

**The development and evaluation of analytical
methods for the analysis of trace levels of moisture
in high purity gas samples**

By

B.L. Hickman Mosdell

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DECLARATION

I, BL Hickman Mosdell, hereby declare that the work on which this thesis is based, has not, to my knowledge, previously been submitted for a degree at this or any other university. This work is my own and all reference material that has been used or quoted has been indicated and acknowledged.

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ABSTRACT

Three methods, for the analyses of low levels of moisture in gas samples, were developed and optimized. The analytical techniques included Fourier Transform Infrared Spectroscopy (FTIR) and Pulsed Discharge Helium Ionization/Gas Chromatography (PDHID/GC).

The methods included the direct analyses of moisture in gas samples using FTIR as well as the analysis of acetylene (C_2H_2) by FTIR and GC/PDHID. For the latter methods, the purpose was to convert the moisture in a gas sample to C_2H_2 by hydrolization of the calcium carbide (CaC_2) with moisture to C_2H_2 and then analyze the resulting C_2H_2 content by FTIR or GC/PDHID. The C_2H_2 result was then converted back to moisture to obtain the moisture content of the sample.

The FTIR moisture method developed provided eleven different wavenumbers for quantitation providing a wide analytical scope, specifically in complex gas matrices, where there is often peak overlap between matrix and moisture. A heated eight meter glass long path gas cell and a mercury cadmium telluride (MCT) detector were utilized. The FTIR method required much greater volumes of sample than the GC method but allowed for direct analysis of moisture without prior conversion to acetylene. Moisture permeation standards were used for calibration and the LOD's ranged from 0.5 to 1 ppm with quantification possible from 0.5 to 10ppm.

For the FTIR C_2H_2 method various concentration ranges were established from 50 up to 2000 ppm. Three wavenumbers were evaluated for C_2H_2 and methane was introduced as an internal standard. The use of methane as an internal standard provided better r^2 values on the calibration data than for the tests run without internal standard.

A gas chromatographic (GC), pulsed discharge helium ionization detector (PDHID) method for the determination of moisture content in small

quantities of gases, based on the conversion of the moisture to acetylene (C_2H_2) prior to analysis, was developed. The method developed on the GC/PDHID for C_2H_2 , provided a quantitation range from 0.6 to 7.7 ppm. Conversion of the moisture to acetylene was achieved by hydrolysing an excess of calcium carbide (CaC_2) in a closed reaction vessel with a measured volume of a sample containing a known quantity of moisture. The gaseous reaction mixture was transferred, using helium (He) carrier gas, to a GC/PDHID, set up with "sample injection and heart cut to detector" to prevent matrix disturbances on the PDHID, for analysis. The acetylene concentration values thus obtained were converted back to moisture values and percentage recoveries calculated. A similar conversion process was applied on FTIR.

The conversion of moisture to C_2H_2 using CaC_2 was tested and proven to be viable. Quantification was not possible as the available sample holder could not be adequately sealed to prevent air ingress. This led to higher C_2H_2 values than expected. This process can be optimized by the design and production of a sealed sample holder.

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TABLE OF CONTENTS

Declaration.....	ii
Abstract.....	iii
Acknowledgements.....	v
Table of contents	vi
Abbreviations	xi
List of Figures	xii
List of Tables.....	xvi
Chapter 1: INTRODUCTION AND BACKGROUND.....	1
1.1. Introduction.....	1
1.2. Purpose of the study.....	3
1.3. Objectives of the study	3
1.4. Importance of the study	4
Chapter 2: LITERATURE REVIEW	6
2.1. Introduction and background	6
2.2. Methods for moisture analysis	14
2.3. Chemical processes involving moisture.....	15
2.4. Infrared spectroscopy	17
Introduction	17
Theory of infrared absorption	19
Instrumentation	23

	Measurement of gas samples on FTIR	33
	Measurement parameters for FTIR	33
2.5.	Gas chromatography	34
	Introduction	34
	Theory of GC.....	35
	Instrumentation	39
2.6.	Using a permeation tube to create a range of moisture standards for calibration	43
	Chapter 3: RESEARCH METHODOLOGY	49
3.1.	Introduction.....	49
3.2.	Section 1: FTIR experimental work.....	50
	Commercial instrumentation.....	50
	Consumables	50
	Gases.....	50
	Reference standards.....	51
	FTIR instrument set up and optimization.....	51
3.3.	Method 1: H ₂ O analysis on FTIR	57
	General	57
	Variation of gases used for dilutions	57
	Optimizing the glass gas cell temperature	57
	Moisture permeation reference standard: KINTEK.....	58
	Calculations to obtain ppmv values from dilutions.....	61

	Peak selection.....	61
	Calibration for moisture	62
	Use of methane to prove stability of FTIR system.....	62
	CH ₄ as internal standard for moisture analyses	64
3.4.	Method 2: C ₂ H ₂ analysis on FTIR	64
	General	64
	Background	64
	Summary of acetylene reference standards tested:	64
	Standard 1 (Matheson 0.15% Reference standard)	65
	Standard 2 (C ₂ H ₂ Standard certified in-house).....	67
	Standard 2 with internal standard.....	68
	Standard 3 (Air Liquide C ₂ H ₂ Reference Standard).....	69
	Standard 3 with internal standard.....	70
3.5.	Section 2: GC experimental Work	71
	Commercial instrumentation.....	71
	Consumables	71
	Gases.....	72
	Reference standards.....	72
3.6.	GC/PDHID set up and optimization	72
	General	72
	Valve configuration.....	72
3.7.	GC/PDHID experimental work	76

General	76
Dilution of standards using mass flow controllers.....	76
Calculations to obtain ppmv values for dilutions.....	77
3.8. Section 3: Conversion of moisture to C ₂ H ₂	77
Consumables	77
Optimization of the conversion process using vials.....	78
Sample holder for conversion process	78
Chapter 4: RESULTS AND DISCUSSION	80
4.1. Method 1: H ₂ O analysis on FTIR	80
Optimization of the glass cell temperature	80
Calibration results for moisture.....	80
4.2. Determining the suitability of methane as internal standard	87
Methane as internal standard for moisture	88
4.3. Method 2: C ₂ H ₂ analysis on FTIR	89
Calibration results for Standard 1: no internal standard	89
Calibration results for Standard 2: no internal standard	93
Calibration results for Standard 2 using CH ₄ as internal standard	99
Calibration results for Standard 3: no internal standard	105
Calibration results for Standard 3 using CH ₄ as internal standard	111
4.4. Statistics	116

