷ 7.36 = 13.3 ppm ϕ

Toluene 96.9 ppm ÷ 7.36 = 13.2 ppm $\phi-CH_3$

Ethyl Benzene 96.6 ÷ 7.36 = 13.1 ppm

p-Xylene 97.2 ppm ÷ 7.36 = 13.2 ppm

m-Xylene 96.0 ÷ 7.36 = 13.0 ppm

o-Xylene 96.9 ÷ 7.36 = 13.2 ppm

HPLC pump started only pumping at ½ rate. One head (right one) would not pump. Took off check valves - couldn't make it work. Replaced HPLC pump. Started at 1.0 ml/min measured ~ 0.95 ml/min Adjust to 1.1 ml/min & measured

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1.1 mL/min 90

1.1 mL/min = 9.78 ~~LPM~~ % moisture

Started moisture collection run. FTIR vs. Method 4

Jeff recorded a new formaldehyde reference spectra from the Scott cylinder. Concentration = 4.70 ppm

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7/13/94 FTIR Formaldehyde Validation

acetaldehyde & acrolein std - Channel 1 set @ 1.74 on

MFM measured 2.04 }
2.05 } 2.04
2.04 }

Collected Formaldehyde samples M301-713-1B
M301-713-2B
for beginning of run

Gas flowrate = 14.62 LPM water 1.336 Lpm gas

Formaldehyde @ 370 ug/mL solution = 20.3 ppm In blue recalculated from recert of cylinder

Acetaldehyde 55.4 Recert 48.0 $\frac{14.62}{2.04}$ = 7.1667 $\frac{55.4}{7.17}$ = 7.73 ppm 6.70

Acrolein 55.2 55.2/7.17 = 7.70 ppm

Initial check of spiking w/ spiked ambient air

	Calculated conc(ppm)	Measured Conc(ppm)				mean of 4	Rec
Formaldehyde	20.3	23.4	24.95	21.75	24.0	23.5/20.3	116%
Acetaldehyde	7.73	6.46	6.60	6.41	6.58	6.51/7.73	84%
Acrolein	7.70	8.42	8.36	8.37	8.31	8.37/7.70	109%

Stack gas

formaldehyde	20.8	19.9	19.5	19.47	19.9 ± 0.61
acetaldehyde	2.70	2.79	3.26	3.38	
acrolein	-4.7	-4.99	-5.10	-4.93	

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Recorded by L Olofe Date 7/13/94

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Values in blue pen are derived from updated FTIR methods & are used in 301 Calculation

Started spiking @ 11:13 Am

aldehyde flow 2.04
water (gas) flow 1.34
3.38

$\frac{3.38}{14.62}$ = 0.231 dF = 0.769

Native formaldehyde = 19.5 ~~*~~ X 0.231 = 4.49 19.5 − 4.49 = 15.0 ppm native

20.3 spike + 15.0 native = 35.3 total

Measured $\frac{38.86 \text{ ppm}}{35.31}$ = 110% second $\frac{39.38}{35.31}$ = 112%

Unspiked acetal 3.87
acrolein 1.99

From data pair #1 above

Bias = Mean spiked − Mean unspiked − Calculated spikes

B = 39.1 − 15.0 − 20.3 Measured acetal 9.82
acrolein

B = 3.82 ppm

Run #2 native = 18.64 form acet 2.78 acro −5.84

formaldehyde 18.64 × 0.769 (dil fact) = 14.33

14.33 + 20.3 spike = 34.63 theoretical formaldehyde

acetaldehyde
2.78 × 0.769 = 2.14 + 7.73 = 9.87 ppm
3.28

acrolein
−5.84 × 0.769 = −4.49 + 7.70 = 3.21 ppm
1.16

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Measured	(ppm)	Calc.	% Recovery
Formaldehyde	36.62	34.63	106
Acetaldehyde	9.19 9.69	9.87	
Acrolein	5.17	3.21	

discharge pressure increased during run # 2 390 psig → 412 psig opened valve to let off some of pressure. ~~Bo~~ Pressure reduced to during [illegible] for run #3

Run #3

	(ppm)	(0.769) ppm from % in spiked		Total in Spiked Spiked measured	[illegible] spiked calculated
Formaldehyde	20.69	15.91	~~36.24~~	44.58	36.21
acetaldehyde	3.28 3.81	2.52		10.37 10.66	10.25
acrolein	-6.64 1.48	-5.11		4.39 10.36	2.59

Note: Engine #3 tripped off during native measurement on run #3 discharged pressure from ~~440~~ 411 to 306 — Reduced load on the engine.

Run #4

	Native ppm	Native % in spiked	Calculated spike	Measured spike
Formaldehyde	23.28	17.90	38.2	46.9
Acetaldehyde	4.63 5.11	3.56	11.29	11.29 11.77
Acrolein	-5.90 1.76	-4.54	3.16	4.15 10.38

Run #5

Formaldehyde	24.09	18.53	38.83	42.2
Acetaldehyde	4.97 5.47	3.82	~~11.55~~ 11.94	10.95 11.45
Acrolein	-6.24 1.97	-4.80	2.90	4.17 10.21

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(all ppm)

Run #6	Native	(0.769) Calculated Native	Calculated Spiked	Measured Spiked
Formaldehyde	23.35	17.96	38.26	37.20
Acetaldehyde	4.82 5.33	3.71	11.43	10.59 11.10
Acrolein	-6.42 1.85	-4.94	2.76	4.23 10.11

NOx going up slightly - load may be changing some

Run #7				
Formaldehyde	22.66	17.43	37.73	35.37
Acetaldehyde	4.73 5.22	3.64	11.38	9.88 10.38
Acrolein	-6.01 1.93	-4.62	3.08	5.16 10.10

Run #8				
Formaldehyde	19.58	15.06	35.36	39.24
Acetaldehyde	3.55 4.04	2.73	10.46	9.67 10.16
Acrolein	-5.35 1.78	-4.11	3.59	5.07 10.02

Run #9				
Formaldehyde	19.55	15.0	35.33	38.87
Acetaldehyde	3.50 4.0	2.69	10.42	9.91 10.40
Acrolein	-5.22 1.73	-4.01	3.69	5.32 10.59

[illegible] in spreadsheet M301ALD.WQ1

Run #10				
Formaldehyde	19.88	15.29	35.59	36.40
Acetaldehyde	3.18 3.68	2.45	10.18	9.24 9.73
Acrolein	-5.79 1.31	-4.45	3.25	4.76 9.86

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Run #11 Native Measured Spiked

Formal 20.19 15.53

Acetaldehyde 3.42 3.91 2.63 35.83 38.82

Acrolein -5.52 1.85 -4.24 10.36 9.56 10.06

5.46 4.84 10.38

Run #12

35.71

Form 20.04 15.41 ~~41.80~~ LDO

Acet 3.59 4.08 2.76 41.8

Acrolein -5.85 1.75 -4.50 10.49 9.78 10.28

3.20 4.69 10.08

Run #13

Formaldehyde 20.09 15.45 35.75

Acetaldehyde 3.40 3.90 2.61 ~~37.63~~ 37.43

Acrolein -5.67 1.74 -4.36 10.34 9.35 9.86

3.34 4.98 10.15

Run #14 ~~19.87~~ LDO

Form 19.87 15.28 35.58 39.47

Acet 3.36 3.85 2.58 10.31 9.73 10.24

Acrolein -5.32 1.99 -4.09 3.61 5.15 10.07

Run #15

Formaldehyde 19.90 15.30

Acet 3.19 3.78 2.45 35.60 42.71

Acrolein -5.39 1.93 -4.14 10.18 9.50 10.0

3.56 5.04 10.01

Run #16

35.53

Form 19.8 15.23 ~~36.26~~ LDO 39.82

Acet 2.86 3.35 2.20 9.93 9.47 9.96

Acrolein -5.07 1.77 -3.90 3.80 ~~4.81~~ 5.01 10.04

Acetaldehyde Bias -0.68 $SD_1^2 = 0.42$ $SD_{11}^2 = 0.53$ LDO

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Last 12 Runs M301 calcs Formaldehyde (New 301 Method)

$B = 2.85$

$$t = \frac{2.85}{\sqrt{\frac{(2.30)^2+(1.62)^2}{12}}} \quad \sqrt{\frac{5.29+2.62}{12}} = \frac{2.85}{0.812}$$

$3.51 > 2.228$

$= 3.51$ Signif

$$CF = \frac{1}{1+\frac{B}{CS}} \quad \frac{1}{1+\frac{2.85}{20.3}} = 0.877$$

incorrect SD calculated incorrectly see spreadsheet M301AL2.WQ1 for calcs of std dev

$$F = \frac{S_u^2}{S_s^2} \quad \frac{(1.62)^2}{(2.30)^2} = \frac{2.62}{5.29} = 0.495$$

$$SD_{pooled} = \sqrt{\frac{2.62+5.29}{2}} = \sqrt{3.955} = 1.99$$

$$RSD = \left(\frac{1.99}{20.75 \text{ (undiluted)}}\right) = 9.58\%$$

$$RSD = \left(\frac{1.99}{15.96 \text{ diluted}}\right) = 12.5\%$$

Corrected:

$$F = \frac{S_u^2}{S_s^2} \quad \frac{(0.923)^2}{(2.371)^2} \quad \frac{0.852}{5.622} = 0.152$$

$$SD_{pooled} = \sqrt{\frac{0.852+5.622}{2}} = 1.80$$

$$RSD = \frac{1.80}{20.75} = 0.0867 = 8.7\%$$

EPA old spreadsheet Formeold.wq1 EPA New Spreadsheet Formenew.WQ1

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Last 12 Runs M301 calcs for Acetaldehyde (New 301 Method)

$B = S_m - M_m - CS$ $B = 9.80 - 2.86 - 7.73$

$B = -0.79$

$$t = \frac{|B|}{\sqrt{\frac{SD_s^2 + SD_m^2}{12}}} = \frac{0.79}{\sqrt{\frac{0.25 + 0.50}{12}}} = \frac{0.79}{0.25} = 3.15$$

$3.15 > 2.228$

$$CF = \frac{1}{1 + \frac{B}{CS}} \quad \frac{1}{1 + \frac{0.79}{7.73}} = 0.907 \quad F = \frac{0.5}{0.25} = 2$$

$$SD_{pooled\,\cancel{F}\,H_2O} = \sqrt{\frac{0.25 + 0.50}{2}} = 0.61$$

$$\cancel{H_2O\; SD_{pooled} = \sqrt{0.25 + 0.5}} \quad RSD = \frac{0.61}{3.71} \times 100 = 16.4\%$$

$$SD_{pooled\,(dil)} = \sqrt{\frac{0.29 + 0.25}{2}} = 0.52 \quad RSD = \frac{0.52}{3.71} \times 100 = 14\%$$

The acrolein method was revised to use a stronger, cleaner band for quantitation. This affected the acetaldehyde quantitation. Formaldehyde was not affected. The spreadsheet was revised to reflect the new quantitation M301AL2.WQ1 New calcs next two pages

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Revised Acetaldehyde M301 Calculations (New 301)
(Last 12 runs)

$B = S_m - M_m - CS$ M_m = from corrected (for dilution) unspiked

$B = 10.3 - 3.24 - \cancel{7.33}$ 7.73 JRD

$B = -\cancel{0.27}$ RAS -0.67

SD_u^2 = std dev. for uncorrected unspiked sample.

$t = \sqrt{\frac{(0.50)^2 + (0.71)^2}{12}} = \sqrt{\frac{0.7541}{12}}$

$t = \frac{0.27}{\sqrt{0.0628}} = \cancel{4.2994}$ JRD $= 1.077$

t calc using std dev from corrected unspiked sample

$t = \frac{|B|}{\sqrt{\frac{(0.50)^2 + (0.54)^2}{12}}} = \frac{|B|}{\sqrt{\frac{0.5416}{12}}} = \frac{0.27}{0.21} = 1.27$

No need to calculate correction factor - bias not significant in either case.

$F = \frac{S_u^2}{S_s^2} = \frac{0.516}{0.25} = 2.07$ ← with uncorrected unspiked (can use pooled SD_s)

$F = \frac{0.292}{0.25} = 1.17$ (can use pooled SD_s)

See Note p. 43

SD pooled (uncorrected) $= \sqrt{\frac{(0.50)^2 + (0.71)^2}{2}} = 0.614$

SD pooled (corrected) $= \sqrt{\frac{(0.50)^2 + (0.54)^2}{2}} = 0.52$

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See note

$RSD_{uncorrected} = \frac{0.614}{4.22} \times 100$

$= 14.55$

Sm = mean of unspiked uncorrected for di

$RSD_{corrected} = \frac{0.52}{3.24} \times 100$

$= 16.05$

Sm = mean of unspiked corrected for dil

★ Note: F, SD pooled & RSD above are incorrect due to the way the SD of differences were calculated.
See spreadsheet M301KL2.WQ1 for std. dev calcs

$F = \frac{S_u^2}{S_s^2}$ ~~$(0.54)^2$~~ LAD $\frac{(0.38)^2}{(0.26)^2} = \frac{0.144}{0.068} = 2.13$

(Can use pooled SD)

$SD_{pooled} = \sqrt{\frac{0.144 + 0.068}{2}} = \sqrt{0.106} = 0.326$

$RSD = \frac{0.326}{4.22} \times 100 = 7.72\%$

EPA "old" M301 Spreadsheet ACETEOLD.WQ1

EPA "new" M301 Spreadsheet ACETENEW.WQ1

Witnessed & Understood by me,

Date

Invented by

Recorded by

Date 7/13/94

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Acrolein Method 301 Calculations (Revised Method 301)
(Last 12 runs)

$B = S_m - M_m - CS$

M_m = Corrected ~~spikes~~ unspiked (LAO)
(corrected for dilution)

$B = 10.14 - 1.38 - 7.70$

$B = 1.06$

t_u = uncorrected for dilution

$$t_u = \frac{1.06}{\sqrt{\frac{(0.19)^2 + (0.18)^2}{12}}} = \frac{1.06}{\sqrt{\frac{0.036 + 0.0324}{12}}} = \sqrt{0.0057}$$

$$t_u = \frac{1.06}{0.076 \; \cancel{3.249 \times 10^{-7}} \text{ LAO}} = 13.64$$ (significant)

t_c = Corrected for dilution

$$t_c = \frac{1.06}{\sqrt{\frac{(0.19)^2 + (0.14)^2}{12}}} = \frac{1.06}{\sqrt{0.036 + 0.0196}} = \sqrt{0.0046}$$

$$t_c = \frac{1.06}{0.0681} = 15.6$$ (significant)

$$CF_\mu = \frac{1}{1 + \frac{1.06}{7.70}} = 0.879$$

see spreadsheet

$$F = \frac{s_u^2}{s_s^2} = \frac{(0.16)^2}{(0.232)^2} = \frac{0.0256}{0.0538} = 0.4756$$ (can pool SDs)

$$S_{pooled} = \sqrt{\frac{0.0256 + 0.0538}{2}} = 0.199$$

$$RSD = \frac{0.199}{1.80} \times 100 = 11.1\%$$

Calculated w/ EPA M301 "old" spreadsheet ACROEOLC

"new" spreadsheet ACROENEW.WQ1

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Witnessed & Understood by me.	Date	Invented by	Date 7/13/94
		Recorded by L A Ogle	

TITLE

Project No.
Book No. 28805

RADIAN CORPORATION

From Page No.

7/14/94

Run 1 9:32:48 Start time for first criteria pollutant & H_2O validation run

Run 2 11:11:00 start time

Run 3 13:04 " "

Run 4 14:36 " "

Run 5 16 ~~18~~:03 " " After Run 5 the load on the engine was increased (increased suction pressure)

Run 6 ~~18~~ 17 ~~19~~:42 " "

Run 7 19:22 " "

Run 8 20:48 " "

Run 9 22:09 " "

CO	Spreadsheet	COENEW.WQ1
CO_2	"	CO2ENEW.WQ1
NO_x	"	NOXENEW.WQ1
H_2O	"	H2OENEW.WQ1

Witnessed & Understood by me, Date

Invented by

Recorded by Date 7/14/94

To Page No.

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"OLD" EPA 301 Calculations (Spreadsheets)

CO Spreadsheet = COEOLD.WQ1

CO_2 " = CO2EOLD.WQ1

NO_x " = NOXEOLD.WQ1

H_2O " = H2OEOLD.WQ1

To Page No.

Witnessed & Understood by me.	Date	Invented by Recorded by	Date 7/14/94

Criteria Pollutant Validation

* approximate w/ NO_2

Run	CO		CO_2		NOx		Water		THC	
	CEM	FTIR	CEM	FTIR	CEM	FTIR	M4	FTIR	CEM	F
1	103.1	103.6	4.17	4.22	447.6	443.5*	9.52	9.55	992.8	
2	103.3	102.2	4.24	4.23	518.9	485.0*	10.50	9.43	847.7	
3	103.3	98.8	4.22	4.22	539.0	515*	10.2	9.26	844.6	
4	103.1	97.3	4.20	4.22	567.0	536*	10.1	9.24	839.7	
5	103.9	96.6	4.17	4.19	506.3	467*	10.6	9.38	849.6	
Changed load on engine (higher load)										
6	101.6	95.1	4.27	4.33	768.4	712*	10.1	9.55	832.3	
7	103.0	106.1	429	4.46	764.2	763*	10.4	10.3	849.9	
8	100.8	104.1	4.25	4.42	724.9	721*	9.93	9.99	834.2	
9	99.6	107.1	4.24	4.42	663.1	669	10.95	10.0	807.8	

Critical t value for 9 runs = 1.397

Mean of NOx CEM measurement = 611.04

RSD = 2.16%
(RSD of validated CEM method)

$RSD = \frac{SD}{mean} \times 100$ $SD = \frac{RSD \times mean}{100}$

$SD = \frac{2.16 \times 611.04}{100} = 13.2$

Witnessed & Understood by me.

Date 7/14/94

Invented by

Recorded by

Date

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Channel 1 set @ 1.50 Measured 1.78 & 1.78

Channel 2 set @ 1.77 Measured 2.06

Project # 58085

Formaldehyde cylinder # ALM041182 4.7ppm

from Scott Gases, Plumsteadville, PA (215)-766-8861

Quantitation for certification - Certified master gas

±2% of analysis -

Blend tolerance ± 10%

Impinger method 2,4-DNPH in acetonitrile - Direct HPLC injection for quantitation.

Permeation devices used to put formaldehyde in cylinder.

(215) 766-8861 Ken Wong

FINAL FORMALDEHYDE CONCENTRATIONS FOR CALCULATIONS (FROM FORMALIN SOLUTION ANALYSIS)

Pretest	A	360 ug/mL	Post test	A	420 ug/mL
	B	360		B	390
	C	390		C	370
				D	380

Mean of all formalin analyses = 380 ug/mL

See page 54.