Linear regression analyses	116
Evaluating the results of the regression analysis	116
4.5. Method 3: analysis on GC/PDHID	123
Calibration results for C ₂ H ₂	123
4.6. Conversion of moisture to C ₂ H ₂	123
4.7. In summary	124
Chapter 5: CONCLUSIONS AND RECOMMENDATIONS	126
References.....	129
APPENDIX 1:.....	136
APPENDIX 2:.....	137
APPENDIX 3:.....	157

ABBREVIATIONS

APIMS	atmospheric pressure ionization mass spect.
atm	atmosphere
cm	centimeters
CEPA	California Environmental Protection Agency
COA	Certificate of Analysis
CRDS	Cavity Ring-Down Spectroscopy
DTGS	Deuterated Triglycine Sulphate Detector
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
FPD	Flame Photometric Detector
GC	Gas Chromatograph
GSV	Gas Sampling Valve
He-PDPID	Helium Pulsed Discharge Photo Ionization
HETP	Height Equivalent Theoretical Plate
HPLC	High Pressure Liquid Chromatography
HSGC	High Speed Gas Chromatography
HS-GC	Head Space Capillary Gas Chromatography
Hz	Hertz
ILS	Intracavity Laser Spectroscopy
IMS	Ion Mobility Spectrometry
IR	Infrared
KBr	Potassium Bromide
Kg	Kilogram
LDR	Linear Dynamic Range
LOD	Limit of Detection
LPG	Liquid Petroleum Gas
MCTD	Mercury Cadmium Telluride Detector
MSD	Mass Selective Detector
NECSA	Nuclear Energy Corporation South Africa
PAL	Pelindaba Analytical Laboratories
PDD	Pulsed Discharge Detector
pg	Picogram
PDED	Pulsed Discharge Emission Detector
ppbv	parts per billion volume
ppm	parts per million
pptv	parts per trillion volume
RGA	Refinery Gas Analyzer
SOP	Standard Operating Procedure
SSS	Scientific Supply Services cc
TCD	Thermal Conductivity Detector
TDLAS	Tunable Diode Laser Absorption
UV	Ultraviolet
WGSR	Water-Gas Shift Reaction

LIST OF FIGURES

Figure 1: Schematic diagram of the equipment used for simultaneous determination of dissolved gases and moisture by the HS-GS technique. This represents the standby position. ⁽¹³⁾	11
Figure 2: Reverse water gas shift reaction in an Inconel reactor. 900°C, ambient pressure, $[H_2]_0 = [CO_2]_0$. Equilibrium conversion for these conditions is 55%. ⁽¹⁵⁾	13
Figure 3: The electromagnetic spectrum ⁽²³⁾	18
Figure 4: Stretching and bending vibrational modes for H_2O ⁽²¹⁾	20
Figure 5: Stretching and bending vibrational modes for CO_2 ⁽²¹⁾	21
Figure 6: General regions of the IR spectrum ⁽²⁷⁾	23
Figure 7: Simplified optical layout of a typical FTIR spectrometer. ⁽²⁸⁾	24
Figure 8: Schematic diagram of the optical layout of a Michelson interferometer ⁽³¹⁾	25
Figure 9: Infrared Substrate Comparison (Wavelength Range for N-BK7 is Representative for the Majority of Substrates Used for Visible Wavelengths such as B270, N-SF11, BOROFLOAT®, etc.) ⁽³⁶⁾	28
Figure 10: A136 Variable gas cell 0.8-8 m.	30
Figure 11: Optics for a Long path gas cell ⁽³⁸⁾	31
Figure 12: Images on mirror M2 ⁽³⁸⁾	31
Figure 13: A typical chromatogram for a two component mixture. ⁽⁴²⁾	37
Figure 14: Sample injection-Valco 6 port valve. ⁽⁴⁹⁾	39
Figure 15: Cross section of the PDHID). ⁽⁵¹⁾	42
Figure 16: A basic permeation tube device ⁽⁵⁴⁾	45
Figure 17: A typical permeation system flow ⁽⁵⁵⁾	48
Figure 18: Top view of Bruker Tensor 27 FTIR showing various compartments ⁽⁵⁶⁾	52
Figure 19: Schematic of FTIR set up for experimental work	54
Figure 20: Plot of H_2O concentration versus cell temperature for glass cell	58
Figure 21: Typical permeation tube and permeation tube holder ⁽⁵⁸⁾	59

Figure 22: Typical FTIR spectra of H ₂ O indicating peaks selected for quantitation	61
Figure 23: Typical FTIR spectra of CH ₄ indicating peak selected for quantitation	63
Figure 24: Spectrum obtained for Standard 1	66
Figure 25: Overlay of Standard 1 with a >94% C ₂ H ₂ standard. The insert shows a close up of the peaks at 1350 and 1305 cm ⁻¹	66
Figure 26: Spectrum obtained for Standard 2	68
Figure 27: Spectrum obtained on analysing Standard 2 using CH ₄ as internal standard at 3017 cm ⁻¹	69
Figure 28: Spectrum obtained for Standard 3	70
Figure 29: Spectrum obtained on analysing Standard 3 with CH ₄ as internal standard at 3017 cm ⁻¹	71
Figure 30: In position A on the left, the sample loop is filled and in position B on the right, the contents of the loop are injected onto the column. ⁽⁵⁹⁾ ..	73
Figure 31: In position A on the left, the sample loop is loaded/column 1 is backflushed and in position B on the right, the sample is sent to the columns ⁽⁶⁰⁾	74
Figure 32: In position A on the left, the sample loop is loaded in the initial step and in the second step the heart cut is sent to the detector. In position B on the right, the loop contents are sent to the column in the initial step and in the second step the end cut is sent to waste. ⁽⁶¹⁾	75
Figure 33: Sample holder for CaC ₂ /H ₂ O reaction.....	79
Figure 34: Linear calibration curve for moisture at 3854 cm ⁻¹ with a working range between 0.514 and 9.890 ppm	81
Figure 35: Quadratic calibration curve for moisture at 3854 cm ⁻¹ with a working range 0.514 to 9.890 ppm.....	84
Figure 36: Linear calibration curve for CH ₄ at 3017 cm ⁻¹ with a working range between 0.198 and 4.729 ppm	87
Figure 37: Quadratic calibration curve for CH ₄ at 3017 cm ⁻¹ with a working range between 0.198 and 4.729 ppm	88

Figure 38: Linear calibration curve obtained for Standard 1 for C ₂ H ₂ at 3313/3266 cm ⁻¹	90
Figure 39: Linear calibration curve obtained for Standard 1 for C ₂ H ₂ at 1305 cm ⁻¹	90
Figure 40: Quadratic calibration curve obtained for Standard 1 for C ₂ H ₂ at 3313/3266 cm ⁻¹	92
Figure 41: Quadratic calibration curve obtained for Standard 1 for C ₂ H ₂ at 1305 cm ⁻¹	92
Figure 42: Linear calibration curve obtained for Standard 2 for C ₂ H ₂ at 3313/3266 cm ⁻¹	94
Figure 43: Linear calibration curve obtained for Standard 2 for C ₂ H ₂ at 1350 cm ⁻¹	94
Figure 44: Linear calibration curve obtained for Standard 2 for C ₂ H ₂ at 1305 cm ⁻¹	95
Figure 45: Quadratic calibration curve obtained for Standard 2 for C ₂ H ₂ at 3313/3266 cm ⁻¹	97
Figure 46: Quadratic calibration curve obtained for Standard 2 for C ₂ H ₂ at 1350 cm ⁻¹	97
Figure 47: Quadratic calibration curve obtained for Standard 2 for C ₂ H ₂ at 1305 cm ⁻¹	98
Figure 48: Linear calibration curve obtained for Standard 2 for C ₂ H ₂ at 3313/3266 cm ⁻¹ using CH ₄ as internal standard.....	100
Figure 49: Linear calibration curve obtained for Standard 2 for C ₂ H ₂ at 1350 cm ⁻¹ using CH ₄ as internal standard.....	100
Figure 50: Linear calibration curve obtained for Standard 2 for C ₂ H ₂ at 1305 cm ⁻¹ using CH ₄ as internal standard.....	101
Figure 51: Quadratic calibration curve obtained for Standard 2 for C ₂ H ₂ at 3313/3266 cm ⁻¹ using CH ₄ as internal standard.....	103
Figure 52: Quadratic calibration curve obtained for Standard 2 for C ₂ H ₂ at 1350 cm ⁻¹ using CH ₄ as internal standard.....	103
Figure 53: Quadratic calibration curve obtained for Standard 2 for C ₂ H ₂ at 1305 cm ⁻¹ using CH ₄ as internal standard.....	104

Figure 54: Linear calibration curve for Standard 3 for C ₂ H ₂ at 1313/3266 cm ⁻¹ with a working range between 94.804 and 291.265 ppm	106
Figure 55: Linear calibration curve for Standard 3 for C ₂ H ₂ at 1305 cm ⁻¹ with a working range between 94.804 and 291.265 ppm	106
Figure 56: Linear calibration curve for Standard 3 for C ₂ H ₂ at 1350 cm ⁻¹ with a working range between 94.804 and 291.265 ppm	107
Figure 57: Quadratic calibration curve for Standard 3 for C ₂ H ₂ at 1313/3266 cm ⁻¹ with a working range between 94.804 and 291.265 ppm	109
Figure 58: Quadratic calibration curve for Standard 3 for C ₂ H ₂ at 1350 cm ⁻¹ with a working range between 94.804 and 291.265 ppm	109
Figure 59: Quadratic calibration curve for Standard 3 for C ₂ H ₂ at 1305 cm ⁻¹ with a working range between 94.804 and 291.265 ppm	110
Figure 60: Linear calibration curve obtained for Standard 3 for C ₂ H ₂ at 3313/3266 cm ⁻¹ using CH ₄ as internal standard.....	112
Figure 61: Linear calibration curve obtained for Standard 3 for C ₂ H ₂ at 1350 cm ⁻¹ using CH ₄ as internal standard.....	112
Figure 62: Quadratic calibration curve obtained for Standard 3 for C ₂ H ₂ at 3313/3266 cm ⁻¹ using CH ₄ as internal standard.....	114
Figure 63: Quadratic calibration curve obtained for Standard 3 for C ₂ H ₂ at 1350 cm ⁻¹ using CH ₄ as internal standard.....	114
Figure 64: Examples of residual plots ⁽⁶²⁾	117
Figure 65: Typical excel regression data. Red/bold data indicates components used in calculations.	118

LIST OF TABLES

Table 1: FTIR window materials and properties ⁽²⁾	29
Table 2: Label descriptions for Figure 18	52
Table 3: FTIR Settings	56
Table 4: Dilution of moisture permeation standard to obtain calibration levels.....	60
Table 5: Dilution of CH ₄ reference standard to obtain calibration levels ..	63
Table 6: Dilution of Standard 1 using mass flow controllers and nitrogen as diluent	65
Table 7: Dilution of Standard 2 using mass flow controllers and nitrogen as diluent	67
Table 8: Dilutions of Standard 2 using mass flow controllers and 9.9 ppm CH ₄ standard in nitrogen as diluent	68
Table 9: Dilution of Standard 3 using mass flow controllers and nitrogen as diluent	69
Table 10: Dilutions of Standard 3 using mass flow controllers and 102 ppm CH ₄ standard as diluent	70
Table 11: Dilution of C ₂ H ₂ standard using mass flow controllers	77
Table 12: Summary of linear regression data for moisture standard: Confidence intervals for the intercept.....	81
Table 13: Summary of linear regression data for moisture standard: Regression data for t test.....	82
Table 14: Summary of linear regression data for moisture standard: LOD and LOQ values	83
Table 15: Summary of linear regression data for moisture standard: P values	83
Table 16: Summary of quadratic regression data for moisture standard: Regression data for t test.....	85
Table 17: Summary of quadratic regression data for moisture standard: LOD and LOQ values.....	86

Table 18: Summary of quadratic regression data for moisture standard: P values.	86
Table 19: Summary of linear regression data for Standard 1 (C ₂ H ₂): Confidence intervals of the intercept.	91
Table 20: Summary of linear regression data for Standard 1 (C ₂ H ₂): Regression data for t test.	91
Table 21: Summary of linear regression data for Standard 1 (C ₂ H ₂): LOD and LOQ values.	91
Table 22: Summary of linear regression data for Standard 1 (C ₂ H ₂): P values.	91
Table 23: Summary of quadratic regression data for Standard 1 (C ₂ H ₂): Confidence intervals of the intercept.	93
Table 24: Summary of quadratic regression data for Standard 1 (C ₂ H ₂): Regression data for t test.	93
Table 25: Summary of quadratic regression data for Standard 1 (C ₂ H ₂): LOD and LOQ values.	93
Table 26: Summary of quadratic Excel regression data for Standard 1 (C ₂ H ₂): P values.	93
Table 27: Summary of linear regression data for Standard 2 (C ₂ H ₂): Confidence intervals of the intercept.	95
Table 28: Summary of linear regression data for Standard 2 (C ₂ H ₂): Regression data for t test.	96
Table 29: Summary of linear regression data for Standard 2 (C ₂ H ₂): LOD and LOQ values.	96
Table 30: Summary of linear regression data for Standard 2 (C ₂ H ₂): P values.	96
Table 31: Summary of quadratic regression data for Standard 2 (C ₂ H ₂): Confidence intervals (no internal standard)	98
Table 32: Summary of quadratic regression data for Standard 2 (C ₂ H ₂): Regression data for t test (no internal standard)	98
Table 33: Summary of quadratic regression data for Standard 2 (C ₂ H ₂): LOD and LOQ values (no internal standard)	99