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Cylinder No. CC119231
C.G.A. Valve 350
Order # 2369488 Date 7-7-94
Pressure: 150 PSIA Volume 10.65 FT^3

O-Xylene	97.1 ppm
M-Xylene	96.2 ppm
P-Xylene	97.9 ppm
Ethyl Benzene	96.8 ppm
Toluene	97.0 ppm
Benzene	97.7 ppm
Nitrogen	Balance

H. P. Gas Products, Inc.
4428 Shell Dock Road
Baytown, TX 77520
Phone (713) 383-7236
Fax No. (713) 573-9267

Cylinder No. CC107397
C.G.A. Valve 350
Order # 2369488 Date 7-7-94
Pressure: 150 PSIA Volume: 10.65 FT^3

O-Xylene	96.9 ppm
M-Xylene	96.0 ppm
P-Xylene	97.2 ppm
Ethyl Benzene	96.6 ppm
Toluene	96.9 ppm
Benzene	97.6 ppm
Nitrogen	Balance

H. P. Gas Products, Inc.
4428 Shell Dock Road
Baytown, TX 77520
Phone (713) 383-7236
Fax No. (713) 573-9267

Cylinder No. CC13019
C.G.A. Valve 350
Order # 2369488 Date 7-7-94
Pressure: 150 PSIA Volume 10.65 FT^3

O-Xylene	96.4 ppm
M-Xylene	95.5 ppm
P-Xylene	96.7 ppm
Ethyl Benzene	96.1 ppm
Toluene	96.4 ppm
Benzene	97.0 ppm
Nitrogen	Balance

H. P. Gas Products, Inc.
4428 Shell Dock Road
Baytown, TX 77520
Phone (713) 383-7236
Fax No. (713) 573-9267

Witnessed & Understood by me,	Date	Invented by	Date 7/15/94
		Recorded by L D Ogle	

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RADIAN CORPORATION Project No.____ Book No 28805 TITLE ____

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Using information on p. $\overset{35}{\cancel{29}}$ ADD developed during validation and average concentration of formaldehyde of 380 µg/mL$^{p(52)}$, we calculate the formaldehyde spike level at:

$$380\,\mu g/mL \times \frac{1\,mL}{min} = \frac{380\,\mu g}{min} \times \frac{1\,\mu mole}{30.03\,\mu g} \times \frac{24.04\,\mu L}{\mu mole} = \frac{304.2\,\mu g}{min}$$

$$\frac{304.2\,\frac{\mu L\ \cancel{\mu g}}{min}\ \text{formaldehyde}}{14.62\ \frac{\text{liters gas}}{min}} = 20.8\ \frac{\mu L}{L}\ \text{formaldehyde}$$

To Page No.____

Witnessed & Understood by me.	Date	Invented by	Date
		Recorded by	7/27/94

APPENDIX E.5

Certification Sheets

Scott Specialty Gases, Inc.

Shipped From: 3714 LAPAS DRIVE
HOUSTON TX 77023
Phone: 713-644-4820 Fax: 713-644-0244

CERTIFICATE OF ANALYSIS

RADIAN CORPORATION
HOWARD GOAD
15508 BRATTON LANE

AUSTIN TX 78728

PROJECT #: 04-26842-003
PO#: 222483
ITEM #: 0402A2004924AL
DATE: 10/04/93

CYLINDER #: AAL18772
FILL PRESSURE: 2000 PSI
BLEND TYPE : CERTIFIED MASTER GAS

ANALYTICAL ACCURACY: +/- 2%
PRODUCT EXPIRATION: 10/02/94

COMPONENT	REQUESTED GAS CONC MOLES		ANALYSIS (MOLES)	
ACROLEIN	50.	PPM	50.	PPM
NITROGEN		BAL		BAL

ANALYST: Laurence Bledsoe APPROVED BY:

PLUMSTEADVILLE, PENNSYLVANIA / TROY, MICHIGAN · HOUSTON, TEXAS / DURHAM, NORTH CAROLINA
SOUTH PLAINFIELD, NEW JERSEY FREMONT, CALIFORNIA WAKEFIELD, MASSACHUSETTS / LONGMONT, COLORADO

Scott Specialty Gases, Inc.

Shipped From:
3714 LAPAS DRIVE
HOUSTON TX 77023
Phone: 713-644-4820
Fax: 713-644-0244

CERTIFICATE OF ANALYSIS

RADIAN CORPORATION
HOWARD GOAD
15508 BRATTON LANE

AUSTIN TX 78728

PROJECT #: 04-26842-002
PO#: 222483
ITEM #: 04020222 4AL
DATE: 10/04/93

CYLINDER #: AAL13957
FILL PRESSURE: 2000 PSI
BLEND TYPE : CERTIFIED MASTER GAS
ANALYTICAL ACCURACY: +/- 2%
PRODUCT EXPIRATION: 9/30/94

COMPONENT	REQUESTED GAS CONC MOLES	ANALYSIS (MOLES)
ACETALDEHYDE	50. PPM	50. PPM
NITROGEN	BAL	BAL

ANALYST: Lawrence Bledsoe

APPROVED BY:

Scott Specialty Gases, Inc.

Shipped From: 6141 EASTON ROAD
PLUMSTEADVILLE PA 18949-0310
Phone: 215-766-8861
PO BOX 310
Fax: 215-766-2070

CERTIFICATE OF ANALYSIS

RADIAN CORPORATION
ROHLACK/MCDONALD
8501 MOPAC BOULEVARD

AUSTIN TX 78759

PROJECT #: 01-57645-002
PO#: 234945
ITEM #: 0102A3014814AL
DATE: 6/15/94

CYLINDER #: ALM041267

ANALYTICAL ACCURACY: +/- 2%

BLEND TYPE : CERTIFIED MASTER GAS

COMPONENT	REQUESTED GAS CONC MOLES		ANALYSIS (MOLES)	
ACETALDEHYDE	50.	PPM	55.4	PPM
ACROLEIN	50.	PPM	55.2	PPM
NITROGEN		BAL		BAL

ANALYTICAL METHOD: G.C. F.I.D.

ANALYST:
RENE J. BEDOYA

Scott Specialty Gases, Inc.

Shipped From:
6141 EASTON ROAD
PLUMSTEADVILLE PA 18949-0310
PO BOX 310
Phone: 215-766-8861
Fax: 215-766-2070

CERTIFICATE OF ANALYSIS

RADIAN CORPORATION

C/O COLUMBIA GAS TRANS
1258 HURRICANE ROAD
PIKEVILLE KY 41501

PROJECT #: 01-58085-001
PO#: 234292
ITEM #: 0102F2002204AL
DATE: 7/06/94

CYLINDER #: ALM041182

BLEND TYPE : CERTIFIED MASTER GAS

ANALYTICAL ACCURACY: +/-10%
PRODUCT EXPIRATION: 1/06/95

COMPONENT	REQUESTED GAS CONC MOLES		ANALYSIS (MOLES)	
FORMALDEHYDE	5.	PPM	4.7	PPM
NITROGEN		BAL		BAL

ANALYST: for K.W.
KEN WONG

H.P. Gas Products, Inc.

MAILING ADDRESS
P.O. Box 2074, Baytown, TX 77522-2074

LOCATION
4428 Shell Dock Rd., Baytown, TX 77520

Phone: (713) 383-7236 • Fax: (713) 383-7237

CERTIFIED GAS STANDARD FOR INSTURMENT CALIBRATION (+OR- 2%)

CYLINDER NUMBER: A8415

COMPONENT:	CONCENTRATION: (MOLE %)
Carbon Monoxide	99.7 ppm
Nitrogen	Balance

* 6 MONTH SHELF LIFE FROM DATE OF MANUFACTURE.

MAKE DATE: 06-09-94
EXP. DATE: 12-09-94

Becky Vasquez
APPROVAL

H.P. Gas Products, Inc.

MAILING ADDRESS
P.O. Box 2074, Baytown, TX 77522-2074

LOCATION
4428 Shell Dock Rd., Baytown, TX 77520

Phone: (713) 383-7236 • Fax: (713) 383-7237

CERTIFIED GAS STANDARD FOR INSTURMENT CALIBRATION (+OR- 2%)

CYLINDER NUMBER: GG7324

COMPONENT:	CONCENTRATION: (MOLE %)
Ethylene	100.0 ppm
Nitrogen	Balance

* 6 MONTH SHELF LIFE FROM DATE OF MANUFACTURE.

MAKE DATE: 06-09-94
EXP. DATE: 12-09-94

Becky Vasquez
APPROVAL

H.P. Gas Products, Inc.

MAILING ADDRESS
P.O. BOX 2074, BAYTOWN, TX 77522-2074

LOCATION
4428 SHELL DOCK RD., BAYTOWN, TX 77520

PHONE: (713) 383-7236 • FAX: (713) 383-7237

CERTIFIED GAS STANDARD FOR INSTURMENT CALIBRATION (+OR- 2%)

CYLINDER NUMBER: GG2091

COMPONENT:	CONCENTRATION: (MOLE %)
Nitric Oxide	506 ppm
Nitrogen	Balance
Nitrogen Dioxide	3 ppm

* 6 MONTH SHELF LIFE FROM DATE OF MANUFACTURE.

MAKE DATE: 06-09-94
EXP. DATE: 12-09-94

Becky Vasquez
APPROVAL

H.P. Gas Products, Inc.

MAILING ADDRESS
P.O. Box 2074, Baytown, TX 77522-2074

LOCATION
4428 Shell Dock Rd., Baytown, TX 77520

Phone: (713) 383-7236 • Fax: (713) 383-7237

CERTIFIED GAS STANDARD FOR INSTRUMENT CALIBRATION (+OR- 2%)

CYLINDER NUMBER: CC25449

COMPONENT:	CONCENTRATION: (MOLE %)
Nitric Oxide	1978 ppm
Nitrogen	Balance
Nitrogen Dioxide	27 ppm

* 12 MONTH SHELF LIFE FROM DATE OF MANUFACTURE.

MAKE DATE: 05-26-94
EXP. DATE: 05-26-95

Becky Vasquez
APPROVAL

Scott Specialty Gases, Inc.

ipped 1750 EAST CLUB BLVD.
om: DURHAM NC 27704
Phone: 919-220-0803 Fax: 919-220-0808

CERTIFICATE OF ANALYSIS

ADIAN CORPORATION
300 PERIMETER PARK
ORRISVILLE NC 27560

PROJECT #: 12-05412-010
PO#: 222409
ITEM #: 12024520 4AL
DATE:10/11/93

CYLINDER #: AAL13097 ANALYTICAL ACCURACY: +/-2%

BLEND TYPE : CERTIFIED MASTER GAS

OMPONENT	REQUESTED GAS CONC MOLES		ANALYSIS (MOLES)	
ARBON DIOXIDE	3.5	PCT	3.49	PCT
ARBON MONOXIDE	500.	PPM	500.	PPM
YGEN	3.	PCT	3.00	PCT
ITROGEN		BAL		BAL

NALYST: J. ERNST APPROVED BY: Alan Barber
A. BARBER

Scott Specialty Gases, Inc.

Shipped From: 1750 EAST CLUB BLVD.
DURHAM NC 27704
Phone: 919-220-0803
Fax: 919-220-0808

CERTIFICATE OF ANALYSIS

RADIAN CORPORATION
900 PERIMETER PARK
MORRISVILLE NC 27560

PROJECT #: 12-05412-005
PO#: 222409
ITEM #: 12024520 4AL
DATE:10/11/93

CYLINDER #: ALM039911

ANALYTICAL ACCURACY: +/-2%

BLEND TYPE : CERTIFIED MASTER GAS

COMPONENT	REQUESTED GAS CONC MOLES		ANALYSIS (MOLES)	
CARBON DIOXIDE	18.	PCT	17.97	PCT
CARBON MONOXIDE	2.	PCT	2.00	PCT
OXYGEN	20.9	PCT	20.9	PCT
NITROGEN		BAL		BAL

ANALYST: J. ERNST

APPROVED BY: Alan Barber
A. BARBER

APPENDIX F

EXTRACTIVE FTIR PROTOCOL

See Appendix B--FTIR Test Protocol (Addendum)

APPENDIX G

METHOD 301 SPREADSHEET PRINTOUTS

VALIDATION OF FTIR FOR THE ANALYSIS OF FORMALDEHYDE

ANALYTE SPIKING: QUAD TRAINS

FEDERAL REGISTER CALCULATION METHOD

ENTER VALUE OF SPIKED LEVEL (CS)= 20.800

Dilution Factor for Unspiked Samples = 0.769

ENTER SPIKED AND UNSPIKED CONCENTRATIONS (COMPARABLE UNITS ASSUMED)

CONCENTRATION IN PPM (WET)

	SPIKED SAMPLES		UNSPIKED SAMPLES					
RUN #	A	B	C	D	A-B	(A-B)^2	C-D	(C-D)^2
1	42.15	37.16	24.01	23.27	4.99	24.90	0.74	0.55
2	35.29	39.76	22.58	19.50	-4.47	19.98	3.08	9.49
3	38.79	36.28	19.47	19.80	2.51	6.30	-0.33	0.11
4	38.74	41.74	20.11	19.96	-3.00	9.00	0.15	0.02
5	37.35	39.38	20.02	19.78	-2.03	4.12	0.24	0.06
6	42.62	39.74	19.83	19.71	2.88	8.29	0.12	0.01

AVERAGE: Sm= 39.08 Mm= 20.67

STANDARD DEVIATION:

SPIKED SDs= 2.46

UNSPIKED SDu= 0.92

RELATIVE STD RSDs= 6.3% (acceptable)

RELATIVE STD RSDu= 4.5% (acceptable)

BIAS:

Corrected Unspiked Conc = 15.90

B= 2.388

STD OF MEAN SDm= 2.627

t-VALUE= 0.909

CRITICAL t-VALUE= 2.201
(n=12, alpha=95%)

Bias not statistically significant, CF not needed.

VALIDATION OF FTIR FOR THE ANALYSIS OF ACETALDEHYDE

ANALYTE SPIKING: QUAD TRAINS

FEDERAL REGISTER CALCULATION METHOD

ENTER VALUE OF SPIKED LEVEL (CS)= 6.700

Dilution Factor for Unspiked Samples = 0.769

ENTER SPIKED AND UNSPIKED CONCENTRATIONS (COMPARABLE UNITS ASSUMED)

CONCENTRATION IN PPM (WET)

	SPIKED SAMPLES		UNSPIKED SAMPLES					
RUN #	A	B	C	D	A-B	(A-B)^2	C-D	(C-D)^2
1	11.45	11.10	5.47	5.33	0.35	0.12	0.14	0.02
2	10.38	10.16	5.22	4.04	0.22	0.05	1.18	1.39
3	10.40	9.73	4.00	3.68	0.67	0.45	0.32	0.10
4	10.06	10.28	3.91	4.08	-0.22	0.05	-0.17	0.03
5	9.86	10.24	3.90	3.85	-0.38	0.14	0.05	0.00
6	10.00	9.96	3.78	3.35	0.04	0.00	0.43	0.18

AVERAGE: Sm= 10.30 Mm= 4.22

STANDARD DEVIATION:

SPIKED SDs= 0.26

UNSPIKED SDu= 0.38

RELATIVE STD RSDs= 2.5% (acceptable)

RELATIVE STD RSDu= 9.0% (acceptable)

BIAS:

Corrected Unspiked Conc = 3.24

B= 0.358

STD OF MEAN SDm= 0.461

t-VALUE= 0.778

CRITICAL t-VALUE= 2.201
(n=12, alpha=95%)

Bias not statistically significant, CF not needed.

VALIDATION OF FTIR FOR THE ANALYSIS OF ACROLEIN

NOTE: CORRECTED FOR 23.7% DIFFERENCE BETWEEN MEASURED AND CYLINDER
ANALYTE SPIKING: QUAD TRAINS
FEDERAL REGISTER CALCULATION METHOD
ENTER VALUE OF SPIKED LEVEL (CS)= 7.700
Dilution Factor for Unspiked Samples = 0.769
ENTER SPIKED AND UNSPIKED CONCENTRATIONS (COMPARABLE UNITS ASSUMED)

CONCENTRATION IN PPM (WET)

	SPIKED SAMPLES		UNSPIKED SAMPLES					
RUN #	A	B	C	D	A-B	(A-B)^2	C-D	(C-D)^2
1	7.79	7.71	1.50	1.41	0.08	0.01	0.09	0.01
2	7.71	7.65	1.47	1.36	0.06	0.00	0.11	0.01
3	8.80	7.52	1.32	1.00	1.28	1.64	0.32	0.10
4	7.92	7.69	1.41	1.34	0.23	0.05	0.07	0.00
5	7.74	7.68	1.33	1.52	0.06	0.00	-0.19	0.04
6	7.64	7.66	1.47	1.35	-0.02	0.00	0.12	0.01

AVERAGE: Sm= 7.79 Mm= 1.37

STANDARD DEVIATION:

SPIKED SDs= 0.38

UNSPIKED SDu= 0.12

RELATIVE STD RSDs= 4.8% (acceptable)

RELATIVE STD RSDu= 8.9% (acceptable)

BIAS:

Corrected Unspiked Conc = 1.06
B= -0.964

STD OF MEAN SDm= 0.396

t-VALUE= 2.432

CRITICAL t-VALUE= 2.201
(n=12, alpha=95%)

Bias is statistically significant

CORRECTION FACTOR= 1.143 (Acceptable)

VALIDATION OF NOx BY COMPARISON OF FTIR TO CEM

METHOD COMPARISON: PAIRED TRAIN SPREADSHEET

FEDERAL REGISTER METHOD OF CALCULATION

ENTER STANDARD DEVIATION OF VALIDATED METHOD: 13.20

Standard Deviation of Validated Method based on 2.16% RSD of 611.08 ppm

ENTER SAMPLE CONCENTRATIONS (ASSUMED TO BE IN COMPARABLE UNITS)

CONCENTRATION IN PPM ON A DRY BASIS

RUN #	PROPOSED	VALIDATED	DI(V-P)	DI^2
1	446.76	447.94	1.18	1.39
2	492.92	520.17	27.25	742.56
3	519.4	538.31	18.91	357.59
4	543.7	566.99	23.29	542.42
5	474.12	506.61	32.49	1055.60
6	724.36	768.43	44.07	1942.16
7	773.39	763.77	-9.62	92.54
8	724.91	724.54	-0.37	0.14
9	681.21	662.93	-18.28	334.16
AVERAGE:	597.86	611.08	13.21	563.17
TOTAL:	5380.77	5499.69	118.92	5068.5718
COUNT:			9	

STANDARD DEVIATION:

DIFFERENCE (SDd)= 20.91 corrected error in formula

PROPOSED (SDp)= 7.708 added @if statement

VARIANCE:

PROPOSED METHOD (Sp^2)= 59.417

VALIDATED METHOD (Sv^2)= 174.240

Proposed Variance Acceptable
(F-Factor=1.0)

BIAS:

t-VALUE= 1.896

CRITICAL t-VALUE= 1.397
(n=9,alpha=80%)

Bias Statistically Significant

CORRECTION FACTOR (CF)= 1.022 (acceptable)

VALIDATION OF CO BY COMPARISON OF FTIR TO CEM

METHOD COMPARISON: PAIRED TRAIN SPREADSHEET

FEDERAL REGISTER METHOD OF CALCULATION

ENTER STANDARD DEVIATION OF VALIDATED METHOD: 10.00

Standard Deviation of Validated Method Assumed to be 2% of Span

ENTER SAMPLE CONCENTRATIONS (ASSUMED TO BE IN COMPARABLE UNITS)

CONCENTRATION IN PPM ON A DRY BASIS

RUN #	PROPOSED	VALIDATED	DI(V-P)	DI^2
1	106.51	103.14	-3.37	11.36
2	103.51	103.27	-0.24	0.06
3	103.01	103.32	0.31	0.10
4	101.66	103.1	1.44	2.07
5	101.07	103.91	2.84	8.07
6	99.38	101.55	2.17	4.71
7	109.17	102.99	-6.18	38.19
8	106.8	100.08	-6.72	45.16
9	111.76	99.6	-12.16	147.87
AVERAGE:	104.76	102.33	-2.43	28.62
TOTAL:	942.87	920.96	-21.91	257.5751
COUNT:			9	

STANDARD DEVIATION:

DIFFERENCE (SDd)= 5.05 corrected error in formula

PROPOSED (SDp)= 3.573322336 added @if statement

VARIANCE:

PROPOSED METHOD (Sp^2)= 12.769

VALIDATED METHOD (Sv^2)= 100.000

Proposed Variance Acceptable
(F-Factor=1.0)

BIAS:

t-VALUE= 1.445

CRITICAL t-VALUE= 1.397
(n=9,alpha=80%)

Bias Statistically Significant

CORRECTION FACTOR (CF)= 0.976 (acceptable)

VALIDATION OF CO2 BY COMPARISON OF FTIR TO CEM

METHOD COMPARISON: PAIRED TRAIN SPREADSHEET
FEDERAL REGISTER METHOD OF CALCULATION
ENTER STANDARD DEVIATION OF VALIDATED METHOD: 0.11

ENTER SAMPLE CONCENTRATIONS (ASSUMED TO BE IN COMPARABLE UNITS)

CONCENTRATION IN PERCENT ON A DRY BASIS

RUN #	PROPOSED	VALIDATED	DI(V-P)	DI^2
1	4.22	4.17	-0.05	0.00
2	4.29	4.24	-0.05	0.00
3	4.26	4.22	-0.04	0.00
4	4.26	4.2	-0.06	0.00
5	4.24	4.17	-0.07	0.00
6	4.36	4.27	-0.09	0.01
7	4.47	4.29	-0.18	0.03
8	4.41	4.25	-0.16	0.03
9	4.47	4.24	-0.23	0.05
AVERAGE:	4.33	4.23	-0.10	0.01
TOTAL:	38.98	38.05	-0.93	0.1341
COUNT:			9	

STANDARD DEVIATION:

DIFFERENCE (SDd)=	0.07	corrected error in formula
PROPOSED (SDp)=	0.048741332	added @if statement

VARIANCE:

PROPOSED METHOD (Sp^2)=	0.002
VALIDATED METHOD (Sv^2)=	0.012

Proposed Variance Acceptable
(F-Factor=1.0)

BIAS:

t-VALUE=	4.498
CRITICAL t-VALUE= (n=9,alpha=80%)	1.397

Bias Statistically Significant

CORRECTION FACTOR (CF)= 0.976 (acceptable)

VALIDATION OF WATER BY COMPARISON OF FTIR TO CEM

METHOD COMPARISON: PAIRED TRAIN SPREADSHEET

FEDERAL REGISTER METHOD OF CALCULATION

ENTER STANDARD DEVIATION OF VALIDATED METHOD: 0.23

ENTER SAMPLE CONCENTRATIONS (ASSUMED TO BE IN COMPARABLE UNITS)

	CONCENTRATION IN PERCENT			
RUN #	PROPOSED	VALIDATED	DI(V-P)	DI^2
1	9.55	9.63	0.08	0.01
2	10.37	10.6	0.23	0.05
3	10.07	10.2	0.13	0.02
4	10.13	10.1	-0.03	0.00
5	10.32	10.6	0.28	0.08
6	10.58	10.1	-0.48	0.23
7	10.24	10.4	0.16	0.03
8	9.99	9.9	-0.09	0.01
9	10.02	11	0.98	0.96
AVERAGE:	10.14	10.28	0.14	0.15
TOTAL:	91.27	92.53	1.26	1.380
COUNT:			9	

STANDARD DEVIATION:

DIFFERENCE (SDd)=	0.39	corrected error in formula
PROPOSED (SDp)=	0.158	added @if statement

VARIANCE:

PROPOSED METHOD (Sp^2)=	0.025
VALIDATED METHOD (Sv^2)=	0.053

Proposed Variance Acceptable
(F-Factor=1.0)

BIAS:

t-VALUE=	1.083
CRITICAL t-VALUE= (n=9,alpha=80%)	1.397

Bias Not Statistically Significant, CF not needed.

APPENDIX H

DRAFT REVISED METHOD 301

Received
7/7/94

OPTIONAL FORM 99 (7-90)

FAX TRANSMITTAL

	# of pages ► 13
To Phyllis O'Hara	From Gary McAlister
Dept./Agency	Phone # 541-1062
Fax # 460-1631	Fax # 541-1039

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DRAFT

* * * * *

6. CALCULATIONS

Data resulting from the procedures specified in Section 5.0 shall be treated as follows to determine bias, correction factors, RSDs, precision, and data acceptance.

6.1 Isotopic Spiking. Analyze the data for isotopic spiking tests as outlined in Sections 6.1.1 through 6.1.3.

6.1.1 Bias Analysis.

6.1.1.1 Bias. Calculate the numerical value of the bias using the results from the analysis of the isotopically spiked field samples and the calculated value of the isotopically labeled spike:

$$B = S_m - CS \qquad \text{Eq. 301-1}$$

where:

B = Bias at the spike level.

S_m = Mean of the measured values of the isotopically spiked samples.

CS = Calculated value of the isotopically labeled spike.

6.1.1.2 t-Test. Test the bias for statistical significance by calculating the t-statistic using Equation 301-2. Use the standard deviation determined in Section 6.1.3.1.

$$t = \frac{|B|}{\frac{SD_s}{\sqrt{n}}} \qquad \text{Eq. 301-2}$$

Compare the calculated t-value with the critical value of the two-sided t-distribution at the 95-percent confidence level and n-1 degrees of freedom. This critical value is 2.201 for the eleven degrees of freedom when the procedure specified in Section 5.1.2 is followed. If the calculated t-value is greater than the critical value, the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.1.2 Calculation of a Correction Factor. If the t-test does not show that the bias is statistically significant, use all analytical results without correction and proceed to the precision evaluation. If the method's bias is statistically significant, calculate the correction factor, CF, using the following equation:

$$CF = \frac{1}{1 + \frac{B}{CS}} \qquad \text{Eq. 301-4}$$

301-3

If the CF is outside the range of 0.70 to 1.30, the data and method are considered unacceptable. For correction factors within the range, multiply all analytical results by the CF to obtain the final values.

6.1.3 Precision

6.1.3.1 Standard Deviation. Calculate the standard deviation of the S_i values as follows:

$$SD = \sqrt{\frac{\sum (S_i - S_n)^2}{(n-1)}} \qquad \text{Eq. 301-4}$$

where:

S_i = Measured value of the isotopically labeled analyte in the i-th field sample,

n = Number of isotopically spiked samples, 12.

6.1.3.2 RSD. Calculate the RSD as follows:

$$RSD = \left(\frac{SD_s}{S_m}\right) \times 100 \qquad \text{Eq. 301-5}$$

where S_m is the measured mean of the isotopically labeled spiked samples. The data and proposed method are unacceptable if the RSD is greater than 50 percent.

6.2 Comparison with Validated Method. Analyze the data for comparison with a validated method as outlined in Sections 6.2.1 or 6.2.2, as appropriate. Conduct these procedures in order to determine if a proposed method produces results equivalent to a validated method. Make all necessary bias corrections for the validated method, as appropriate. If the data from proposed method fail either test, the data and the proposed test method are unacceptable. For highly variable sources, additional precision checks may be necessary. The analyst should consult with the Administrator if a highly variable source is suspected.

6.2.1 Paired Sampling Systems.

6.2.1.1 Bias Analysis.

6.2.1.1.1 Determine the standard deviation, SD_d, of the differences, d_i's, of the paired samples using Equation 301-6.

$$SD_d = \sqrt{\frac{\sum_{i}^{N} (d_i - d_m)^2}{n-1}} \qquad \text{Eq. 301-6}$$

where:

d_i = The difference between the i-th pair of samples.

d_m = The mean of the paired sample differences.

6.2.1.1.2 t-Test. Test the bias for statistical significance by calculating the t-statistic and determine if the mean of the differences between the proposed method and the validated method is significant at the 80-percent confidence level.

Calculate the value of the t-statistic using the following equation:

$$t = \frac{|d_m|}{\frac{SD_d}{\sqrt{n}}} \qquad \text{Eq.301-7}$$

where n is the total number of paired samples. For the procedure in Section 5.2.1, n equals nine. Compare the calculated t-statistic with the corresponding value from the table of the t-statistic. When nine runs are conducted, as specified in Section 5.2.1, the critical value of the t-statistic is 1.397 for eight degrees of freedom. If the calculated t-value is greater than the critical value, the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.2.1.2 Calculation of a Correction Factor. If the statistical test cited above does not show a significant bias with respect to the reference method, assume that the proposed method is unbiased and use all analytical results without correction. If the method's bias is statistically significant, calculate the correction factor, CF, as follows:

$$CF = \frac{1}{1 + \frac{d_m}{V_m}} \qquad \text{Eq. 301-8}$$

where V_m is the mean of the validated method's values. Multiply all analytical results by CF to obtain the final values. The data and the proposed method are unacceptable if the correction factor is outside the range of 0.9 to 1.10.

6.2.1.3 Precision. Compare the variance of the proposed method to that of the validated method. If a significant difference is determined using the F-test, the proposed method and the results are rejected. Proposed methods demonstrating F-values equal to or less than the critical value have acceptable precision. This procedure requires the standard deviation of the validated method, SD_v, to be known. Use the value furnished with the method. If the standard deviation of the validated method is not available, the paired replicate sampling procedure may not be used.

6.2.1.3.1 Calculate the variance of the validated method, S_v^2, using the following equation:

$$S_v^2 = SD_v^2 \qquad \text{Eq. 301-9}$$

where:

SD_v = Standard deviation provided with the validated method.

6.2.1.3.2 Pooled Variance. Calculate the pooled variance of both methods, S^2_{pooled}, as follows:

$$S^2_{pooled} = \frac{\sum_{1}^{N} d_i^2}{2(n-1)} \qquad \text{Eq. 301-9}$$

If the proposed method has a bias, all data points must be multiplied by CF before calculating the d_i's.

6.2.1.3.3 Proposed Method Variance. Calculate the variance of the proposed method, S^2_p, from the S^2_{pooled} using the following equation.

$$S^2_p = 2S^2_{pooled} - SD_v^2 \qquad \text{Eq. 301-10}$$

(If $S^2_v > S^2_{pooled}$, let $S^2_p = S^2_{pooled}/2$).

6.2.1.4 The F-test. Determine if the variance of the proposed method is significantly different from that of the validated method by performing the F-test. Calculate the experimental F-value using the following equation:

$$F = \frac{S_p^2}{S_v^2} \qquad \text{Eq. 301-12}$$

Compare the experimental F value with the critical value of F at a 95% confidence level. The critical value should be less than 4.03 when the procedure specified in section 5.2.1 for paired trains is followed. If the calculated F is greater than the critical value, the difference in precision is significant and the data and proposed method are unacceptable.

6.2.2 Quadruplet Replicate Sampling Systems.

6.2.2.1 Bias Analysis. Test the bias for statistical significance at the 80 percent confidence level by calculating the t-statistic.

6.2.2.1.1 Bias. Determine the bias which is defined as the mean of the differences between the proposed method and the validated method (d_m). The following equation is used to calculate d_i:

$$d_i = \frac{(V_{1_i} + V_{2_i})}{2} - \frac{(P_{1_i} + P_{2_i})}{2} \qquad \text{Eq. 301-12}$$

and:

V_{1i} = First measured value with the validated method in the i-th sample.

V_{2i} = Second measured value with the validated method in the i-th sample.

P_{1i} = First measured value with the proposed method in the i-th sample.

P_{2i} = Second measured value with the proposed method in the i-th sample.

6.2.2.1.2 Standard Deviation of the Differences. Calculate the standard deviation of the differences, SD_d, using Equation 301-6.

6.2.2.1.3 T-test. Calculate the t-statistic using Equation 301-7 where n is the total number of test sample differences (d_i). For the procedure in Section 5.2.1, n equals four. Compare the calculated t-statistic with the corresponding value from the table of the t-statistic and determine if the mean is significant at the 80-percent confidence level. When four runs are conducted, as specified in Section 5.2.1, the critical value of the t-statistic is 1.638 for three degrees of freedom. If the calculated t-value is greater than the critical value, the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.2.2.2 Correction Factor Calculation. If the method's bias is statistically significant, calculate the correction factor, CF, using Equation 301-8. Multiply all analytical results by CF to obtain the final values. The data and the proposed method are unacceptable if the correction factor is outside the range of 0.9 to 1.10.

6.2.2.3 Precision. Compare the variance of the proposed method to that of the validated method. If a significant difference is determined using the F-test, the proposed method and the results are rejected. Proposed methods demonstrating F-values equal to or less than the critical value have acceptable precision.

6.2.2.3.1 Proposed Method Variance. Calculate the variance of the proposed method, S_p^2, using the following equation:

$$S^2 = \frac{\sum d_i^2}{2n} \qquad \text{Eq. 301-14}$$

where the d_i's are the differences between the i-th pair of samples collected with the proposed method. Use the published values for the variance of the validated method. If there are no published values, calculate the variance of the validated method using Equation 301-14.

6.2.2.3.2 The F-test. Determine if the variance of the proposed method is greater than that of the validated method by calculating the F-value using Equation 301-12. Compare the experimental F value with the critical value of F. The critical value is 6.68 for the 95% confidence level when the procedure specified in section 5.2.1 for quadruplet trains is followed. If the calculated F is greater than the critical value, the difference in precision is significant, and the data and the proposed method are unacceptable.

6.3 Analyte Spiking. Analyze the data for analyte spike testing as outlined in Sections 6.3.1 through 6.3.3.

6.3.1 Bias Analysis.

6.3.1.1 Bias. Calculate the numerical value of the bias using the results from the analysis of the spiked field samples, the unspiked field samples, and the calculated value of the spike:

$$B = S_m - M_m - CS \qquad \text{Eq. 301-15}$$

where:

B = Bias at the spike level.

S_m = Mean of the spiked samples.

M_m = Mean of the unspiked samples.

CS = Calculated value of the spiked level.

6.3.1.2 Test the bias for statistical significance by calculating the t- statistic using Equation 301-16 and comparing it with the critical value of the two-sided t-distribution at the 95-percent confidence level and n-2 degrees of freedom. This critical value is 2.228 for the ten degrees of freedom. n=2*trains

$$t = \frac{|B|}{\sqrt{\frac{SD_s^2 + SD_u^2}{12}}} \qquad \text{Eq. 301-16}$$

6.3.2 Calculation of a Correction Factor. If the t-test shows that the bias is not statistically significant, use all analytical results without correction. If the method's bias is statistically significant, calculate the correction factor using Equation 301-3. If the CF is outside the range of 0.70 to 1.30, the data and method are considered unacceptable. For correction factors within the range, multiply all analytical results by the CF to obtain the final values.

6.3.3 Precision. Calculate the standard deviation and the RSD of the proposed method.

6.3.3.1 Spiked Samples. Calculate the difference, d_i, between the pairs of the spiked proposed method measurements for each replicate sample set. Determine the standard deviation (SD_s) of the spiked values using the following equation:

$$SD_s = \sqrt{\frac{\sum d_{is}^2}{2n}} \qquad \checkmark \qquad \text{Eq. 301-17}$$

where: d_{is} = Difference between the i-th pair of spiked samples.

n = Number of paired samples.

6.3.3.2 Unspiked Samples. Calculate the standard deviation of the unspiked values using the following equation.

$$SD_u = \sqrt{\frac{\sum d_{iu}^2}{2n}} \qquad \checkmark \qquad \text{Eq. 301-18}$$

where: d_{iu} = Difference between the i-th pair of unspiked samples.

n = Number of paired samples.