Table 34: Summary of quadratic regression data for Standard 2 (C ₂ H ₂): P values (no internal standard).....	99
Table 35: Summary of linear regression data for Standard 2 (C ₂ H ₂): Confidence intervals (with internal standard)	101
Table 36: Summary of linear regression data for Standard 2 (C ₂ H ₂): Regression data for t test (with internal standard).....	101
Table 37: Summary of linear regression data for Standard 2 (C ₂ H ₂): LOD and LOQ values (with internal standard).....	102
Table 38: Summary of linear regression data for Standard 2 (C ₂ H ₂): P values (with internal standard)	102
Table 39: Summary of quadratic regression data for Standard 2 (C ₂ H ₂): Confidence intervals (with internal standard)	104
Table 40: Summary of quadratic regression data for Standard 2 (C ₂ H ₂): Regression data for t test (with internal standard).....	104
Table 41: Summary of quadratic regression data for Standard 2 (C ₂ H ₂): LOD and LOQ values (with internal standard)	105
Table 42: Summary of quadratic regression data for Standard 2 (C ₂ H ₂): P values (with internal standard)	105
Table 43: Summary of linear regression data for Standard 3 (C ₂ H ₂): Confidence intervals (no internal standard)	107
Table 44: Summary of linear regression data for Standard 3 (C ₂ H ₂): Regression data for t test (no internal standard)	107
Table 45: Summary of linear regression data for Standard 3 (C ₂ H ₂): LOD and LOQ values (no internal standard)	108
Table 46: Summary of linear regression data for Standard 3 (C ₂ H ₂): P values (no internal standard).....	108
Table 47: Summary of quadratic regression data for Standard 3 (C ₂ H ₂): Confidence intervals (no internal standard)	110
Table 48: Summary of quadratic regression data for Standard 3 (C ₂ H ₂): Regression data for t test (no internal standard)	110
Table 49: Summary of quadratic regression data for Standard 3 (C ₂ H ₂): LOD and LOQ values (no internal standard).....	111

Table 50: Summary of quadratic regression data for Standard 3 (C ₂ H ₂): P values (no internal standard).....	111
Table 51: Summary of linear regression data for Standard 3 (C ₂ H ₂): Confidence intervals (with internal standard)	113
Table 52: Summary of linear regression data for Standard 3 (C ₂ H ₂): Regression data for t test (with internal standard).....	113
Table 53: Summary of linear regression data for Standard 3 (C ₂ H ₂): LOD and LOQ values (with internal standard).....	113
Table 54: Summary of Linear regression data for Standard 3 (C ₂ H ₂): P values (with internal standard)	113
Table 55: Summary of quadratic regression data for Standard 3 (C ₂ H ₂): Confidence intervals (with internal standard)	115
Table 56: Summary of quadratic regression data for Standard 3 (C ₂ H ₂): Regression data for t test (with internal standard).....	115
Table 57: Summary of quadratic regression data for Standard 3 (C ₂ H ₂): LOD and LOQ values (with internal standard)	115
Table 58: Summary of quadratic regression data for Standard 3 (C ₂ H ₂): P values (with internal standard)	115
Table 59: Comparison of moisture measurement techniques.....	126

CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1. Introduction

In a number of specialty gas applications, the analysis of water vapor, often referred to as moisture, is of high importance. The biggest driver for the development and advancement of trace moisture analysis techniques has, to date, been the microelectronics industry. The reason for this is that even trace levels of water in process gases can affect device performance and hence analytical techniques must be capable of detecting water vapor from ppmv right down to sub-ppbv levels.

More than 50 different gaseous chemical components are used in the production of various semiconductor devices. These are generally classified by their handling and distribution as either bulk or specialty gases. Bulk gases include nitrogen, oxygen, helium, argon and hydrogen, all gases which are relatively inert and nontoxic. These gases are used for purge procedures at large flow rates which include removal of residual components from previous process steps or purging of ambient components.⁽¹⁾

The challenge of measuring water vapor at trace levels is largely due to the adsorptive nature of the water molecule on metal and other surfaces. In addition, the range of gas matrices that can potentially interfere with the measurement process is huge and includes oxides, halides, hydrides, corrosive gases, hydrocarbons and many more. Over the years a range of techniques have been investigated as no single approach has been found that can meet all the analysis requirements. These include Gas chromatography (GC), mass spectrometry (MS), ion mobility spectrometry (IMS) and spectroscopic methods such as Fourier Transform infrared (FTIR), tunable diode laser absorption spectroscopy (TDLAS) and cavity ring down spectroscopy (CRDS).⁽²⁾

This project initially started with the development of a FTIR method for moisture analysis on Nitrogen Trifluoride (NF_3) gas produced at NECSA by the Pelchem plant facilities. The NF_3 production facility at the Pelchem site in Pelindaba, South Africa was constructed in the year 2000 with the purpose of producing NF_3 , the primary uses of which included chamber-cleaning gas in chemical vapor deposition semiconductor production processes and in liquid crystal display production processes. NF_3 is also used as an etchant in semiconductor manufacturing and provides the benefit of lower perfluorocarbon emissions as compared to alternate cleaning gases. The NF_3 facility at Pelchem was designed to supply grades of product for each of the afore mentioned applications. One of the Pelchem analytical specifications included low moisture content and a method was developed in-house, using FTIR, to determine the moisture content in NF_3 . The method utilized a BOMEM FTIR, a mercury cadmium telluride detector (MCT) and a two meter corrosive resistant long path gas cell. Method validation data sourced from internal validation documents indicated that a method detection limit (LOD) of 0.4 ppmv had been achieved for the measurement of moisture in NF_3 matrix. ⁽³⁾ Later studies performed at NECSA utilizing a similar system but with a ten meter gas cell replacing the original two meter gas cell and a deuterated triglycine sulphate detector (DTGS) and using helium as the matrix gas produced a LOD of 1.77 ppmv. ⁽⁴⁾ The discrepancy in these two LOD's could not be explained adequately specifically as the helium method should have produced a much lower LOD with the use of a longer gas cell path although the DTGS detector is less sensitive than the MCT detector.

Many queries had previously been received at PAL requesting analyses for moisture in various gas types and this together with the earlier validation results obtained by the Pelchem group for moisture analyses in NF_3 and PAL's results for moisture in helium led to the initiation of this study.

1.2. Purpose of the study

The purpose of this project was to develop methods by which low parts per million volume (ppmv) concentrations of moisture, specifically in gas samples, could be analyzed. Initially analysis of moisture would be performed using FTIR and a permeation standard. This method was to serve as both a comparative and backup method. This was to be followed by a process in which moisture present in gas samples was to be converted to acetylene (C_2H_2) or carbon dioxide (CO_2) and then analyzed by FTIR and gas chromatography (GC). The C_2H_2 or CO_2 results would then be calculated back to moisture values.

1.3. Objectives of the study

The first objective of this project was the setup of a FTIR for moisture analysis as both a comparative and backup method. For this method the moisture was to be read directly on FTIR without conversion to C_2H_2 or CO_2 .

The second objective of this project was the setup of a FTIR for C_2H_2 and CO_2 analysis. The purpose of this was to convert moisture in gas samples into C_2H_2 or CO_2 and analyzing using FTIR.

The third objective was the setup and optimization of a GC/ PDHID for C_2H_2 and CO_2 analysis. The purpose of this was to convert moisture in gas samples into C_2H_2 or CO_2 and analyzing using GC/PDHID.

The fourth objective was the design of a conversion system whereby the moisture in gas samples could be converted, stoichiometrically, to either C_2H_2 or CO_2 prior to analysis using GC/PDHID or FTIR.

The fifth objective of this project was based on the success of the conversion process. If the conversion was effective, method validation of the conversion methods would be undertaken and the methods implemented for commercial purposes in the laboratory.

Hypothesis

Hypothesis 1:

Is it possible to make use of an industrial process method to stoichiometrically convert the moisture in a gas sample to an organic compound such as C_2H_2 which is more readily analyzed on a GC than moisture?

Hypothesis 2:

Is it possible to make use of an industrial process method to stoichiometrically convert the moisture in a gas sample to a permanent gas type such as CO_2 which is more readily analyzed on a GC than water?

Hypothesis 3:

Is the analysis of C_2H_2 or CO_2 more effective than the analysis of moisture, due to the ingress of atmospheric moisture everywhere, using a FTIR as the analytical technique?

Hypothesis 4:

Can parts ppmv levels of moisture be detected using a FTIR with an eight meter path length glass cell and a MCT detector?

1.4. Importance of the study

A reliable and accurate method with which to measure moisture in gas samples is required for a laboratory wishing to specialize in gas analyses. Previous discussions with companies such as Afrox SA, who are currently only able to reach concentration levels of 1 ppm and greater on their moisture analyses in gas samples, led to the conclusion that this type of analyses is an urgent requirement in the gas industry. Conversion of moisture to acetylene should allow for small sample volumes to be used and ppmv values to be achieved using GC/PDHID. Larger samples would be required for FTIR analyses but in theory the conversion process should

be effective for these analyses using FTIR. Additionally it should be possible to set up a FTIR method for the direct analyses of moisture in the ppmv ranges although this method would require large amounts of sample as cell conditioning for moisture takes much longer than for an organic compound such as C_2H_2 .

CHAPTER 2: LITERATURE REVIEW

2.1. Introduction and background

Precise analysis of natural gas is important for determining the price, calorific value, identification of source and gas quality. In natural gas there are a number of components from C_1 to C_{10} hydrocarbons, including isomers. Their physical properties are similar and the composition ratio of major to minor components is high, making quantification by ordinary analytical means difficult. Two analytical methods most frequently used in the industry are ASTM D-1945 and GPA standard 2261 multi-column technique. These methods encompass the use of a ten port valve, two six port valves and several columns. Recently a simpler technique using an alternative system with two gas chromatographs (GC-GC) and four columns was introduced. In this system the first GC is equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) and the second GC is equipped with a TCD and a flame photometric detector (FPD). The FID was used to characterize hydrocarbons, the TCD for permanent gases such as oxygen, nitrogen, carbon dioxide and the FPD for sulfur components. Using these combined techniques, a complex mixture of C_1 to C_{10} hydrocarbons, permanent gases and sulphur compounds could be well characterized with good resolution and repeatability.⁽⁵⁾

Afore mentioned systems addressed the analyses and characterization of natural gas components and set the benchmark for this type of analyses. However, the detection limits obtained for these methods do not meet the requirements of the semiconductor industry where trace levels of impurities in high purity gases need to be determined. Quantification of trace levels was made possible by the introduction of the pulsed discharge helium ionization detector (PDHID) in 1992.⁽⁶⁾ It provided advantages with simple configuration, convenience, high sensitivity and good versatility. As helium passes through the ionization chamber, the analyte(s) eluting

through the GC capillary column are ionized by the helium metastables and photons and transfer the signal to the electrometer. Since the ionization potential of the metastable helium is higher than that of all species, with the exception of the argon ion, all other compounds can thus be ionized by the helium. For this reason the PDHID has become the most universal detector, capable of detecting H_2 , O_2 , CO_2 , H_2O as well as a variety of organic compounds ranging from light hydrocarbons to high molecular weight pesticides and metal complexes. Its sensitivity towards hydrocarbons is in the order of 1 pg s^{-1} .⁽⁵⁾ Introduction of the PDHID meant that the TCD and FID could effectively be replaced by one detector thus eliminating the complexities of using two different detectors.

According to Roberge et al,⁽⁷⁾ a PDHID was used, under appropriate separation conditions, to detect hydrogen and methane from the matrix components of human breath samples. The sensitivity of this method is over an order of magnitude better than published methods using a FID and a TCD and has an additional advantage of detecting both analytes with only one detector. Limits of detection (LOD) were 0.3 ppm for both hydrogen and methane and the method had a linear dynamic range (LDR) of three orders of magnitude ($0.3 - 400 \text{ ppm, v v}^{-1}$). The PDHID was also compared to the FID and TCD with regards to selectivity, sensitivity and reproducibility for high-speed gas chromatography (HSGC). It was shown that the PDHID is as sensitive as the FID for fast separations but was limited by the difficulty of resolving analyte peaks from O_2 and N_2 matrices. The PDHID was at least three orders of magnitude more sensitive than the TCD for all analytes examined⁽⁷⁾

Although the PDHID allowed for simplification of the analytical method and detection at low concentrations, other problems were encountered with the determination of trace impurities in pure gases. GC/PDHID systems with packed columns are commonly used in this role because of their universal detection capability and high sensitivity. The challenge of this analysis is

the difficult separation and quantitation of trace impurities often eluting adjacent to or within the peak of the main component/matrix. One solution is the removal of the matrix by separators but this is only applicable for a limited number of gases and is often not cost effective due to the limited lifetime of the separators. Additionally, interference between the separator and gas molecules has been observed. An alternative method is the use of multiple capillary columns and column switching techniques. The separation of the trace impurities and the matrix was also improved by the use of capillary columns in place of packed column. However, the matrix still flowed through the analytical column to the detector saturating both the columns and PDHID with the matrix. In addition, trace levels of impurities remained embedded in the shoulder of the matrix peak making detection and quantitation difficult ⁽⁸⁾