6.3.3.3 Pooled Standard Deviation. Calculate the pooled standard deviation of the spiked and unspiked samples if the

APPENDIX I

DRAFT REVISED METHOD 301 SPREADSHEET PRINTOUTS

VALIDATION OF FTIR FOR THE ANALYSIS OF FORMALDEHYDE

ANALYTE SPIKING: QUAD TRAINS NUMBER OF RUNS = 6
DRAFT REVISED CALCULATION METHOD
ENTER VALUE OF SPIKED LEVEL (CS)= 20.600
DILUTION FACTOR FOR UNSPIKED SAMPLES = 0.769
ENTER SPIKED AND UNSPIKED CONCENTRATIONS (COMPARABLE UNITS ASSUMED)

CONCENTRATION IN PPM (WET)

	SPIKED SAMPLES		UNSPIKED SAMPLES		SPIKED SAMPLES		UNSPIKED SAMPLES		Corrected SPIKED SAMPLES		Corrected UNSPIKED SAMPLES		Corrected SPIKED SAMPLES		Corrected UNSPIKED SAMPLES	
RUN #	A	B	C	D	A-B	(A-B)^2	C-D	(C-D)^2	A	B	C	D	A-B	(A-B)^2	C-D	(C-D)^2
1	42.15	37.16	24.01	23.27	4.99	24.90	0.74	0.55	37.81	33.33	21.54	20.87	4.48	20.04	0.66	0.44
2	35.29	39.76	22.68	19.60	-4.47	19.98	3.08	9.49	31.66	35.67	20.25	17.49	-4.01	16.08	2.76	7.63
3	38.79	36.28	19.47	19.80	2.51	6.30	-0.33	0.11	34.80	32.54	17.46	17.76	2.25	5.07	-0.30	0.09
4	38.74	41.74	20.11	19.96	-3.00	9.00	0.15	0.02	34.75	37.44	18.04	17.90	-2.69	7.24	0.13	0.02
5	37.35	39.38	20.02	19.78	-2.03	4.12	0.24	0.06	33.50	35.32	17.96	17.74	-1.82	3.32	0.22	0.05
6	42.62	39.74	19.83	19.71	2.88	8.29	0.12	0.01	38.23	35.65	17.79	17.68	2.58	6.67	0.11	0.01

AVERAGE: Sm= 39.083 Mm= 20.67 SUM ds^2 = 72.596 SUM du^2 = 10.237 Sm= 35.058 Mm = 18.541 SUM ds^2 = 58.41324065 SUM ds^2 = 8.237319068

STANDARD DEVIATION:

SPIKED SDs= 2.46

UNSPIKED SDu= 0.92

POOLED SD (SDpooled)= 1.858

RELATIVE STD RSD= 9.0% (Acceptable)
RSD = SDpooled/Mm

Corrected

SPIKED SDs= 2.21

UNSPIKED SDu= 0.83

POOLED SD (SDpooled)= NA

RELATIVE STD RSD= 6.3% (Acceptable)
RSD = SDs/Sm

BIAS: CORRECTED UNSPIKED CONCS = 15.90

B= 2.388

Experimental F = 0.141
F Bounds = 0.140 7.146
F TEST => Pooled

Experimental F = 0.061
F Bounds = 0.140 7.146
F TEST => Spike

STD OF MEAN SDm= 0.758

t-VALUE= 3.149

CRITICAL t-VALUE= 2.228
(n= 12 ,alpha=95%)

Bias is statistically significant

CORRECTION FACTOR= 0.897 (Acceptable)

VALIDATION OF FTIR FOR THE ANALYSIS OF ACETALDEHYDE

ANALYTE SPIKING: QUAD TRAINS NUMBER OF RUNS = 6

DRAFT REVISED CALCULATION METHOD

ENTER VALUE OF SPIKED LEVEL (CS)= 6.700

DILUTION FACTOR FOR UNSPIKED SAMPLES = 0.769

ENTER SPIKED AND UNSPIKED CONCENTRATIONS (COMPARABLE UNITS ASSUMED)

CONCENTRATION IN PPM (WET)

	SPIKED SAMPLES		UNSPIKED SAMPLES		SPIKED SAMPLES		UNSPIKED SAMPLES		Corrected SPIKED SAMPLES		Corrected UNSPIKED SAMPLES		Corrected SPIKED SAMPLES		Corrected UNSPIKED SAMPLES	
RUN #	A	B	C	D	A-B	(A-B)^2	C-D	(C-D)^2	A	B	C	D	A-B	(A-B)^2	C-D	(C-D)^2
1	11.45	11.10	5.47	5.33	0.35	0.12	0.14	0.02	10.87	10.54	5.19	5.06	0.33	0.11	0.13	0.02
2	10.38	10.16	5.22	4.04	0.22	0.05	1.18	1.39	9.85	9.64	4.95	3.83	0.21	0.04	1.12	1.25
3	10.40	9.73	4.00	3.68	0.67	0.45	0.32	0.10	9.87	9.24	3.80	3.49	0.64	0.40	0.30	0.09
4	10.06	10.28	3.91	4.08	-0.22	0.05	-0.17	0.03	9.55	9.76	3.71	3.87	-0.21	0.04	-0.16	0.03
5	9.86	10.24	3.90	3.85	-0.38	0.14	0.05	0.00	9.36	9.72	3.70	3.65	-0.36	0.13	0.05	0.00
6	10.00	9.96	3.78	3.35	0.04	0.00	0.43	0.18	9.49	9.45	3.59	3.18	0.04	0.00	0.41	0.17

AVERAGE: Sm= 10.302 Mm= 4.22 SUM ds^2 = 0.814 SUM du^2 = 1.731 Sm= 9.779 Mm = 4.003 SUM ds^2 = 0.733613041 SUM ds^2 = 1.559400749

STANDARD DEVIATION:

SPIKED SDs= 0.26

UNSPIKED SDu= 0.38

POOLED SD (SDpooled)= 0.326

RELATIVE STD RSD= 7.7% (Acceptable)

RSD = SDpooled/Mm

BIAS: CORRECTED UNSPIKED CONCS = 3.24

B= 0.358

STD OF MEAN SDm= 0.133

t-VALUE= 2.696

CRITICAL t-VALUE= 2.228

(n= 12 ,alpha=95%)

Bias is statistically significant

CORRECTION FACTOR= 0.949 (Acceptable)

Experimental F = 2.126

F Bounds = 0.140 7.146

F TEST => Pooled

Corrected

SPIKED SDs= 0.25

UNSPIKED SDu= 0.36

POOLED SD (SDpooled)= 0.328163876

RELATIVE STD RSD= 8.2% (Acceptable)

RSD = SDpooled/Mm

Experimental F = 2.123

F Bounds = 0.140 7.146

F TEST => Pooled

VALIDATION OF FTIR FOR THE ANALYSIS OF ACROLEIN

NOTE: CORRECTED FOR 23.7% DIFFERENCE BETWEEN MEASURED AND CYLINDER
ANALYTE SPIKING: QUAD TRAINS NUMBER OF RUNS = 6
DRAFT REVISED CALCULATION METHOD
ENTER VALUE OF SPIKED LEVEL (CS)= 7.700
DILUTION FACTOR FOR UNSPIKED SAMPLES = 0.769
ENTER SPIKED AND UNSPIKED CONCENTRATIONS (COMPARABLE UNITS ASSUMED)

	CONCENTRATION IN PPM (WET)							
	SPIKED SAMPLES		UNSPIKED SAMPLES		SPIKED SAMPLES		UNSPIKED SAMPLES	
RUN #	A	B	C	D	A-B	(A-B)^2	C-D	(C-D)^2
1	7.79	7.71	1.50	1.41	0.08	0.01	0.09	0.01
2	7.71	7.65	1.47	1.36	0.06	0.00	0.11	0.01
3	8.80	7.52	1.32	1.00	1.28	1.64	0.32	0.10
4	7.92	7.69	1.41	1.34	0.23	0.05	0.07	0.00
5	7.74	7.68	1.33	1.52	0.06	0.00	-0.19	0.04
6	7.64	7.66	1.47	1.35	-0.02	0.00	0.12	0.01

AVERAGE: Sm= 7.793 Mm= 1.37 SUM ds^2 = 1.705 SUM du^2 = 0.178

STANDARD DEVIATION:

SPIKED SDs= 0.38

UNSPIKED SDu= 0.12

POOLED SD (SDpooled)= NA

RELATIVE STD RSD= 4.8% (Acceptable)
RSD = SDs/Sm

BIAS: CORRECTED UNSPIKED CONCS = 1.06

B= -0.964

Experimental F = 0.104
F Bounds = 0.140 7.146
F TEST => Spike

STD OF MEAN SDm= 0.114

t-VALUE= 8.426

CRITICAL t-VALUE= 2.228
(n= 12 ,alpha=95%)

Bias is statistically significant

CORRECTION FACTOR= 1.143
(Acceptable)

VALIDATION OF NOx BY COMPARISON OF FTIR TO CEM

METHOD COMPARISON: PAIRED TRAIN SPREADSHEET

DRAFT REVISED CALCULATION METHOD

ENTER STANDARD DEVIATION OF VALIDATED METHOD: 13.20

Standard Deviation of Validated Method based on 2.16% RSD of 611.08 ppm

ENTER SAMPLE CONCENTRATIONS (ASSUMED TO BE IN COMPARABLE UNITS)

	CONCENTRATION IN PPM ON A DRY BASIS					Corrected			
RUN #	PROPOSED	VALIDATED	DI(V-P)	(DI-DM)^2	DI^2	Proposed	DI(V-P)	(DI-DM)^2	DI^2
1	446.76	447.94	1.18	144.80	1.3924	456.42	-8.48	76.84	71.92
2	492.92	520.17	27.25	197.03	742.5625	503.58	16.59	265.66	275.28
3	519.4	538.31	18.91	32.45	357.5881	530.63	7.68	54.66	58.97
4	543.7	566.99	23.29	101.64	542.4241	555.46	11.53	126.51	133.02
5	474.12	506.61	32.49	371.59	1055.6001	484.37	22.24	481.91	494.63
6	724.36	768.43	44.07	952.13	1942.1649	740.02	28.41	790.61	806.97
7	773.39	763.77	-9.62	521.36	92.5444	790.11	-26.34	709.09	693.96
8	724.91	724.54	-0.37	184.51	0.1369	740.58	-16.04	266.68	257.43
9	681.21	662.93	-18.28	991.83	334.1584	695.94	-33.01	1108.69	1089.65
AVERAGE:	597.68	611.08	13.21	388.58	563.176	610.79	0.29	431.22	431.30
TOTAL:	5380.77	5499.69	118.92	3497.24	5068.5718	5497.12	2.57	3880.99	3881.72
COUNT:			9						

STANDARD DEVIATION:

DIFFERENCE (SDd)= 20.91

VARIANCE:

		CORRECTED FOR BIAS	
POOLED VARIANCE (Spooled^2) =	316.786	POOLED VARIANCE (Spooled^2) =	242.608
VALIDATED METHOD (Sv^2)=	174.240	VALIDATED METHOD (Sv^2)=	174.240
PROPOSED METHOD (Sp^2)=	459.331	PROPOSED METHOD (Sp^2)=	310.975
Experimental F-value =	2.636	Experimental F-value =	1.785
F-Factor (95% confidence) =	4.026	F-Factor (95% confidence) =	4.026
Proposed Variance Acceptable		Proposed Variance Acceptable	

BIAS:

t-VALUE= 1.696

CRITICAL t-VALUE= 1.397

(n = 9 , alpha=80%)

Bias Statistically Significant

CORRECTION FACTOR (CF)= 1.022 1+(dm/Vm) (Acceptable)

VALIDATION OF CO BY COMPARISON OF FTIR TO CEM

METHOD COMPARISON: PAIRED TRAIN SPREADSHEET

DRAFT REVISED CALCULATION METHOD

ENTER STANDARD DEVIATION OF VALIDATED METHOD: 10.00

Standard Deviation of Validated Method Assumed to be 2% of Span

ENTER SAMPLE CONCENTRATIONS (ASSUMED TO BE IN COMPARABLE UNITS)

	CONCENTRATION IN PPM ON A DRY BASIS					Corrected			
RUN #	PROPOSED	VALIDATED	DI(V-P)	(DI-DM)^2	DI^2	Proposed	DI(V-P)	(DI-DM)^2	DI^2
1	106.51	103.14	-3.37	0.88	11.3569	103.98	-0.84	0.80	0.70
2	103.51	103.27	-0.24	4.82	0.0576	101.05	2.22	4.69	4.94
3	103.01	103.32	0.31	7.53	0.0961	100.56	2.76	7.30	7.62
4	101.66	103.1	1.44	15.01	2.0736	99.24	3.86	14.44	14.89
5	101.07	103.91	2.84	27.62	8.0656	98.67	5.24	26.90	27.50
6	99.38	101.55	2.17	21.20	4.7089	97.02	4.53	20.04	20.56
7	109.17	102.99	-6.18	14.03	38.1924	106.57	-3.58	13.25	12.84
8	106.8	100.08	-6.72	18.37	45.1584	104.26	-4.18	17.95	17.47
9	111.76	99.6	-12.16	94.59	147.8656	109.10	-9.50	91.38	90.27
AVERAGE:	104.76	102.33	-2.43	22.69	28.6195	102.27	0.06	21.86	21.87
TOTAL:	942.87	920.96	-21.91	204.24	257.5761	920.44	0.52	196.78	196.79
COUNT:			9						

STANDARD DEVIATION:

DIFFERENCE (SDd)= 5.05

VARIANCE:		CORRECTED FOR BIAS	
POOLED VARIANCE (Spooled^2) =	16.098	POOLED VARIANCE (Spooled^2) =	12.299
VALIDATED METHOD (Sv^2)=	100.000	VALIDATED METHOD (Sv^2)=	100.000
PROPOSED METHOD (Sp^2)=	5.049	PROPOSED METHOD (Sp^2)=	6.150
Experimental F-value =	0.050	Experimental F-value =	0.061
F-Factor (95% confidence) =	4.026	F-Factor (95% confidence) =	4.026
Proposed Variance Acceptable		Proposed Variance Acceptable	

BIAS:

t-VALUE= 1.445

CRITICAL t-VALUE= 1.397

(n = 9 , alpha=80%)

Bias Statistically Significant

CORRECTION FACTOR (CF)= 0.976 1+(dm/Vm) (Acceptable)

VALIDATION OF CO2 BY COMPARISON OF FTIR TO CEM

METHOD COMPARISON: PAIRED TRAIN SPREADSHEET

DRAFT REVISED CALCULATION METHOD

ENTER STANDARD DEVIATION OF VALIDATED METHOD: 0.11

ENTER SAMPLE CONCENTRATIONS (ASSUMED TO BE IN COMPARABLE UNITS)

CONCENTRATION IN PERCENT ON A DRY BASIS

RUN #	PROPOSED	VALIDATED	DI(V-P)	(DI-DM)^2	DI^2	Corrected Proposed	DI(V-P)	(DI-DM)^2	DI^2
1	4.22	4.17	-0.05	0.00	0.0025	4.12	0.05	0.00	0.00
2	4.29	4.24	-0.05	0.00	0.0025	4.19	0.05	0.00	0.00
3	4.26	4.22	-0.04	0.00	0.0016	4.16	0.06	0.00	0.00
4	4.26	4.2	-0.06	0.00	0.0036	4.16	0.04	0.00	0.00
5	4.24	4.17	-0.07	0.00	0.0049	4.14	0.03	0.00	0.00
6	4.36	4.27	-0.09	0.00	0.0081	4.25	0.02	0.00	0.00
7	4.47	4.29	-0.18	0.01	0.0324	4.36	-0.07	0.01	0.01
8	4.41	4.25	-0.16	0.00	0.0256	4.30	-0.05	0.00	0.00
9	4.47	4.24	-0.23	0.02	0.0529	4.36	-0.12	0.02	0.01
AVERAGE:	4.33	4.23	-0.10	0.00	0.0149	4.23	0.00	0.00	0.00
TOTAL:	38.98	38.05	-0.93	0.04	0.1341	38.03	0.02	0.04	0.04
COUNT:			9						

STANDARD DEVIATION:

DIFFERENCE (SDd)= 0.07

VARIANCE:

		CORRECTED FOR BIAS	
POOLED VARIANCE (Spooled^2) =	0.008	POOLED VARIANCE (Spooled^2) =	0.002
VALIDATED METHOD (Sv^2)=	0.012	VALIDATED METHOD (Sv^2)=	0.012
PROPOSED METHOD (Sp^2)=	0.004	PROPOSED METHOD (Sp^2)=	0.001
Experimental F-value =	0.346	Experimental F-value =	0.092
F-Factor (95% confidence) =	4.026	F-Factor (95% confidence) =	4.026
Proposed Variance Acceptable		Proposed Variance Acceptable	

BIAS:

t-VALUE= 4.496

CRITICAL t-VALUE= 1.397

(n = 9 , alpha=80%)

Bias Statistically Significant

CORRECTION FACTOR (CF)= 0.976 1+(dm/Vm) (Acceptable)

VALIDATION OF WATER BY COMPARISON OF FTIR TO CEM

METHOD COMPARISON: PAIRED TRAIN SPREADSHEET

DRAFT REVISED CALCULATION METHOD

ENTER STANDARD DEVIATION OF VALIDATED METHOD: 0.23

ENTER SAMPLE CONCENTRATIONS (ASSUMED TO BE IN COMPARABLE UNITS)

	CONCENTRATION IN PERCENT					Corrected			
RUN #	PROPOSED	VALIDATED	DI(V-P)	(DI-DM)^2	DI^2	Proposed	DI(V-P)	(DI-DM)^2	DI^2
1	9.55	9.63	0.08	0.00	0.0064	9.68	-0.05	0.00	0.00
2	10.37	10.6	0.23	0.01	0.0529	10.51	0.09	0.01	0.01
3	10.07	10.2	0.13	0.00	0.0169	10.21	-0.01	0.00	0.00
4	10.13	10.1	-0.03	0.03	0.0009	10.27	-0.17	0.03	0.03
5	10.32	10.6	0.28	0.02	0.0784	10.46	0.14	0.02	0.02
6	10.58	10.1	-0.48	0.38	0.2304	10.72	-0.62	0.39	0.39
7	10.24	10.4	0.16	0.00	0.0256	10.38	0.02	0.00	0.00
8	9.99	9.9	-0.09	0.05	0.0081	10.13	-0.23	0.05	0.05
9	10.02	11	0.98	0.71	0.9604	10.16	0.84	0.71	0.71
AVERAGE:	10.14	10.28	0.14	0.13	0.1533	10.28	0.00	0.13	0.13
TOTAL:	91.27	92.53	1.26	1.20	1.38	92.51	0.02	1.21	1.21
COUNT:			9						

STANDARD DEVIATION:

DIFFERENCE (SDd)= 0.39

VARIANCE:

		CORRECTED FOR BIAS	
POOLED VARIANCE (Spooled^2) =	0.086	POOLED VARIANCE (Spooled^2) =	0.076
VALIDATED METHOD (Sv^2)=	0.053	VALIDATED METHOD (Sv^2)=	0.053
PROPOSED METHOD (Sp^2)=	0.120	PROPOSED METHOD (Sp^2)=	0.098
Experimental F-value =	2.261	Experimental F-value =	1.861
F-Factor (95% confidence) =	4.026	F-Factor (95% confidence) =	4.026
Proposed Variance Acceptable		Proposed Variance Acceptable	

BIAS:

t-VALUE= 1.053

CRITICAL t-VALUE= 1.397

(n = 9 , alpha=80%)

Bias Not Statistically Significant, CF not needed.

APPENDIX J

PAIRED SAMPLING DATA

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 1 on July 14, 1994

FTIR Data

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
09:31:47	95474.70	38210.10	96.51	395.97	42243.27	106.69	437.76	5.19	443
09:36:46	95409.20	38168.90	96.04	401.08	42194.66	106.17	443.36	5.32	449
09:41:46	95593.50	38121.90	96.27	396.26	42151.29	106.45	438.14	5.45	444
09:46:45	96282.60	38118.60	96.27	390.62	42133.16	106.41	431.76	5.14	437
09:51:45	96022.20	38136.90	96.74	394.66	42188.76	107.01	436.59	5.47	442
09:56:44	95853.50	38256.80	96.27	397.57	42312.61	106.48	439.71	5.31	445
10:01:44	95546.00	38148.40	96.04	395.10	42178.37	106.19	436.84	5.14	442
10:06:43	95100.60	38090.10	95.81	398.29	42093.19	105.88	440.15	5.34	445
10:11:43	95073.90	38133.00	96.74	398.87	42139.35	106.90	440.78	5.21	446
10:16:42	94986.20	38184.10	96.04	404.56	42191.73	106.12	447.02	5.37	452
10:21:42	95433.60	38153.70	96.27	401.06	42178.99	106.43	443.37	5.47	449
10:26:41	95762.00	38342.20	96.27	406.32	42402.77	106.47	449.35	5.77	455
10:31:41	95763.30	38312.00	96.04	405.15	42369.44	106.21	448.05	5.63	454
Average	95494.72	38182.75	96.26	398.88	42213.51	106.42	440.98	5.37	446

TEST 1: CRITERIA POLLUTANTS ON DRY BASIS
BASED ON METHOD 4 MOISTURE DETERMINATIONS

METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
9.63	4.23	106.79	443.36
	4.22	106.28	449.12
	4.22	106.53	443.93
	4.22	106.53	437.38
	4.22	107.05	442.19
	4.23	106.53	445.24
	4.22	106.28	442.34
	4.21	106.02	446.07
	4.22	107.05	446.50
	4.23	106.28	453.05
	4.22	106.53	449.28
	4.24	106.53	455.39
	4.24	106.28	453.95
	4.22	106.51	446.76

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 1 on July 14, 1994

FTIR Data Run 1

Time	H2O %	CO2 % (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 % (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
09:31:47	9.55	3.82	96.51	395.97	4.23	106.69	437.76	5.19	442.96
09:36:46	9.54	3.82	96.04	401.08	4.22	106.17	443.36	5.32	448.68
09:41:46	9.56	3.81	96.27	396.26	4.22	106.45	438.14	5.45	443.59
09:46:45	9.53	3.81	96.27	390.62	4.22	106.41	431.76	5.14	436.90
09:51:45	9.60	3.81	96.74	394.66	4.22	107.01	436.59	5.47	442.06
09:56:44	9.50	3.83	96.27	397.57	4.23	106.48	439.71	5.31	445.02
10:01:44	9.55	3.81	96.04	395.10	4.22	106.19	436.84	5.14	441.98
10:06:43	9.51	3.81	95.81	398.29	4.21	105.88	440.15	5.34	445.49
10:11:43	9.51	3.81	96.74	398.87	4.22	106.90	440.78	5.21	445.99
10:16:42	9.50	3.82	96.04	404.56	4.23	106.12	447.02	5.37	452.40
10:21:42	9.54	3.82	96.27	401.06	4.22	106.43	443.37	5.47	448.84
10:26:41	9.58	3.83	96.27	406.32	4.24	106.47	449.35	5.77	455.12
10:31:41	9.58	3.83	96.04	405.15	4.24	106.21	448.05	5.63	453.68
Average	9.55	3.82	96.26	398.88	4.22	106.42	440.99	5.37	446.36

CEM Data Run 1

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
09:32:48	13.72	763.67	4.15	454.01	716.76	102.96
09:33:48	13.72	781.43	4.14	445.60	716.12	102.87
09:34:48	13.72	784.64	4.13	450.39	716.30	102.37
09:35:48	13.71	802.96	4.12	447.02	715.81	101.48
09:36:48	13.71	787.52	4.13	445.84	715.63	102.48
09:37:48	13.71	772.54	4.12	448.75	717.01	103.54
09:38:48	13.72	805.36	4.14	440.87	716.41	102.55
09:39:48	13.72	782.45	4.13	441.38	715.53	102.78
09:40:48	13.72	775.97	4.13	445.14	717.48	102.02
09:41:48	13.72	768.83	4.12	438.48	716.79	103.31
09:42:48	13.73	782.16	4.14	441.40	716.48	103.33
09:43:48	13.73	769.54	4.14	435.38	716.64	103.20
09:44:48	13.74	788.56	4.14	439.52	716.87	103.41
09:45:48	13.73	762.88	4.16	430.40	715.82	102.95
09:46:48	13.73	819.82	4.17	443.35	716.80	102.66
09:47:48	13.74	778.68	4.17	439.15	716.77	102.81
09:48:48	13.72	786.13	4.18	445.19	717.11	103.08
09:49:48	13.73	784.82	4.19	442.45	717.08	103.04
09:50:48	13.71	791.31	4.20	440.44	716.21	102.38
09:51:48	13.73	803.08	4.17	443.09	716.15	103.73
09:52:48	13.73	792.61	4.18	447.37	717.12	103.90
09:53:48	13.73	786.10	4.19	443.49	717.19	102.64
09:54:48	13.73	796.24	4.19	441.27	717.10	103.00
09:55:48	13.72	794.44	4.20	449.53	717.52	102.90
09:56:48	13.73	795.03	4.20	444.08	716.94	102.69
09:57:48	13.72	797.10	4.21	449.85	717.29	103.65
09:58:48	13.73	802.54	4.20	447.55	716.71	102.69
09:59:48	13.72	794.27	4.19	439.24	717.48	103.48
10:00:48	13.73	809.40	4.20	443.28	716.89	103.86
10:01:48	13.72	793.48	4.21	448.16	717.30	102.89
10:02:48	13.72	828.52	4.20	457.10	718.01	102.80
10:03:48	13.74	772.06	4.20	440.56	717.95	102.23
10:04:48	13.72	754.51	4.20	447.17	717.15	102.96
10:05:48	13.72	781.81	4.20	448.75	717.01	102.62
10:06:48	13.73	785.48	4.20	443.76	716.84	103.03
10:07:48	13.71	776.12	4.20	449.91	716.97	104.13
10:08:48	13.72	804.15	4.20	448.88	717.91	104.13
10:09:48	13.73	769.10	4.19	450.61	717.46	104.19
10:10:48	13.74	798.41	4.19	442.84	717.89	103.32
10:11:48	13.73	790.36	4.19	444.72	717.46	104.24
10:12:48	13.73	820.01	4.18	452.77	718.51	103.71
10:13:48	13.72	819.48	4.18	454.79	717.79	103.19
10:14:48	13.72	790.92	4.18	459.50	718.50	102.23
10:15:48	13.72	785.20	4.18	454.40	718.18	102.33
10:16:48	13.72	800.72	4.17	447.57	717.95	103.14
10:17:48	13.71	787.15	4.16	449.28	718.38	103.01
10:18:48	13.71	808.61	4.16	448.97	718.61	103.13
10:19:48	13.70	818.84	4.16	454.34	718.10	103.26
10:20:48	13.70	767.24	4.17	450.09	717.96	103.53
10:21:48	13.71	794.54	4.17	452.63	718.23	103.30
10:22:48	13.71	794.24	4.17	452.55	718.60	104.28
10:23:48	13.70	813.21	4.17	453.35	718.06	103.63
10:24:48	13.72	811.46	4.16	455.88	718.29	104.16
10:25:48	13.71	799.36	4.17	456.71	718.59	103.37
10:26:48	13.72	818.86	4.17	454.56	718.22	102.44
10:27:48	13.71	804.42	4.16	452.86	718.48	103.23
10:28:48	13.71	788.66	4.16	451.01	717.85	103.54
10:29:48	13.71	803.14	4.16	449.04	719.22	103.52
10:30:48	13.70	807.31	4.17	459.43	719.28	103.20
10:31:48	13.69	797.38	4.17	461.35	719.13	102.95
10:32:48	13.70	790.19	4.16	467.16	718.36	103.74
Average	13.72	792.74	4.17	447.94	717.45	103.14

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 2 on July 14, 1994

FTIR Data Run 2

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
11:15:28	105300.00	38400.80	93.97	429.43	42464.84	103.92	474.88	6.04	480.92
11:20:27	104800.00	38446.10	93.97	430.93	42493.23	103.87	476.29	5.90	482.19
11:25:27	104300.00	38335.00	93.06	431.68	42349.63	102.81	476.89	6.13	483.01
11:30:26	103800.00	38325.20	92.84	436.34	42317.19	102.51	481.79	6.38	488.17
11:35:26	103700.00	38357.10	92.61	437.85	42350.63	102.25	483.44	6.47	489.90
11:40:25	103400.00	38303.20	92.38	432.28	42278.09	101.97	477.14	6.38	483.51
11:45:25	103300.00	38261.70	91.93	438.30	42251.27	101.46	483.75	6.28	490.04
11:50:24	103400.00	38320.90	92.16	435.74	42295.20	101.71	480.93	6.77	487.70
11:55:24	103400.00	38306.50	92.16	436.64	42282.55	101.72	481.96	6.57	488.54
12:00:23	103600.00	38270.80	91.93	437.25	42248.39	101.49	482.69	6.23	488.92
12:05:23	103100.00	38294.70	91.93	438.00	42254.46	101.44	483.29	6.66	489.95
12:10:22	102700.00	38285.40	91.48	435.44	42207.58	100.91	480.30	6.46	486.76
Average	103733.33	38325.82	92.54	434.99	42316.09	102.17	480.28	6.36	486.63

TEST 2: CRITERIA POLLUTANTS ON DRY BASIS BASED ON METHOD 4 MOISTURE DETERMINATIONS

METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
10.60	4.30	105.12	486.39
	4.30	105.12	487.92
	4.29	104.10	488.99
	4.29	103.84	494.45
	4.29	103.59	496.23
	4.28	103.34	489.91
	4.28	102.83	496.56
	4.29	103.08	494.17
	4.28	103.08	494.99
	4.28	102.83	495.32
	4.28	102.83	496.59
	4.28	102.33	493.53
AVERAGE	4.29	103.51	492.92

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 2 on July 14, 1994

FTIR Data Run 2

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
11:15:28	10.53	3.84	93.97	429.43	4.25	103.92	474.88	6.04	480.92
11:20:27	10.48	3.84	93.97	430.93	4.25	103.87	476.29	5.90	482.19
11:25:27	10.43	3.83	93.06	431.68	4.23	102.81	476.89	6.13	483.01
11:30:26	10.38	3.83	92.84	436.34	4.23	102.51	481.79	6.38	488.17
11:35:26	10.37	3.84	92.61	437.85	4.24	102.25	483.44	6.47	489.90
11:40:25	10.34	3.83	92.38	432.28	4.23	101.97	477.14	6.38	483.51
11:45:25	10.33	3.83	91.93	438.30	4.23	101.46	483.75	6.28	490.04
11:50:24	10.34	3.83	92.16	435.74	4.23	101.71	480.93	6.77	487.70
11:55:24	10.34	3.83	92.16	436.64	4.23	101.72	481.96	6.57	488.54
12:00:23	10.36	3.83	91.93	437.25	4.22	101.49	482.69	6.23	488.92
12:05:23	10.31	3.83	91.93	438.00	4.23	101.44	483.29	6.66	489.95
12:10:22	10.27	3.83	91.48	435.44	4.22	100.91	480.30	6.46	486.76
Average	10.37	3.83	92.54	434.99	4.23	102.17	480.28	6.36	486.63

Note: Water and CO Recalculated using band areas

CEM Data Run 2

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
11:15:09	13.68	856.15	4.23	510.68	717.41	103.73
11:16:10	13.68	852.52	4.22	510.91	717.58	102.74
11:17:09	13.68	832.86	4.21	508.94	717.89	103.28
11:18:09	13.68	834.87	4.22	506.63	717.42	103.40
11:19:09	13.68	852.25	4.22	506.97	718.05	103.70
11:20:09	13.69	839.34	4.23	508.58	717.98	102.94
11:21:09	13.69	830.18	4.23	504.36	716.95	104.13
11:22:09	13.69	857.88	4.23	512.08	716.80	103.24
11:23:09	13.69	866.00	4.24	512.47	717.31	103.49
11:24:09	13.69	845.69	4.24	523.06	717.58	102.58
11:25:09	13.70	848.90	4.22	509.31	716.43	103.30
11:26:09	13.69	841.27	4.24	522.86	717.79	103.08
11:27:09	13.69	859.09	4.24	531.71	716.77	103.46
11:28:09	13.69	835.18	4.24	509.30	717.25	102.84
11:29:09	13.69	858.68	4.24	522.75	717.17	103.67
11:30:09	13.70	839.77	4.24	518.19	716.54	103.00
11:31:10	13.70	829.58	4.24	516.41	718.28	102.05
11:32:09	13.68	867.20	4.24	530.78	716.58	102.74
11:33:09	13.69	855.22	4.24	521.59	718.38	103.84
11:34:09	13.70	875.79	4.24	523.52	717.78	102.70
11:35:09	13.69	848.38	4.25	518.94	717.23	103.05
11:36:09	13.71	846.46	4.23	514.95	717.83	102.80
11:37:09	13.70	840.52	4.24	518.54	717.86	103.32
11:38:09	13.69	857.88	4.24	516.14	716.95	103.57
11:39:09	13.71	846.03	4.24	519.16	717.94	103.20
11:40:09	13.70	841.03	4.25	517.30	717.13	103.07
11:41:09	13.69	825.92	4.25	520.87	717.15	103.22
11:42:09	13.70	832.61	4.25	526.86	718.61	103.11
11:43:09	13.71	852.52	4.24	524.78	717.80	102.59
11:44:09	13.70	838.73	4.25	526.59	718.31	103.40
11:45:09	13.69	823.25	4.26	518.27	718.24	103.40
11:46:09	13.70	835.19	4.25	517.44	718.03	103.06
11:47:10	13.70	839.03	4.25	515.64	717.98	102.84
11:48:09	13.70	834.22	4.25	516.28	717.74	103.05
11:49:09	13.71	836.73	4.24	534.64	718.49	103.38
11:50:09	13.71	829.18	4.24	523.46	716.90	102.90
11:51:09	13.71	826.58	4.23	523.62	718.41	103.52
11:52:09	13.70	857.33	4.24	522.48	717.44	103.40
11:53:09	13.70	817.21	4.23	520.98	718.26	103.26
11:54:09	13.70	816.02	4.24	520.23	717.76	102.62
11:55:09	13.70	871.67	4.23	532.77	717.44	103.00
11:56:09	13.70	849.58	4.24	530.37	718.82	104.33
11:57:10	13.68	821.14	4.24	515.11	718.31	103.88
11:58:09	13.68	843.28	4.25	519.46	717.61	103.17
11:59:09	13.68	853.50	4.25	531.48	718.52	102.91
12:00:09	13.68	847.50	4.25	531.07	717.69	103.70
12:01:09	13.68	874.33	4.25	536.87	718.10	103.68
12:02:10	13.68	833.18	4.25	521.59	717.23	104.10
12:03:09	13.68	817.65	4.25	521.22	719.50	104.18
12:04:09	13.70	839.22	4.25	525.16	717.84	102.93
12:05:09	13.70	851.04	4.25	526.36	717.53	103.50
12:06:09	13.70	850.96	4.25	522.36	717.45	103.20
12:07:09	13.70	824.88	4.23	518.27	719.63	103.10
12:08:09	13.71	863.67	4.23	524.11	717.65	103.95
12:09:09	13.71	876.24	4.23	530.51	718.75	103.28
12:10:09	13.70	829.89	4.24	518.41	718.78	103.41
12:11:09	13.70	830.76	4.23	514.46	719.01	103.59
Average	13.69	843.89	4.24	520.17	717.79	103.27

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 3 on July 14, 1994

FTIR Data Run 3

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
01:08 PM	100300.00	38476.40	93.62	465.05	42402.92	103.39	512.51	7.21	519.72
01:13 PM	100800.00	38396.00	92.40	457.96	42315.34	102.11	504.68	7.14	511.82
01:18 PM	100500.00	38309.20	92.40	457.04	42217.05	102.09	503.66	7.46	511.12
01:23 PM	101200.00	38191.80	92.40	453.05	42092.20	102.12	499.32	7.32	506.64
01:28 PM	100500.00	38335.80	92.40	459.03	42257.76	102.14	506.00	7.32	513.32
01:33 PM	101300.00	38318.60	92.40	458.11	42224.58	102.13	504.81	7.55	512.36
01:38 PM	100500.00	38165.80	92.40	454.73	42058.64	102.13	501.12	6.96	506.07
01:43 PM	100300.00	38214.80	92.40	458.73	42110.11	102.05	505.49	7.46	512.95
01:48 PM	101700.00	38206.00	92.40	459.80	42126.50	102.10	506.96	7.07	514.03
01:53 PM	100300.00	38205.40	92.40	464.12	42095.62	102.08	511.38	7.42	518.81
01:58 PM	99600.00	38247.60	92.40	464.74	42128.57	102.10	511.90	7.67	519.57
02:03 PM	101000.00	38269.90	92.40	465.67	42164.57	102.18	513.30	7.37	520.68
Average	100666.67	38278.39	92.50	459.84	42184.49	102.22	506.76	7.33	514.09

TEST 3: CRITERIA POLLUTANTS ON DRY BASIS BASED ON METHOD 4 MOISTURE DETERMINATIONS

METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
10.20	4.28	104.25	525.06
	4.28	102.90	517.11
	4.27	102.90	516.41
	4.25	102.90	511.83
	4.27	102.90	518.49
	4.27	102.90	517.70
	4.25	102.90	513.34
	4.26	102.90	518.29
	4.25	102.90	519.10
	4.25	102.90	524.27
	4.26	102.90	525.20
	4.26	102.90	525.94
AVERAGE	4.26	103.01	519.40

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 3 on July 14, 1994

FTIR Data Run 3

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
01:08 PM	10.03	3.85	93.62	465.05	4.24	103.39	512.51	7.21	519.72
01:13 PM	10.08	3.84	92.40	457.96	4.23	102.11	504.68	7.14	511.82
01:18 PM	10.05	3.83	92.40	457.04	4.22	102.09	503.66	7.46	511.12
01:23 PM	10.12	3.82	92.40	453.05	4.21	102.12	499.32	7.32	506.64
01:28 PM	10.05	3.83	92.40	459.03	4.23	102.14	506.00	7.32	513.32
01:33 PM	10.13	3.83	92.40	458.11	4.22	102.13	504.81	7.55	512.36
01:38 PM	10.05	3.82	92.40	454.73	4.21	102.13	501.12	6.96	506.07
01:43 PM	10.03	3.82	92.40	458.73	4.21	102.05	505.49	7.46	512.95
01:48 PM	10.17	3.82	92.40	459.80	4.21	102.10	506.96	7.07	514.03
01:53 PM	10.03	3.82	92.40	464.12	4.21	102.08	511.38	7.42	518.81
01:58 PM	9.96	3.82	92.40	464.74	4.21	102.10	511.90	7.67	519.57
02:03 PM	10.10	3.83	92.40	465.67	4.22	102.18	513.30	7.37	520.68
Average	10.07	3.83	92.50	459.84	4.22	102.22	506.76	7.33	514.09