A unique system was designed by which the trace impurities were separated from the matrix in a pre-column by venting the matrix before the target compounds eluted. The trace impurities (together with a small portion of the matrix) were then transferred onto a second column for further separation. This technique, referred to as “heart cutting and back flushing”, was employed on a system equipped with three two-position valves, a two way solenoid valve and four packed columns. This configuration enabled detection and quantitation of trace impurities without interference from peak tailing by the matrix. This method has been applied to H₂, Ar and N₂ respectively. A method detection limit of 100 nl l⁻¹ was achieved and a dynamic range of 100 - 1000 nl l⁻¹ was obtained for methane in argon ⁽⁸⁾

Now that it has been determined that it is possible to analyze effectively for various components such as permanent gases and hydrocarbons at trace levels in high purity gases, the question arises “How to analyze effectively for trace levels of moisture in high purity gases?”

Fourier Transform Infrared (FTIR) spectroscopy is an analytical method that can be optimized for the analysis of corrosive gases and in addition is capable of detecting low ppb levels of water vapor. The detection limit of FTIR spectroscopy combined with classical least squares multivariate calibration is about 20 ppb when using a one meter path length cell and a one minute collection time. Longer collection times or a longer path length cell will provide greater sensitivity but both these options will result in slower measurement speeds. The user can thus trade off speed for sensitivity depending on individual situations. ⁽⁹⁾

An infrared method for the measurement of the moisture content of hydrocarbons in the ppmv range was developed using the conversion of moisture to C_2H_2 with calcium carbide (CaC_2) followed by a subsequent transfer, using a dry carrier gas, of the C_2H_2 , to the infrared cell where it was re-dissolved into carbon tetrachloride and measured. The reason for the conversion of the moisture to C_2H_2 in the hydrocarbon was to eliminate background absorption by the hydrocarbon. ⁽¹⁰⁾

Other instrumental methods currently being used, or in development, for measuring trace moisture at ppbv levels include tunable diode laser absorption spectroscopy (TDLAS), cavity ring-down spectroscopy (CRDS) and intracavity laser spectroscopy (ILS). In addition, sensor-based technologies such as oscillating quartz crystal microbalances, chilled mirror-, capacitor-, and electrolytic-based hygrometers operate in this area. The success of each trace moisture method is dependent on the degree to which the different process gases interfere with the measurement process.

Very few references were found with regards to the analysis of moisture using gas chromatography. R.P. Badoni and A. Jayaraman ⁽¹¹⁾ analyzed for moisture using a gas chromatograph coupled to a Thermal Conductivity Detector (GC/TCD) but this was only really effective for water contents greater than 50%. California Environmental Protection Agency (CEPA)

brought out a standard operating procedure (SOP) for the determination of moisture in consumer products using a GC/TCD.⁽¹²⁾ This method has a detection limit of 1.0 mg ml⁻¹.

J. Albert et al⁽¹³⁾ developed a method whereby mineral oil was analyzed for dissolved gases, H₂, O₂, N₂, CO, CO₂, CH₄, C₂H₆, C₂H₄, C₂H₂ and C₃H₈, using static headspace capillary gas chromatography (HSGC). High voltage transformers are susceptible to malfunctions such as arcing, overheating and partial discharges, which always result in the chemical decomposition of the mineral oil and cellulose insulation. Several gases, totally or partially dissolved in the oil, are produced. A headspace sampler device was used to equilibrate the sample species in a two phase system under controlled temperature and agitation conditions. A portion of the equilibrated species was then automatically split-injected into two chromatographic channels mounted on the same GC for separation. The hydrocarbons and the lighter gases were separated on the first channel by a GS-Q column coupled with a Molsieve 5-A column via a bypass valve, while the moisture was separated on the second channel using a Stabilwax column. The analytes were detected using two PDHID's. The performance of the method was established using equilibrated vials containing known amounts of gas mixture, water and blank oil. Detection limits for the method were established between 0.08 µl l⁻¹ and 6 µl l⁻¹ for the dissolved gases, excluding O₂, N₂ and CO₂ where higher values were observed mostly due to air ingress during sampler operations, and detection limits of 0.1 µg g⁻¹ were established for the dissolved water. Ten consecutive measurements in the high and low levels of the calibration curves showed a precision better than 12% and 6% respectively in all cases. Figure 1 below depicts the experimental setup for this process.

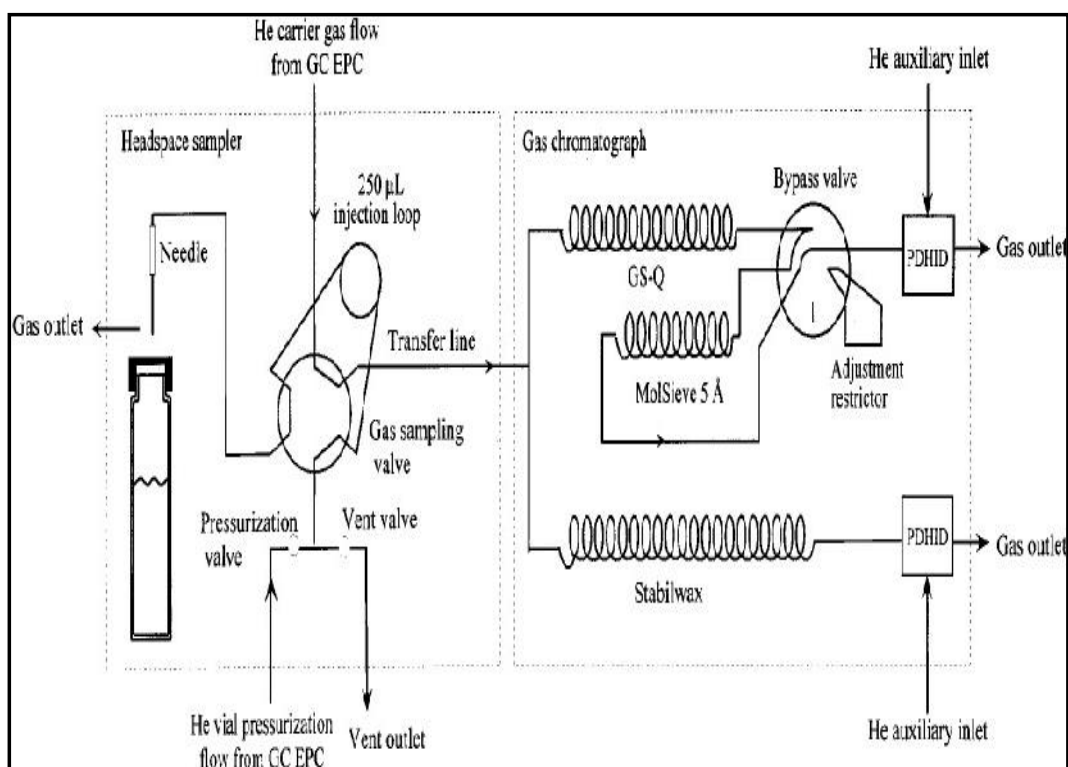


Figure 1: Schematic diagram of the equipment used for simultaneous determination of dissolved gases and moisture by the HS-GS technique. This represents the standby position. ⁽¹³⁾

The FTIR is an obvious choice as there are currently methods available for this technique with regards to moisture analysis and these go down to ppb levels. ⁽⁹⁾ The drawback of FTIR is that a fairly large amount of sample is required for the analysis and this is not always available.