Note: Water and CO recalculated using band areas

CEM Data Run 3

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
13:07:55	13.63	816.91	4.23	539.39	717.46	103.51
13:08:55	13.62	825.88	4.23	536.73	717.29	103.51
13:09:55	13.62	845.21	4.22	533.45	717.28	103.31
13:10:55	13.63	832.09	4.23	537.51	717.40	103.49
13:11:55	13.65	841.19	4.21	537.62	717.70	102.68
13:12:55	13.64	841.83	4.22	535.05	717.36	102.97
13:13:55	13.65	825.41	4.22	533.65	717.56	103.14
13:14:55	13.64	842.86	4.22	541.29	716.88	103.29
13:15:55	13.64	863.08	4.22	533.12	718.31	102.92
13:16:55	13.63	841.92	4.23	535.07	717.24	103.06
13:17:55	13.64	844.27	4.22	532.65	717.81	103.63
13:18:55	13.64	841.72	4.23	533.24	717.51	103.54
13:19:55	13.65	832.34	4.22	532.13	717.53	103.22
13:20:55	13.66	847.44	4.23	527.53	716.86	103.51
13:21:55	13.63	854.69	4.23	526.37	717.61	103.04
13:22:55	13.64	838.34	4.23	529.05	718.11	104.02
13:23:55	13.63	846.03	4.23	534.32	717.14	104.04
13:24:55	13.63	829.92	4.22	535.86	717.60	103.30
13:25:55	13.64	850.24	4.23	539.00	716.95	103.09
13:26:55	13.63	867.58	4.23	541.57	717.84	103.22
13:27:55	13.64	839.32	4.23	535.05	717.59	103.63
13:28:55	13.65	850.30	4.22	535.61	717.57	103.20
13:29:55	13.64	842.07	4.21	543.47	716.58	103.04
13:30:55	13.65	855.78	4.23	539.23	716.67	102.97
13:31:55	13.64	836.02	4.22	534.54	717.31	104.63
13:32:55	13.64	858.46	4.22	536.60	718.27	104.04
13:33:55	13.65	846.06	4.22	535.80	717.83	103.71
13:34:55	13.65	873.21	4.22	537.77	717.94	103.06
13:35:55	13.65	845.98	4.21	536.97	717.73	102.34
13:36:55	13.64	833.38	4.22	530.79	716.60	103.87
13:38:02	13.65	830.05	4.21	533.86	718.89	103.65
13:38:55	13.65	843.72	4.21	532.71	717.75	103.20
13:39:55	13.64	851.40	4.21	545.99	716.46	103.19
13:40:55	13.64	840.26	4.20	545.26	718.51	103.20
13:41:55	13.64	817.07	4.20	534.31	718.49	103.30
13:42:55	13.65	854.40	4.21	537.36	717.87	103.72
13:43:55	13.65	850.44	4.20	540.95	717.26	102.76
13:44:55	13.64	882.62	4.20	548.67	718.10	103.26
13:45:55	13.64	850.68	4.21	538.36	717.87	102.67
13:46:55	13.63	839.79	4.20	537.50	717.77	102.54
13:47:55	13.63	853.06	4.21	545.04	718.42	103.21
13:48:55	13.64	849.17	4.20	542.03	716.97	103.33
13:49:55	13.64	870.49	4.20	548.58	718.87	103.68
13:50:55	13.64	862.38	4.20	558.43	718.54	102.49
13:51:55	13.64	860.00	4.20	552.96	717.98	103.15
13:52:55	13.63	857.28	4.21	553.32	717.89	103.87
13:53:55	13.63	871.17	4.20	545.76	717.84	103.37
13:54:55	13.64	820.64	4.21	538.52	717.93	103.33
13:55:55	13.65	826.49	4.21	529.63	718.31	102.21
13:56:55	13.64	827.45	4.21	537.38	717.74	104.71
13:57:55	13.64	883.02	4.21	541.96	718.23	102.93
13:58:55	13.65	850.64	4.21	534.96	718.39	103.12
13:59:55	13.63	833.03	4.21	538.10	718.25	103.86
14:00:55	13.62	841.58	4.22	544.22	718.03	104.12
14:01:55	13.62	865.36	4.20	538.66	717.03	103.31
14:02:55	13.63	852.72	4.20	540.66	718.40	102.57
Average	13.64	846.36	4.22	538.31	717.74	103.32

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 4 on July 14, 1994

FTIR Data Run 4

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
02:36 PM	89800.00	32899.10	74.99	382.57	35638.16	81.96	416.96	6.05	423.01
02:41 PM	101900.00	38384.90	92.40	476.24	42340.80	102.25	525.40	7.78	533.17
02:46 PM	100600.00	38390.00	92.40	483.61	42304.75	102.16	532.92	7.66	540.58
02:51 PM	101500.00	38340.50	91.19	479.53	42264.54	100.85	528.61	7.63	536.23
02:56 PM	101700.00	38266.00	91.19	476.87	42170.05	100.85	525.52	7.91	533.43
03:01 PM	101300.00	38276.90	91.19	478.12	42179.30	100.90	528.86	8.22	535.08
03:06 PM	101500.00	38220.10	91.19	478.59	42086.62	100.78	527.00	7.58	534.59
03:11 PM	99900.00	38288.10	91.19	482.19	42171.18	100.79	531.10	8.12	539.22
03:15 PM	101000.00	38336.10	91.19	485.18	42235.11	100.88	534.52	7.91	542.43
03:20 PM	101500.00	38255.70	91.19	485.81	42161.33	100.89	535.41	8.29	543.70
03:25 PM	101300.00	38209.80	91.19	483.29	42069.96	100.80	532.37	8.12	540.49
03:30 PM	102000.00	38263.90	91.19	485.81	42132.22	100.71	534.92	8.12	543.04
03:35 PM	101200.00	38257.90	91.19	484.39	42117.42	100.79	533.26	8.17	541.43
Average	101275.08	37899.83	91.39	474.02	41684.42	101.05	521.91	7.81	529.72

TEST 4: CRITERIA POLLUTANTS ON DRY BASIS BASED ON METHOD 4 MOISTURE DETERMINATIONS

METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
10.10	3.64	83.41	431.60
	4.27	102.78	537.52
	4.27	102.78	546.60
	4.26	101.43	541.03
	4.26	101.43	538.35
	4.26	101.43	540.05
	4.25	101.43	539.94
	4.26	101.43	544.49
	4.26	101.43	547.60
	4.26	101.43	548.66
	4.25	101.43	545.71
	4.26	101.43	548.51
	4.26	101.43	546.99
AVERAGE	4.25	101.86	543.70

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 4 on July 14, 1994

FTIR Data Run 4

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
02:36 PM	8.96	3.27	74.99	382.57	3.58	81.95	416.96	6.05	423.01
02:41 PM	10.19	3.84	92.40	476.24	4.23	102.25	525.40	7.78	533.17
02:46 PM	10.05	3.84	92.40	483.61	4.23	102.16	532.92	7.66	540.58
02:51 PM	10.15	3.83	91.19	479.53	4.23	100.85	528.61	7.63	536.23
02:56 PM	10.17	3.83	91.19	476.87	4.22	100.85	525.52	7.91	533.43
03:01 PM	10.13	3.83	91.19	478.12	4.22	100.90	528.86	8.22	535.08
03:06 PM	10.15	3.82	91.19	478.59	4.21	100.78	527.00	7.58	534.59
03:11 PM	9.99	3.83	91.19	482.19	4.22	100.79	531.10	8.12	539.22
03:15 PM	10.10	3.83	91.19	485.18	4.22	100.88	534.52	7.91	542.43
03:20 PM	10.15	3.83	91.19	485.81	4.22	100.89	535.41	8.29	543.70
03:25 PM	10.13	3.82	91.19	483.29	4.21	100.80	532.37	8.12	540.49
03:30 PM	10.20	3.83	91.19	485.81	4.21	100.71	534.92	8.12	543.04
03:35 PM	10.12	3.83	91.19	484.39	4.21	100.79	533.26	8.17	541.43
Averages	10.13	3.79	91.39	474.02	4.17	101.05	521.91	7.96	529.87

Note: Water and CO recalculated using band areas

CEM Data Run 4

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
14:35:24	13.61	841.98	4.22	566.35	715.62	103.55
14:36:24	13.63	844.71	4.21	568.36	717.75	103.58
14:37:24	13.62	862.37	4.22	569.35	717.24	103.19
14:38:24	13.62	843.79	4.21	570.03	716.32	103.30
14:39:24	13.61	845.72	4.21	568.86	717.07	103.37
14:40:24	13.63	830.56	4.21	559.58	716.54	103.51
14:41:24	13.61	838.06	4.20	568.42	716.89	102.66
14:42:24	13.61	853.68	4.21	578.88	716.77	104.52
14:43:24	13.63	882.46	4.20	583.49	716.30	103.03
14:44:24	13.64	811.97	4.19	569.81	716.28	102.17
14:45:24	13.63	856.65	4.19	573.06	716.70	102.96
14:46:24	13.61	837.14	4.20	577.00	716.24	102.65
14:47:24	13.63	833.27	4.20	584.93	717.95	102.84
14:48:24	13.62	849.76	4.20	574.85	716.99	103.22
14:49:24	13.63	852.42	4.20	575.10	716.57	102.62
14:50:24	13.64	850.34	4.19	568.92	716.70	102.95
14:51:24	13.63	817.18	4.19	567.77	716.72	103.37
14:52:24	13.64	818.05	4.19	563.43	717.36	102.92
14:53:24	13.63	827.31	4.19	562.86	716.87	102.85
14:54:24	13.62	832.11	4.20	569.42	717.31	103.80
14:55:24	13.62	862.04	4.20	580.02	716.89	103.53
14:56:24	13.63	835.35	4.20	566.76	717.37	103.37
14:57:24	13.63	848.01	4.20	567.88	716.24	103.39
14:58:24	13.63	819.70	4.20	571.57	717.20	102.97
14:59:24	13.63	867.80	4.19	577.83	717.36	103.71
15:00:24	13.63	839.00	4.19	584.64	717.24	103.84
15:01:24	13.63	830.53	4.19	549.73	717.18	103.60
15:02:24	13.63	861.86	4.20	555.66	716.36	103.28
15:03:24	13.66	833.52	4.18	555.22	716.48	102.08
15:04:24	13.65	830.22	4.19	558.48	718.43	103.28
15:05:24	13.64	840.96	4.19	559.80	717.93	102.76
15:06:24	13.63	835.80	4.19	550.14	717.12	102.63
15:07:24	13.63	864.03	4.20	564.64	717.06	102.83
15:08:24	13.63	827.30	4.19	554.32	716.67	102.80
15:09:24	13.63	831.93	4.19	558.03	717.20	102.74
15:10:24	13.61	830.79	4.21	571.96	717.39	102.32
15:11:24	13.62	826.95	4.21	568.74	717.59	103.65
15:12:24	13.63	849.42	4.20	563.68	717.86	102.57
15:13:24	13.63	823.31	4.21	564.84	717.67	103.18
15:14:24	13.64	820.67	4.20	560.49	717.43	103.24
15:15:24	13.63	848.14	4.20	562.56	717.70	102.96
15:16:24	13.62	876.69	4.21	578.19	717.61	103.79
15:17:24	13.64	823.13	4.20	568.29	718.00	103.86
15:18:24	13.64	824.09	4.20	554.18	717.93	103.36
15:19:24	13.62	859.40	4.22	565.38	717.42	102.55
15:20:24	13.63	833.67	4.21	567.19	717.90	102.79
15:21:24	13.63	826.87	4.21	560.48	717.52	103.86
15:22:24	13.63	834.04	4.21	563.13	718.25	103.89
15:23:24	13.64	858.37	4.21	568.91	717.46	102.81
15:24:24	13.64	821.91	4.22	561.51	718.25	102.92
15:25:24	13.64	818.53	4.19	560.21	717.58	103.08
15:26:24	13.64	819.83	4.20	557.80	717.70	103.71
15:27:24	13.64	850.62	4.21	557.58	718.23	103.00
15:28:24	13.64	852.30	4.21	567.48	717.35	102.59
15:29:24	13.64	848.18	4.21	565.26	718.16	102.78
15:30:24	13.64	840.91	4.21	576.55	717.46	103.03
15:31:24	13.65	840.75	4.21	575.24	717.71	103.09
15:32:24	13.64	818.61	4.22	571.50	716.57	103.13
15:33:24	13.65	833.56	4.21	571.92	718.36	102.38
15:34:24	13.65	821.37	4.21	574.69	718.70	102.23
15:35:24	13.65	864.06	4.21	574.29	718.30	102.54
Averages	13.63	838.74	4.20	566.99	717.30	103.10

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 5 on July 14, 1994

FTIR Data Run 5

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
16:02:09	102000.00	38009.20	89.99	423.75	41950.06	99.71	467.69	5.96	473.65
16:07:08	102400.00	37846.60	89.99	419.44	41732.25	99.57	462.50	6.44	468.94
16:12:08	102700.00	37972.20	89.99	420.78	41896.02	99.72	464.28	6.32	470.60
16:17:07	103900.00	37895.30	91.19	418.56	41793.67	101.01	461.61	6.44	468.05
16:22:07	102500.00	37851.60	89.99	411.75	41769.80	99.72	454.38	5.80	460.17
16:27:06	102000.00	37885.00	91.19	413.67	41812.50	101.08	456.56	6.12	462.68
16:32:06	103100.00	37888.60	89.99	413.97	41823.53	99.70	456.98	6.05	463.03
16:37:05	105100.00	37942.30	89.99	417.37	41906.50	99.77	460.97	6.20	467.17
16:42:05	103100.00	38028.00	89.99	417.96	41972.77	99.74	461.30	6.09	467.39
16:47:05	103400.00	37883.00	91.19	417.66	41800.14	101.11	460.85	6.10	466.95
16:52:04	102900.00	37952.10	91.19	414.56	41854.72	101.03	457.18	6.15	463.34
16:57:04	102700.00	38010.70	89.99	422.41	41918.84	99.73	465.84	6.30	472.14
17:02:03	104100.00	38023.30	89.99	426.44	41982.56	99.78	470.84	6.45	477.29
Average	103158.33	37937.45	90.39	418.33	41862.74	100.16	461.61	6.19	467.80

TEST 5: CRITERIA POLLUTANTS ON DRY BASIS
BASED ON METHOD 4 MOISTURE DETERMINATIONS

METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
10.60	4.25	100.66	479.96
	4.23	100.66	475.61
	4.25	100.66	476.99
	4.24	102.00	474.62
	4.23	100.66	466.37
	4.24	102.00	468.84
	4.24	100.66	469.10
	4.24	100.66	473.06
	4.25	100.66	473.60
	4.24	102.00	473.29
	4.25	102.00	469.66
	4.25	100.66	478.79
	4.25	100.66	483.45
AVERAGE	4.24	101.07	474.12

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 5 on July 14, 1994

FTIR Data Run 5

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
16:02:09	10.20	3.80	89.99	423.75	4.20	99.71	467.69	5.96	473.65
16:07:08	10.24	3.78	89.99	419.44	4.17	99.57	462.50	6.44	468.94
16:12:08	10.27	3.80	89.99	420.78	4.19	99.72	464.28	6.32	470.60
16:17:07	10.39	3.79	91.19	418.56	4.18	101.01	461.61	6.44	468.05
16:22:07	10.25	3.79	89.99	411.75	4.18	99.72	454.38	5.80	460.17
16:27:06	10.20	3.79	91.19	413.67	4.18	101.08	456.56	6.12	462.68
16:32:06	10.31	3.79	89.99	413.97	4.18	99.70	456.98	6.05	463.03
16:37:05	10.51	3.79	89.99	417.37	4.19	99.77	460.97	6.20	467.17
16:42:05	10.31	3.80	89.99	417.96	4.20	99.74	461.30	6.09	467.39
16:47:05	10.34	3.79	91.19	417.66	4.18	101.11	460.85	6.10	466.95
16:52:04	10.29	3.80	91.19	414.56	4.19	101.03	457.18	6.15	463.34
16:57:04	10.27	3.80	89.99	422.41	4.19	99.73	465.84	6.30	472.14
17:02:03	10.41	3.80	89.99	426.44	4.20	99.78	470.84	6.45	477.29
Average	10.32	3.79	90.39	418.33	4.19	100.16	461.61	6.21	467.82

Note: Water and CO recalculated using band areas

CEM Data Run 5

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
16:02:13	13.67	838.28	4.15	517.45	717.01	104.08
16:03:13	13.68	825.27	4.14	504.41	715.93	103.68
16:04:13	13.69	830.22	4.14	504.20	716.55	103.52
16:05:13	13.69	852.37	4.14	511.93	715.61	103.97
16:06:13	13.69	855.61	4.14	500.59	717.12	104.00
16:07:13	13.70	883.19	4.13	516.99	716.69	103.52
16:08:13	13.68	846.12	4.15	510.41	718.33	103.49
16:09:13	13.67	862.21	4.16	515.49	716.73	104.56
16:10:13	13.67	866.80	4.17	510.62	717.64	103.02
16:11:13	13.68	822.98	4.15	503.86	716.36	103.12
16:12:13	13.68	851.72	4.16	502.00	720.13	104.09
16:13:13	13.69	844.42	4.15	511.17	716.19	103.93
16:14:13	13.69	863.45	4.14	507.85	718.75	103.78
16:15:13	13.70	848.08	4.14	508.08	718.80	103.62
16:16:13	13.70	848.39	4.15	504.79	718.79	103.91
16:17:13	13.68	844.24	4.16	502.90	719.09	104.10
16:18:13	13.68	844.74	4.16	496.20	718.90	104.06
16:19:13	13.69	820.11	4.15	492.79	718.59	104.27
16:20:13	13.69	843.72	4.15	498.79	719.19	103.47
16:21:13	13.68	848.24	4.17	502.90	718.19	103.65
16:22:13	13.69	848.89	4.16	503.88	718.27	103.60
16:23:13	13.69	857.78	4.16	504.72	717.30	103.26
16:24:13	13.69	860.67	4.17	513.44	720.60	104.72
16:25:13	13.68	848.39	4.17	497.41	718.67	104.12
16:26:13	13.66	854.82	4.18	498.09	718.75	104.16
16:27:13	13.66	875.71	4.17	499.95	718.90	103.82
16:28:13	13.67	840.53	4.17	510.64	718.98	103.78
16:29:13	13.67	836.40	4.16	502.75	718.08	104.06
16:30:13	13.67	855.83	4.17	496.02	717.99	103.94
16:31:13	13.66	829.74	4.17	494.88	717.86	104.28
16:32:13	13.66	862.52	4.17	509.52	720.99	104.25
16:33:13	13.65	868.15	4.18	504.50	719.01	103.18
16:34:13	13.64	873.12	4.20	500.88	718.68	104.80
16:35:13	13.66	866.90	4.18	510.55	718.98	104.47
16:36:13	13.66	858.31	4.18	509.78	719.15	104.20
16:37:13	13.65	868.56	4.17	510.86	718.15	103.64
16:38:13	13.66	844.46	4.17	496.46	719.21	103.22
16:39:13	13.65	857.82	4.19	508.65	719.65	104.28
16:40:13	13.66	848.61	4.17	501.87	719.31	103.73
16:41:13	13.68	845.92	4.16	509.12	718.95	103.86
16:42:13	13.67	824.24	4.16	499.29	719.12	103.54
16:43:13	13.66	845.61	4.18	501.15	718.97	104.49
16:44:13	13.65	854.54	4.19	502.55	718.92	103.72
16:45:13	13.66	849.04	4.18	505.21	718.66	103.61
16:46:13	13.67	843.17	4.18	514.09	719.68	104.12
16:47:13	13.68	830.80	4.16	506.43	719.47	103.56
16:48:13	13.68	845.22	4.17	500.87	719.01	103.76
16:49:13	13.68	847.37	4.16	500.66	719.06	103.39
16:50:13	13.67	845.95	4.18	503.44	719.14	104.50
16:51:13	13.67	835.75	4.19	500.64	718.81	104.40
16:52:13	13.67	846.52	4.18	504.52	719.56	104.13
16:53:13	13.67	842.62	4.17	515.71	719.45	103.51
16:54:13	13.68	824.08	4.18	509.51	719.28	104.18
16:55:13	13.68	823.94	4.19	507.90	719.26	103.72
16:56:13	13.67	830.21	4.20	511.36	718.61	104.94
16:57:13	13.66	884.39	4.20	522.62	719.50	103.88
16:58:13	13.65	841.24	4.21	511.75	719.80	104.03
16:59:13	13.66	863.72	4.21	512.30	719.75	103.98
17:00:13	13.65	837.99	4.21	516.48	719.81	103.30
17:01:13	13.64	862.35	4.22	526.59	719.18	103.89
17:02:13	13.65	868.23	4.21	522.45	719.06	104.33
Averages	13.67	849.83	4.17	506.61	718.65	103.91

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 6 on July 14, 1994

FTIR Data Run 6

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
05:41 PM	105800.00	39252.00	89.99	651.44	43432.79	100.00	720.83	16.28	737.11
05:46 PM	105800.00	39267.30	89.99	658.59	43442.55	100.02	728.61	17.11	745.73
05:51 PM	105700.00	39284.60	88.79	667.56	43437.22	98.60	738.05	17.86	755.91
05:56 PM	105100.00	39350.30	88.79	659.66	43508.80	98.67	729.37	17.10	746.48
06:01 PM	105100.00	39217.80	88.79	647.88	43385.75	98.68	716.41	16.45	732.86
06:06 PM	106600.00	39128.70	88.79	634.26	43261.41	98.71	701.25	16.22	717.47
06:11 PM	106700.00	39164.30	88.79	627.76	43314.63	98.73	694.28	15.50	709.78
06:16 PM	105300.00	38997.00	88.79	624.43	43111.59	98.75	690.31	15.44	705.75
06:21 PM	106400.00	39182.60	89.99	624.78	43334.24	100.01	690.80	15.80	706.61
06:26 PM	107000.00	39163.10	89.99	619.71	43307.34	100.11	685.29	15.99	701.28
06:31 PM	105300.00	39128.70	89.99	615.19	43256.78	100.10	680.12	16.00	696.12
06:36 PM	105300.00	39095.40	88.79	622.16	43202.92	98.60	687.52	16.12	703.64
06:41 PM	105100.00	39084.40	89.99	621.81	43161.88	100.01	686.68	15.93	702.61
Averages	105775.00	39179.00	89.29	636.56	43318.30	99.25	703.81	16.29	720.10

TEST 6: CRITERIA POLLUTANTS ON DRY BASIS
BASED ON METHOD 4 MOISTURE DETERMINATIONS

	METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
	10.10	4.37	100.10	740.92
		4.37	100.10	749.69
		4.37	98.77	760.42
		4.38	98.77	750.87
		4.38	98.77	737.13
		4.35	98.77	721.73
		4.36	98.77	713.79
		4.34	98.77	710.02
		4.36	100.10	710.78
		4.36	100.10	705.32
		4.35	100.10	700.30
		4.35	98.77	708.17
		4.35	100.10	707.59
AVERAGE		4.36	99.36	724.38

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 6 on July 14, 1994

FTIR Data Run 6

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
05:41 PM	10.58	3.93	89.99	651.44	4.34	100.00	720.83	16.28	737.11
05:46 PM	10.58	3.93	89.99	658.50	4.34	100.02	728.61	17.11	745.73
05:51 PM	10.57	3.93	88.79	667.56	4.34	98.60	738.05	17.86	755.91
05:56 PM	10.51	3.94	88.79	659.66	4.35	98.67	729.37	17.10	746.48
06:01 PM	10.51	3.92	88.79	647.88	4.34	98.68	716.41	16.45	732.86
06:06 PM	10.65	3.91	88.79	634.26	4.33	98.71	701.25	16.22	717.47
06:11 PM	10.67	3.92	88.79	627.76	4.33	98.73	694.28	15.50	709.78
06:16 PM	10.53	3.90	88.79	624.43	4.31	98.75	690.31	15.44	705.75
06:21 PM	10.64	3.92	89.99	624.78	4.33	100.01	690.80	15.80	706.61
06:26 PM	10.70	3.92	89.99	619.71	4.33	100.11	685.29	15.99	701.28
06:31 PM	10.53	3.91	89.99	615.19	4.33	100.10	680.12	16.00	696.12
06:36 PM	10.53	3.91	88.79	622.16	4.32	98.60	687.52	16.12	703.64
06:41 PM	10.51	3.91	89.99	621.81	4.32	100.01	686.68	15.93	702.61
Averages	10.58	3.92	89.29	636.56	4.33	99.25	703.81	16.29	720.10

Note: Water and CO recalculated using band areas

CEM Data Run 6

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
17:41:34	13.45	826.24	4.27	787.55	731.01	102.06
17:42:34	13.45	827.65	4.28	793.34	730.79	100.62
17:43:34	13.44	839.17	4.29	801.53	730.60	101.25
17:44:34	13.45	822.35	4.29	787.89	730.52	101.32
17:45:34	13.45	843.42	4.28	803.58	730.48	102.35
17:46:33	13.44	827.97	4.29	803.71	730.62	100.83
17:47:34	13.44	827.60	4.29	811.30	730.59	100.33
17:48:34	13.45	839.83	4.28	815.62	729.53	100.67
17:49:34	13.46	819.98	4.28	805.01	730.25	100.64
17:50:34	13.45	855.25	4.28	803.94	730.40	101.36
17:51:34	13.44	838.24	4.29	798.10	729.88	101.45
17:52:34	13.45	830.56	4.28	783.05	730.69	101.44
17:53:34	13.45	840.67	4.29	805.25	730.60	101.12
17:54:33	13.45	825.11	4.28	811.05	729.86	101.11
17:55:33	13.45	828.30	4.28	796.58	730.19	101.15
17:56:33	13.45	846.69	4.28	799.43	730.57	101.87
17:57:34	13.44	845.67	4.30	793.46	730.72	102.06
17:58:33	13.45	828.44	4.29	788.53	730.02	101.21
17:59:33	13.47	819.78	4.29	774.52	730.56	101.63
18:00:34	13.47	837.27	4.27	770.90	731.22	102.22
18:01:33	13.47	830.09	4.28	775.40	730.59	101.65
18:02:34	13.48	814.78	4.27	764.25	731.07	101.16
18:03:34	13.48	825.99	4.27	764.28	731.15	100.85
18:04:33	13.46	844.93	4.28	768.98	730.26	101.12
18:05:34	13.47	827.38	4.27	764.59	731.43	100.66
18:06:33	13.47	812.43	4.27	754.87	730.87	102.04
18:07:34	13.46	833.94	4.28	757.30	731.51	100.82
18:08:33	13.48	845.12	4.27	785.28	730.54	101.12
18:09:33	13.48	832.09	4.26	752.27	731.37	100.88
18:10:34	13.48	848.73	4.26	759.74	730.65	100.75
18:11:33	13.48	830.65	4.26	761.38	731.09	101.63
18:12:34	13.48	851.23	4.26	756.85	731.66	100.45
18:13:33	13.47	856.38	4.27	757.15	731.70	101.67
18:14:34	13.48	828.51	4.27	752.74	731.36	101.57
18:15:34	13.49	824.29	4.26	757.87	730.68	100.72
18:16:33	13.49	817.95	4.26	754.35	731.43	101.43
18:17:34	13.48	831.33	4.26	750.46	731.78	102.69
18:18:34	13.48	850.31	4.26	754.60	733.34	102.53
18:19:34	13.48	867.14	4.26	768.79	732.84	101.92
18:20:34	13.48	828.62	4.26	748.49	734.02	102.33
18:21:34	13.48	818.63	4.26	743.69	733.18	102.27
18:22:34	13.48	838.55	4.26	751.46	734.42	102.03
18:23:34	13.48	835.68	4.26	755.51	733.97	101.56
18:24:33	13.49	856.13	4.26	758.06	733.71	101.63
18:25:34	13.49	825.32	4.26	742.59	734.27	102.62
18:26:34	13.49	830.33	4.26	746.81	734.59	103.22
18:27:33	13.48	815.39	4.26	744.68	733.81	102.10
18:28:34	13.48	840.22	4.27	742.66	734.20	102.16
18:29:33	13.48	831.95	4.26	742.13	733.78	101.89
18:30:33	13.49	810.54	4.26	744.39	733.92	101.54
18:31:33	13.50	819.98	4.25	739.65	734.35	101.47
18:32:34	13.49	843.45	4.26	761.89	734.36	102.22
18:33:34	13.49	841.55	4.25	759.87	734.25	101.70
18:34:33	13.49	805.65	4.26	743.94	734.29	101.22
18:35:34	13.50	846.86	4.25	750.96	734.45	101.70
18:36:34	13.49	833.09	4.25	759.03	733.98	101.63
18:37:34	13.50	808.30	4.25	751.90	734.73	101.50
18:38:34	13.50	829.39	4.25	754.02	733.97	102.43
18:39:34	13.50	817.19	4.25	741.72	734.52	100.91
18:40:34	13.49	821.88	4.25	749.19	734.00	102.02
Averages	13.47	832.34	4.27	768.43	732.02	101.55

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 7 on July 14, 1994

FTIR Data Run 7

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
19:22:05	97250	40253.00	98.37	689.50	44567.15	108.97	763.78	16.88	780.66
19:27:05	103246	40084.90	98.61	686.77	44699.98	109.96	765.83	17.90	783.74
19:32:05	103567	40103.90	98.14	684.40	44738.17	109.48	763.48	18.20	781.69
19:37:04	102972	40134.10	98.14	686.22	44745.67	109.41	764.99	18.37	783.36
19:42:04	103448	40131.80	98.37	681.13	44762.37	109.72	759.72	18.11	777.82
19:47:03	103161	40068.60	98.14	678.22	44700.88	109.43	756.25	17.77	774.03
19:52:03	103034	40099.80	97.91	674.24	44706.26	109.15	751.69	17.44	769.14
19:57:02	103212	40028.80	97.91	671.53	44635.77	109.17	748.82	17.37	766.19
20:02:02	102938	40072.70	97.44	674.60	44671.02	108.62	752.01	17.59	769.60
20:07:01	102706	40062.20	97.91	671.89	44647.72	109.11	748.79	17.11	765.90
20:12:01	102534	40077.30	97.67	676.77	44656.06	108.83	754.09	17.63	771.73
20:17:00	102518	40064.60	97.67	672.79	44641.10	108.83	749.64	17.43	767.08
20:21:59	100770	39493.50	95.35	657.69	43919.23	106.04	731.39	14.41	745.80
Average	102415	40062	98	677	44622	109	755	17.45	772.10

TEST 7: CRITERIA POLLUTANTS ON DRY BASIS
BASED ON METHOD 4 MOISTURE DETERMINATIONS

METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
10.40	4.49	109.79	786.41
	4.47	110.06	784.38
	4.48	109.53	782.04
	4.48	109.53	784.24
	4.48	109.79	778.29
	4.47	109.53	774.72
	4.48	109.27	769.94
	4.47	109.27	766.85
	4.47	108.75	770.49
	4.47	109.27	766.99
	4.47	109.01	772.96
	4.47	109.01	768.32
	4.41	106.42	748.44
AVERAGE	4.47	109.17	773.39

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 7 on July 14, 1994

FTIR Data Run 7

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
19:22:05	9.72	4.02	98.37	689.50	4.46	108.97	763.78	16.88	780.66
19:27:05	10.32	4.01	98.61	686.77	4.47	109.96	765.83	17.90	783.74
19:32:05	10.36	4.01	98.14	684.40	4.47	109.48	763.48	18.20	781.69
19:37:04	10.30	4.01	98.14	686.22	4.47	109.41	764.99	18.37	783.36
19:42:04	10.34	4.01	98.37	681.13	4.48	109.72	759.72	18.11	777.82
19:47:03	10.32	4.01	98.14	678.22	4.47	109.43	756.25	17.77	774.03
19:52:03	10.30	4.01	97.91	674.24	4.47	109.15	751.69	17.44	769.14
19:57:02	10.32	4.00	97.91	671.53	4.46	109.17	748.82	17.37	766.19
20:02:02	10.29	4.01	97.44	674.60	4.47	108.62	752.01	17.59	769.60
20:07:01	10.27	4.01	97.91	671.89	4.46	109.11	748.79	17.11	765.90
20:12:01	10.25	4.01	97.67	676.77	4.47	108.83	754.09	17.63	771.73
20:17:00	10.25	4.01	97.67	672.79	4.46	108.83	749.64	17.43	767.08
20:21:59	10.08	3.95	95.35	657.69	4.39	106.04	731.39	14.41	745.80
Average	10.24	4.01	97.82	677.37	4.46	108.98	754.85	17.45	772.10

CEM Data Run 7

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
19:22:29	13.47	851.43	4.30	776.10	732.49	103.18
19:23:26	13.46	849.53	4.31	772.89	731.87	103.46
19:24:26	13.48	843.28	4.29	778.75	731.84	103.20
19:25:26	13.48	847.42	4.29	772.74	731.85	103.36
19:26:26	13.49	833.02	4.28	767.98	732.00	103.57
19:27:26	13.49	837.00	4.28	766.42	731.69	102.79
19:28:26	13.49	844.04	4.28	769.44	731.63	103.29
19:29:26	13.48	826.53	4.29	771.83	732.08	103.12
19:30:26	13.48	833.69	4.29	775.20	731.69	103.21
19:31:26	13.47	852.55	4.30	770.20	732.24	103.14
19:32:26	13.47	830.42	4.30	764.70	731.85	102.99
19:33:26	13.49	847.71	4.27	770.29	732.11	102.47
19:34:26	13.49	835.27	4.28	779.43	732.25	102.48
19:35:26	13.47	844.27	4.31	776.11	732.20	102.95
19:36:26	13.48	853.74	4.30	768.80	732.12	102.89
19:37:26	13.47	870.03	4.30	770.67	731.87	103.21
19:38:26	13.47	853.57	4.31	764.23	732.41	102.62
19:39:26	13.48	846.89	4.31	768.91	732.47	103.63
19:40:26	13.48	858.42	4.30	772.73	732.22	104.06
19:41:26	13.48	857.46	4.30	768.99	732.49	104.22
19:42:26	13.48	843.85	4.29	765.15	732.81	102.91
19:43:26	13.48	855.98	4.30	763.69	732.41	103.51
19:44:26	13.47	891.79	4.31	775.25	732.26	103.30
19:45:26	13.49	850.87	4.30	763.67	731.97	103.29
19:46:26	13.48	863.24	4.30	764.43	732.49	103.74
19:47:26	13.49	858.90	4.29	760.92	732.75	101.89
19:48:26	13.48	845.88	4.31	754.65	732.43	101.80
19:49:26	13.49	857.59	4.29	764.40	732.48	103.13
19:50:26	13.48	841.23	4.30	757.93	732.94	103.72
19:51:26	13.48	862.29	4.31	758.96	732.09	103.48
19:52:26	13.48	873.33	4.29	767.42	732.62	103.81
19:53:26	13.48	869.58	4.28	768.09	732.88	103.57
19:54:26	13.48	860.08	4.29	753.45	732.99	103.15
19:55:26	13.48	888.92	4.29	754.44	732.52	103.75
19:56:26	13.48	856.90	4.30	756.31	732.51	103.31
19:57:26	13.48	849.90	4.29	759.13	732.83	102.96
19:58:26	13.49	859.97	4.28	767.95	732.85	101.88
19:59:26	13.49	830.69	4.29	750.71	732.67	102.31
20:00:26	13.47	825.82	4.30	762.95	732.65	103.30
20:01:26	13.47	854.41	4.30	762.32	733.29	102.48
20:02:26	13.49	850.26	4.28	758.59	733.22	102.46
20:03:26	13.48	831.15	4.29	756.72	733.06	102.22
20:04:26	13.46	825.37	4.28	755.78	733.20	103.49
20:05:26	13.48	835.62	4.29	759.19	733.17	102.47
20:06:26	13.49	852.30	4.28	760.94	733.38	103.22
20:07:26	13.49	828.33	4.28	762.90	733.09	102.79
20:08:26	13.49	876.48	4.28	769.12	733.68	102.72
20:09:26	13.49	845.03	4.28	760.00	733.55	101.49
20:10:26	13.48	851.58	4.29	766.69	733.60	102.55
20:11:26	13.49	861.75	4.28	767.12	733.52	102.97
20:12:26	13.48	823.73	4.28	760.39	733.44	102.15
20:13:26	13.48	845.02	4.28	758.44	733.50	102.89
20:14:26	13.46	831.47	4.29	760.03	733.78	103.38
20:15:26	13.48	844.98	4.28	759.08	733.24	103.20
20:16:26	13.48	869.14	4.26	750.25	733.91	102.66
20:17:26	13.47	844.67	4.28	757.71	733.33	102.56
20:18:26	13.46	852.30	4.28	753.24	720.87	102.47
20:19:26	13.47	867.32	4.27	752.42	719.89	103.08
20:20:26	13.47	841.70	4.26	759.59	719.77	103.00
20:21:26	13.45	856.92	4.28	771.59	719.82	102.08
20:22:26	13.35	878.09	4.25	735.61	720.10	103.41
Averages	13.48	850.37	4.29	763.77	731.62	102.99

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 8 on July 14, 1994

FTIR Data Run 8

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
20:47:36	99536	39596.30	93.75	645.56	43973.22	104.11	716.94	13.32	730.25
20:52:37	99543	39401.60	94.06	637.96	43757.34	106.13	708.49	13.34	721.82
20:57:36	101171	39690.50	95.81	651.96	44157.99	106.60	725.36	14.59	739.96
21:02:36	100779	39819.10	96.27	656.62	44281.77	107.06	730.21	15.28	745.49
21:07:35	100918	39874.90	96.04	651.96	44350.69	106.82	725.16	14.66	739.82
21:12:35	99635	39860.20	95.58	655.90	44261.00	106.18	728.65	15.24	743.89
21:17:34	99638	39745.60	96.27	649.84	44153.83	106.95	721.92	15.30	737.21
21:22:34	99331	39783.10	96.14	639.20	44170.59	106.96	709.69	14.53	724.22
21:27:33	99264	39739.50	96.51	639.73	44118.91	107.14	710.23	14.27	724.50
21:32:33	99381	39705.40	96.27	630.92	44086.77	106.90	700.54	14.38	714.92
21:37:32	99644	39765.00	96.97	624.78	44165.85	107.70	693.93	13.79	707.72
21:42:32	99428	39734.10	97.20	620.06	44120.98	107.94	688.52	13.55	702.07
21:47:31	100028	39809.00	97.44	619.19	44233.61	108.27	688.01	13.20	701.21
average	99809	39733	96	640	44143	107	711	14	725

TEST 8: CRITERIA POLLUTANTS ON DRY BASIS
BASED ON METHOD 4 MOISTURE DETERMINATIONS

METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
9.90	4.39	104.05	729.83
	4.37	106.06	721.40
	4.41	106.34	738.21
	4.42	106.85	744.04
	4.43	106.60	738.28
	4.42	106.09	743.22
	4.41	106.86	736.54
	4.42	106.82	723.96
	4.41	107.11	724.30
	4.41	106.85	714.83
	4.41	107.53	707.22
	4.41	107.89	701.75
	4.42	108.14	700.42
AVERAGE	4.41	[illegible]	724.91