Since a PDHID is 500 times more sensitive than a TCD and 50 times more sensitive than a FID ⁽⁸⁾, why not consider this as an option for moisture analysis? The PDHID is a universal detector and can be used for the analysis of certain gases that cannot be detected by an FID e.g. O₂, N₂, Ar, CO and CO₂ and its sensitivity makes it a potentially better choice than a TCD.

The drawback to the PDHID is that exposure to moisture adversely affects its performance. This leads to an alternative suggestion and the pivot on which this proposal is based.

Was it possible to convert the moisture, at whatever levels present in a gas sample, to an alternative component that can be effectively analyzed by a PDHID? Two industrial processes are to be considered for this proposal:

Acetylene production

Calcium carbide is produced industrially in an electric arc furnace from a mixture of lime and coke at approximately 2000°C. The reaction is as follows:



One of the applications that CaC_2 is used for industrially is the production of acetylene. The reaction was discovered by Friederich Wöhler ⁽¹⁴⁾ in 1862 and the reaction equation is as follows:



This reaction is the basis of the industrial manufacture of acetylene and is the major industrial use of calcium carbide.

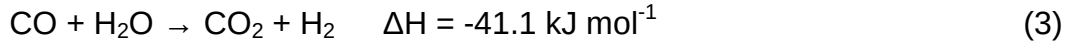
The question arose “Is it possible to make use of this equation to design a reaction vessel, containing calcium carbide which can be forced to react stoichiometrically with moisture from a gas sample, at room temperature, to produce acetylene which can then be analyzed using a GC/PDHID system.

Water gas shift reaction

Another industrial application which may allow for the conversion of moisture to a compound easily analyzed by GC is the water gas shift reaction (WGSR).

The WGSR is an important industrial reaction for the production of chemicals and/or hydrogen. It is an exothermic, equilibrium limited reaction that shows decreasing conversion with increasing temperature. A catalyst

is required at temperatures below 600°C because of the lower reaction rate at low temperatures. ⁽¹⁵⁾ The reaction equation is as follows:



Bustamante et al ⁽¹⁵⁾ experimented with both Inconel (mixture of 72% Nickel, 17% Chromium and 10% Iron) and quartz reactors and found that conversions were very high for small residence times and that these conversions were two orders of magnitude greater using the Inconel reactor compared to the quartz reactor. The result implied that the metal walls of the Inconel reactor catalyzed the reaction. See figure 2 below.

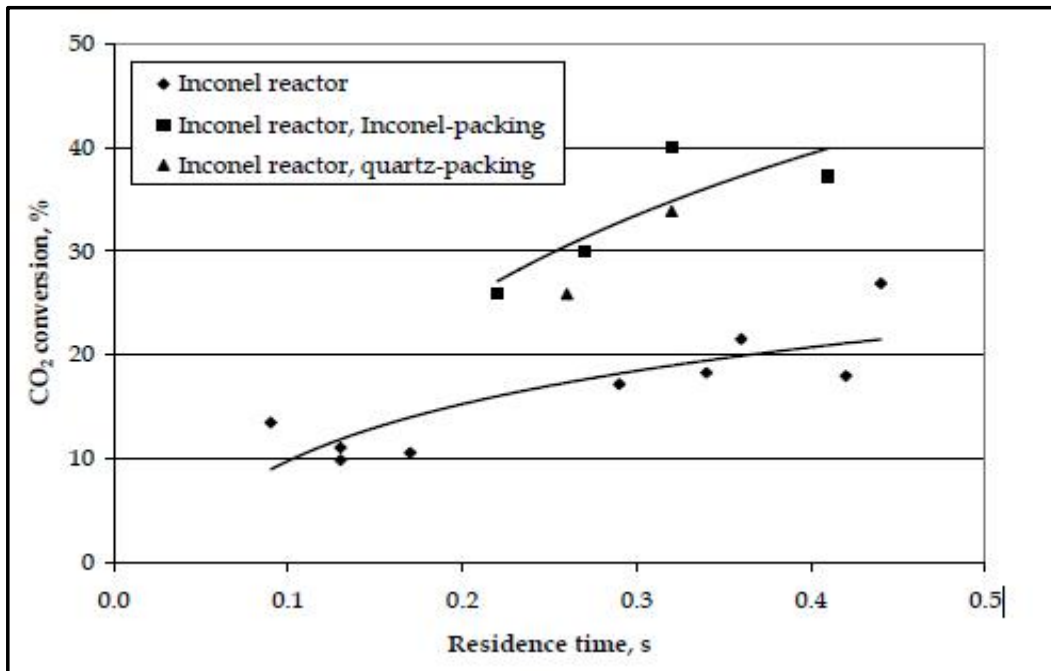


Figure 2: Reverse water gas shift reaction in an Inconel reactor. 900°C, ambient pressure, $[\text{H}_2]_0 = [\text{CO}_2]_0$. Equilibrium conversion for these conditions is 55%. ⁽¹⁵⁾

According to A. Luengnaruemichai et al ⁽¹⁶⁾ there are two types of WGS catalysts which are used commercially. The high temperature shift catalyst is made up of oxides of iron and chromium and is used between 400 - 500°C and will reduce the carbon monoxide to between 2 - 5%. The second catalyst, which is the one being considered for this project, is a low

temperature shift catalyst composed of copper, zinc oxide and alumina and is used between 200 - 400°C to reduce the carbon monoxide concentration to about 1%. The thermodynamics of the WGS reaction are well known in that at high temperatures the conversion is equilibrium limited and at low temperatures it is kinetically limited. Commercially, a combination of the two catalysts is used with in-between cooling. If more active low temperature shift catalysts can be found, the conversion can then approach the equilibrium limit more closely. ⁽¹⁵⁾ The question is whether these catalysts can be used together with the water gas reaction to produce stoichiometric amounts of carbon dioxide and/or hydrogen from a gas sample containing moisture, both of which can be analyzed using GC/PDHID.