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 8 on July 14, 1994

FTIR Data Run 8

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
20:47:36	9.95	3.96	93.75	645.56	4.40	104.11	716.94	13.32	730.25
20:52:37	9.95	3.94	94.06	637.96	4.38	106.13	708.49	13.34	721.82
20:57:36	10.12	3.97	95.81	651.96	4.42	106.60	725.36	14.59	739.96
21:02:36	10.08	3.98	96.27	656.62	4.43	107.06	730.21	15.28	745.49
21:07:35	10.09	3.99	96.04	651.96	4.44	106.82	725.16	14.66	739.82
21:12:36	9.96	3.99	95.58	655.90	4.43	106.18	728.65	15.24	743.89
21:17:34	9.96	3.97	96.27	649.84	4.42	106.95	721.92	15.30	737.21
21:22:34	9.93	3.98	96.14	639.20	4.42	106.96	709.69	14.53	724.22
21:27:33	9.93	3.97	96.51	639.73	4.41	107.14	710.23	14.27	724.50
21:32:33	9.94	3.97	96.27	630.92	4.41	106.90	700.54	14.38	714.92
21:37:32	9.96	3.98	96.97	624.78	4.42	107.70	693.93	13.79	707.72
21:42:32	9.94	3.97	97.20	620.06	4.41	107.94	688.52	13.56	702.07
21:47:31	10.00	3.96	97.44	619.19	4.42	108.27	688.01	13.20	701.21
Average	9.98	3.97	96.23	640.29	4.41	106.90	711.36	14.34	725.70

CEM Data Run 8

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
20:48:03	13.53	775.16	4.26	729.95	720.20	101.20
20:49:03	13.52	849.97	4.26	734.08	719.01	100.67
20:50:03	13.53	824.24	4.26	736.69	719.48	100.69
20:51:03	13.54	806.27	4.26	735.87	719.10	100.98
20:52:03	13.54	838.94	4.26	738.84	719.47	101.05
20:53:03	13.54	816.93	4.25	737.67	719.17	100.64
20:54:03	13.54	828.29	4.25	737.94	719.42	100.68
20:55:03	13.54	835.18	4.27	741.32	725.10	101.27
20:56:03	13.52	852.20	4.27	744.09	728.57	100.87
20:57:03	13.53	904.23	4.27	753.30	728.71	100.91
20:58:03	13.56	843.53	4.26	738.15	729.00	100.97
20:59:03	13.55	853.19	4.26	738.79	728.77	100.65
21:00:03	13.54	853.19	4.28	743.01	727.21	101.20
21:01:03	13.54	852.01	4.28	748.95	727.72	100.56
21:02:03	13.56	856.09	4.27	745.99	727.98	99.87
21:03:03	13.57	869.60	4.25	737.48	727.71	100.07
21:04:03	13.57	860.63	4.25	743.87	728.26	100.00
21:05:03	13.56	858.75	4.27	745.47	728.01	100.59
21:06:03	13.52	833.62	4.29	729.12	728.37	100.03
21:07:03	13.54	827.19	4.29	738.03	727.96	100.28
21:08:03	13.54	818.40	4.28	743.41	728.38	100.89
21:09:03	13.57	832.50	4.25	750.36	728.51	99.32
21:10:03	13.58	832.67	4.25	743.87	727.06	99.38
21:11:03	13.57	827.15	4.25	737.36	727.91	99.76
21:12:03	13.58	850.78	4.25	733.15	728.50	98.31
21:13:03	13.56	850.72	4.26	749.24	728.34	99.40
21:14:03	13.57	836.61	4.25	728.74	728.39	100.00
21:15:03	13.57	827.43	4.25	738.13	728.35	100.16
21:16:03	13.57	844.88	4.26	735.20	729.02	100.53
21:17:03	13.58	860.72	4.24	723.30	729.02	99.51
21:18:03	13.58	827.93	4.24	714.89	729.30	99.92
21:19:03	13.59	830.86	4.23	719.92	728.77	100.00
21:20:03	13.57	830.31	4.24	723.90	728.42	107.37
21:21:03	13.59	836.32	4.23	720.78	728.79	101.22
21:22:03	13.59	844.82	4.22	722.41	729.00	99.72
21:23:03	13.58	844.43	4.24	731.32	727.77	99.58
21:24:03	13.59	816.24	4.24	718.75	728.75	99.30
21:25:03	13.60	848.09	4.23	722.77	727.88	100.33
21:26:03	13.59	831.93	4.24	724.28	729.46	99.43
21:27:03	13.61	841.72	4.23	715.68	728.55	99.50
21:28:03	13.61	857.49	4.23	720.43	728.25	99.16
21:29:03	13.61	831.38	4.24	716.33	729.29	99.55
21:30:03	13.63	846.65	4.22	717.56	729.14	98.52
21:31:03	13.62	837.19	4.22	702.41	728.23	99.39
21:32:03	13.62	832.45	4.23	704.67	728.99	99.07
21:33:03	13.61	824.74	4.24	705.92	728.66	98.66
21:34:03	13.63	815.89	4.23	702.74	728.89	99.59
21:35:03	13.62	826.99	4.24	707.84	729.30	99.32
21:36:03	13.61	836.36	4.25	710.12	728.96	98.89
21:37:03	13.62	826.86	4.25	708.79	729.89	100.05
21:38:03	13.62	811.82	4.25	696.98	729.26	98.98
21:39:03	13.62	815.53	4.26	706.39	729.77	99.42
21:40:03	13.63	815.74	4.24	704.40	729.17	99.35
21:41:03	13.64	807.84	4.23	693.95	729.62	98.62
21:42:03	13.63	807.78	4.23	697.00	729.17	99.71
21:43:03	13.62	818.71	4.24	703.39	729.96	99.97
21:44:03	13.62	815.32	4.24	700.86	729.45	99.88
21:45:03	13.62	803.94	4.25	697.87	729.77	99.45
21:46:03	13.61	813.26	4.25	702.41	729.39	100.31
21:47:03	13.62	831.31	4.25	701.07	730.12	100.27
21:48:03	13.62	802.63	4.25	701.82	729.73	99.95
Average	13.58	833.65	4.25	724.54	727.62	100.08

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 9 on July 14, 1994

FTIR Data Run 9

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
22:08:40	99101	39628.20	98.27	607.39	43987.41	108.87	674.20	12.79	686.99
22:13:39	99342	39669.20	98.14	601.00	44044.68	108.96	667.29	12.86	680.15
22:18:39	99769	39671.70	98.37	597.39	44068.34	109.28	663.60	12.25	675.85
22:23:38	100096	39676.00	98.84	597.56	44091.30	109.84	664.03	12.62	676.65
22:28:38	100345	39844.30	99.08	596.71	44288.44	110.13	663.26	12.26	675.52
22:33:37	100257	39758.50	99.08	593.45	44188.73	110.12	659.58	12.15	671.73
22:38:37	100173	39716.30	99.55	594.99	44137.68	110.63	661.23	12.66	673.88
22:43:36	99905	39674.40	99.55	591.40	44077.99	110.60	657.04	12.25	669.29
22:48:36	100521	39828.60	100.50	596.36	44279.65	111.73	663.01	12.30	675.31
22:53:35	100474	39806.50	100.28	588.49	44252.74	111.46	654.23	12.13	666.36
22:58:35	100390	39817.90	100.74	592.59	44261.30	111.98	658.72	12.13	670.85
23:03:34	101041	39839.30	101.45	595.16	44317.14	112.88	662.06	12.40	674.45
23:08:33	101115	39962.80	101.93	590.20	44480.43	113.40	656.59	12.09	668.68
Average	100184	39763	100	596	44190	111	662	12.34	674.25

TEST 9: CRITERIA POLLUTANTS ON DRY BASIS
BASED ON METHOD 4 MOISTURE DETERMINATIONS

METHOD 4 MOISTURE	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NOX ppm (Dry)
10.95	4.45	108.11	684.86
	4.45	110.21	687.77
	4.46	110.47	683.10
	4.46	111.00	683.66
	4.47	111.26	682.34
	4.46	111.28	678.57
	4.46	111.79	680.81
	4.46	111.79	676.37
	4.47	112.86	681.99
	4.47	112.59	672.99
	4.47	113.13	677.59
	4.47	113.93	680.74
	4.49	114.47	674.86
AVERAGE	4.47	111.76	681.21

GRI FTIR Validation Program - CEM & FTIR Data Comparisons
Criteria Pollutants Data - Run 9 on July 14, 1994

FTIR Data Run 9

Time	H2O (ppm)	CO2 ppm (Wet)	CO (Lo) ppm (Wet)	NO ppm (Wet)	CO2 ppm (Dry)	CO (Lo) ppm (Dry)	NO ppm (Dry)	NO2 ppm (Dry)	NOX ppm (Dry)
22:08:40	9.91	3.96	98.27	607.39	4.40	108.87	674.20	12.79	686.99
22:13:39	9.93	3.97	98.14	601.00	4.40	108.96	667.29	12.86	680.15
22:18:39	9.98	3.97	98.37	597.39	4.41	109.28	663.60	12.25	675.85
22:23:38	10.01	3.97	98.84	597.56	4.41	109.84	664.03	12.62	676.65
22:28:38	10.03	3.98	99.08	596.71	4.43	110.13	663.26	12.26	675.52
22:33:37	10.03	3.98	99.08	593.45	4.42	110.12	659.58	12.15	671.73
22:38:37	10.02	3.97	99.55	594.99	4.41	110.63	661.23	12.66	673.88
22:43:36	9.99	3.97	99.55	591.40	4.41	110.60	657.04	12.25	669.29
22:48:36	10.05	3.98	100.50	596.36	4.43	111.73	663.01	12.30	675.31
22:53:35	10.05	3.98	100.28	588.49	4.43	111.46	654.23	12.13	666.36
22:58:35	10.04	3.98	100.74	592.59	4.43	111.98	658.72	12.13	670.86
23:03:34	10.10	3.98	101.45	595.16	4.43	112.88	662.06	12.40	674.45
23:08:33	10.11	4.00	101.93	590.20	4.45	113.40	656.59	12.09	668.68
Average	10.02	3.98	99.52	595.59	4.42	110.76	661.91	12.34	674.25

CEM Data Run 9

TIME	O2 %	THC ppm	CO2 %	NOx ppm	FTIR mmHg	CO ppm
22:09:25	13.58	793.48	4.21	667.38	727.87	99.18
22:10:25	13.57	823.66	4.23	671.22	727.56	99.37
22:11:25	13.58	821.55	4.22	673.64	727.88	99.88
22:12:25	13.57	804.34	4.22	673.30	727.08	100.22
22:13:25	13.57	817.36	4.21	668.28	727.59	100.23
22:14:25	13.58	799.67	4.22	671.48	727.75	100.78
22:15:25	13.58	813.11	4.21	662.49	728.04	99.78
22:16:25	13.59	820.19	4.22	666.78	727.50	99.33
22:17:25	13.59	803.80	4.22	664.36	727.67	100.18
22:18:25	13.58	804.87	4.22	660.01	727.87	99.75
22:19:25	13.59	830.66	4.23	664.72	727.73	99.92
22:20:25	13.59	804.95	4.23	669.51	727.38	99.39
22:21:25	13.58	821.31	4.22	667.99	728.35	100.30
22:22:25	13.60	825.01	4.23	662.56	728.36	99.38
22:23:25	13.59	795.51	4.23	667.30	727.24	100.36
22:24:25	13.60	806.48	4.23	662.97	728.03	99.99
22:25:25	13.60	826.64	4.24	667.59	728.85	98.40
22:26:25	13.60	824.55	4.24	673.51	727.69	100.28
22:27:25	13.62	829.20	4.24	657.40	729.05	100.11
22:28:25	13.61	815.91	4.23	666.42	727.95	100.45
22:29:25	13.61	797.39	4.24	664.35	728.72	99.43
22:30:25	13.60	819.36	4.25	662.38	728.83	100.32
22:31:25	13.61	786.18	4.25	657.74	728.61	99.68
22:32:25	13.60	803.65	4.25	660.06	728.20	99.29
22:33:25	13.61	801.49	4.24	661.37	729.04	99.24
22:34:25	13.61	782.28	4.24	662.75	728.28	100.03
22:35:25	13.61	809.04	4.25	671.24	728.57	100.13
22:36:25	13.62	808.29	4.24	664.86	729.27	99.16
22:37:25	13.60	805.19	4.24	666.90	728.88	98.88
22:38:25	13.61	781.65	4.25	662.95	728.58	99.87
22:39:25	13.61	789.44	4.24	660.07	729.20	99.97
22:40:25	13.62	788.33	4.24	649.88	728.61	99.58
22:41:25	13.60	787.73	4.24	654.13	729.34	99.19
22:42:25	13.60	841.13	4.24	660.81	728.49	99.10
22:43:25	13.60	803.24	4.25	671.61	728.36	99.93
22:44:25	13.60	809.32	4.25	673.64	729.49	99.59
22:45:25	13.60	784.01	4.24	664.75	728.90	99.66
22:46:25	13.61	804.62	4.25	667.34	729.33	99.56
22:47:25	13.61	796.23	4.25	663.16	729.03	99.33
22:48:25	13.61	788.10	4.25	662.19	729.69	99.80
22:49:25	13.62	821.06	4.25	658.51	728.81	98.89
22:50:25	13.61	795.62	4.24	661.33	729.39	100.02
22:51:25	13.62	834.18	4.24	662.03	729.09	99.39
22:52:25	13.63	802.49	4.25	649.58	729.26	99.21
22:53:25	13.62	797.51	4.24	658.80	729.59	98.56
22:54:25	13.63	791.29	4.24	653.67	729.93	98.88
22:55:25	13.63	814.58	4.24	658.67	729.92	98.98
22:56:25	13.62	774.69	4.25	662.41	730.19	99.11
22:57:25	13.61	781.90	4.26	657.51	729.78	98.86
22:58:25	13.61	814.73	4.26	668.44	730.29	99.72
22:59:25	13.62	816.54	4.26	659.88	730.16	99.91
23:00:25	13.61	853.92	4.27	668.74	730.49	98.89
23:01:25	13.62	796.68	4.25	666.04	729.75	98.79
23:02:25	13.62	817.23	4.26	656.68	730.88	99.31
23:03:25	13.62	830.77	4.26	661.93	730.27	99.87
23:04:25	13.62	811.57	4.26	652.42	730.56	100.73
23:05:25	13.61	810.92	4.26	654.00	730.32	99.46
23:06:25	13.62	798.66	4.26	650.54	731.26	99.03
23:07:25	13.61	827.86	4.26	656.04	729.85	99.65
23:08:26	13.60	839.56	4.27	655.76	730.48	99.84
Average	13.60	808.32	4.24	662.93	728.93	99.60

APPENDIX K

STACK MEASUREMENT METHOD PRECISION DATA

STACK SAMPLING MEASUREMENT PRECISION

MEASUREMENT/METHOD	SPECIFICATION	RSD OR SD	RANGE
TEMPERATURE			
Type K thermocouple	þ1.5% of absolute	þ0.27½F SD	32 to 400½F
Meter temperature	þ5.4½F	þ0.29½F SD	40 to 110½F
Mercury-in-Glass thermometer		þ0.10½F SD	0 to 200½F
Dial thermometers			
PRESSURE/DIFFERENTIAL PRESSURE			
Stack gauge pressure	þ0.1 in.Hg		
Meter gauge pressure			
Atmospheric pressure	þ0.1 in.Hg		
Velocity pressure	þ10.0%		
Orifice pressure differential	þ5.0%		
VELOCITY			
Type S pitot/Method 2		þ2.2% RSD	44.6 to 54.1 fps
Coefficient, Cp	þ0.02	þ0.32% RSD	10 to 100 fps
	þ0.02	þ0.0026 SD	
3D Pitot			
Pitch angle, deg	þ2.0½	þ1.0½ SD	þ40½, 20 to 100 fps
Yaw angle, deg	þ2.0½	þ1.0½ SD	þ40½, 20 to 100 fps
Coefficient, F2	þ3.0%	þ3.0% SD	þ40½, 20 to 100 fps
DRY MOLECULAR WEIGHT			
Orsat/Method 3	þ0.3 lb/lb-mole	þ0.035 lb/lb-mole SD	28.06 to 29.21 lb/lb-mole
Fyrite/Method 3	þ0.3 lb/lb-mole	þ0.044 lb/lb-mole SD	28.06 to 29.21 lb/lb-mole
Method 3A	þ0.3 lb/lb-mole	þ0.035 lb/lb-mole SD	28.06 to 29.21 lb/lb-mole
STACK GAS MOISTURE			
Method 4/5 Impinger		þ0.23% moisture SD	11.7 to 17.5% moisture
PARTICULATE MATTER			
Method 5			81.7 to 254.5 mg/scm
Mass concentration		þ10.4% RSD @ 133 mg/scm	
		þ13.81 mg/scm SD	
METERING SYSTEM			
Sample volume/Method 5	þ2%	þ0.00667 SD	0.97 to 1.03
DGM Audit/Method 5		þ5.0% RSD	
Orifice meter coefficient		þ0.0584 SD	1.6 to 2.0
Diameter of probe nozzle		þ0.0011 SD	3/16 to 0.50 inches
Sample volume/Method 6	þ2%	þ0.0084 SD	0.97 to 1.05
CARBON DIOXIDE			
Orsat/Method 3B	þ0.2% CO2	þ0.20% CO2 SD	1.8 to 3.1% CO2
Method 3A	þ0.2% CO2	þ0.11% CO2 SD	3.9 to 18.4% CO2
	þ0.3% CO2	þ0.16% CO2 SD	3.9 to 18.4% CO2
	þ0.5% CO2	þ0.28% CO2 SD	3.9 to 18.4% CO2
OXYGEN			
Orsat/Method 3B	þ0.2% O2	þ0.32% O2 SD	16.5 to 19.5% O2
Method 3A	þ0.2% O2	þ0.11% O2 SD	1 to 21% O2
	þ0.3% O2	þ0.14% O2 SD	1 to 21% O2
	þ0.5% O2	þ0.19% O2 SD	1 to 21% O2
SULFUR DIOXIDE			
Method 6/Analytical		þ1.3% RSD	
Method 6C		þ2.25% RSD	100 to 2800 ppm
Method 6C		þ2.4 ppm SD	0 to 100 ppm
NITROGEN OXIDES			
Method 7/Analytical		þ6.2% RSD	
Method 7E		þ2.16% RSD	100 to 1000 ppm
Method 7E		þ1.3 ppm SD	0 to 100 ppm
VOST/SEMIVOST			
See attached table			

APPENDIX L

AUDIT RESULT

RADIAN

MEMORANDUM

TO: Ellen Streib, EPA

FROM: Gunseli Sagun Shareef, Radian

COPY: Robin Segall, EPA
Jim Evans, GRI
Jim McCarthy, GRI
Larry Ogle, Radian

DATE: December 21, 1994

SUBJECT: Audit Result

Below you will find the result of the audit cylinder analyzed during the FTIR validation testing conducted in July 1994 under the GRI Air Toxics program:

Cylinder ID	Target Analyte	Measured Concentration (ppm)
695c	Acetaldehyde	ND (DL: 0.3 ppm)

Please call me at 481-0212 if you have any questions.