2.2. Methods for moisture analysis

A number of methods have evolved over the years with regards to moisture analyses. The method most commonly used is the gravimetric drying process which is the most basic and most time consuming of all the available methods. It is also restricted as it principally determines loss on drying and not necessarily the water content. Apart from water, other volatile components of the sample and/or decomposition products are also determined.

Titration methods, in contrast to drying methods, are very specific. Karl Fischer developed the KF titration with which both bound and free water can be determined. The method works over a wide range of concentrations from ppm to % levels. It is based on the Bunsen Reaction, used for the determination of sulfur dioxide in aqueous solutions:

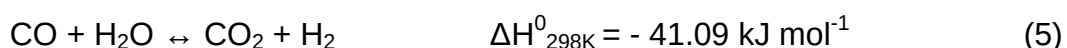


In modern synthetic chemistry dehydration procedures are often performed to ensure experimental reproducibility when water sensitive reagents are used. Despite these precautions, water's pervasiveness,

solubility and propensity to physisorb on reaction vessel surfaces lead to the question “How dry is dry” and this proves difficult to answer if an accurate determination of trace water contaminant at the μg level is required. ⁽¹⁷⁾ Sun et al ⁽¹⁷⁾ have developed a method where the potent dehydrating ability of difluoro(aryl)- λ^3 -iodanes is exploited to develop a convenient ^{19}F -NMR-based aquametry method that is more sensitive than coulometric Karl Fischer titration.

2.3. Chemical processes involving moisture

The Water Gas Shift Reaction (WGSR) is a reaction traditionally used for the production of Hydrogen (H_2) from synthesis gas. The hydrogen is then used for ammonia production in the fertilizer industry, for a variety of operations in the refinery industry and more recently as fuel for power generation and transportation. The reaction is expressed as follows:



The reaction is a moderately exothermic, reversible reaction. The catalyst used initially contained iron and chromium and was capable of catalyzing the reaction at 400 to 500°C and it reduced the exit carbon monoxide content to about 3%. The equilibrium constant for the reaction decreases with increasing temperature. The reaction is thermodynamically favored at low temperatures and kinetically favored at high temperatures. The reaction is also not affected by pressure as there is no change in volume from reactants to products. ⁽¹⁸⁾

Both metals and metal oxides can be used to catalyze the WGSR. Catalysts are classified into two categories namely “High Temperature Shift” catalysts and “Low Temperature Shift” catalysts. The “High Temperature Shift Catalysts are typically an iron oxide chromium oxide catalyst which functions in the range of 310 to 450°C and produce an exit composition of carbon monoxide (CO) at 2 to 4% as the temperature increases but at lower temperatures these catalysts lose their activity. The

“Low Temperature Shift” catalysts are typically copper based catalysts which function at 200°C and can achieve exit composition of CO concentrations at 0.1 to 0.3%. Commercially the WGSR is carried out in two adiabatic stages namely the high temperature shift followed by the low temperature shift with inter-cooling to maintain the inlet temperature. This configuration is necessary as the copper based catalyst is easily poisoned by sulphur compounds coming off the coal or hydrocarbon sources used while the iron based catalysts are sulphur tolerant. Both types of catalysts are commercially available.⁽¹⁸⁾

Acetylene was once a major raw material used for the production of synthetic chemicals such as vinyl chloride, vinyl acetate, acrylonitrile and acetaldehyde. In the mid 1960's, however, acetylene use began to be replaced by ethylene produced from low cost petroleum. Today the major chemical applications for acetylene are for the production of vinyl chloride monomer and 1, 4 butanediol. Non chemical applications include welding and cutting of metals and the production of carbon for batteries. In the United States, the majority of acetylene produced is used as chemical feedstock. It is difficult to transport and is generally used at or near its production site because of its high flammability and combustion heat.⁽¹⁹⁾

Pure acetylene is a colorless, odorless gas. Technical grade acetylene has garlic like odor, attributable to contamination by impurities. Some of these impurities include divinyl sulfide, ammonia, phosphine, arsine, methane, hydrogen sulphide and many others.⁽²⁰⁾

A number of high temperature processes for the production of acetylene have been commercialized via cracking reactions in the 1000 to 1600°C temperature range or synthesis reactions at temperatures above 1600°C. These include a number of processes such as partial oxidation where methane, LPG or light gasolines are pyrolyzed to cracked gases containing acetylene, electric or plasma arc whereby light hydrocarbons are cracked into acetylene using an electric arc and the calcium carbide process where

acetylene is generated by the reaction between calcium carbide and water.

The classical commercial route to acetylene is the calcium carbide route in which lime is reduced by carbon (in the form of coke) in an electrical furnace to yield calcium carbide:



The calcium carbide is then hydrolyzed to produce acetylene:



There are two principal methods for producing acetylene from calcium carbide and these are based on the type of generator used. In the wet generator, the reaction takes place in a cylindrical water shell attached below a carbide feed hopper. The carbide is fed into the water reservoir at a controlled rate until the reaction has run to completion. Calcium hydroxide is obtained as a byproduct in a slurry form containing 10 to 20% hydroxide. For larger scale plants, the dry generation design is more common. This design features a continuous feed of carbide mixed with sufficient water to complete the reaction as well as dissipate the heat generated by the reaction. Typically, a kg of water is used per kg of carbide. The reaction heat is dissipated by water evaporation, leaving a residue of powdered calcium hydroxide with a moisture content of 1 to 6%. Both processes yield acetylene with approximately 99.6% purity by volume after a light scrubbing.⁽¹⁹⁾

2.4. Infrared spectroscopy

Introduction

Infrared spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. A sample is positioned in the path of an IR beam and its absorption of various IR frequencies is measured. This enables determination of the different

chemical functional groups in the sample, as each functional group type absorbs characteristic frequencies of IR radiation. Infrared spectroscopy allows for the analysis of gases, liquids and solids making it a versatile and popular technique with which to determine structural elucidation as well as compound identification.⁽²¹⁾ However, since FTIR functionality is based on the principle that almost all molecules absorb infrared light, monoatomic gases such as He, Ne, Ar and homo-polar diatomic molecules such as H₂, N₂ and O₂, all of which do not absorb infrared light as they do not have dipolar moments, cannot be analyzed or identified using infrared spectroscopy.⁽²²⁾

The term “electromagnetic spectrum” refers to the collection of radiant energy which stretches from cosmic rays to X-rays to visible light to microwaves. Each of these can be considered as wave or particle travelling at the speed of light and each of these waves differ from each other with respect to length and frequency.⁽²¹⁾ See Figure 3 below.

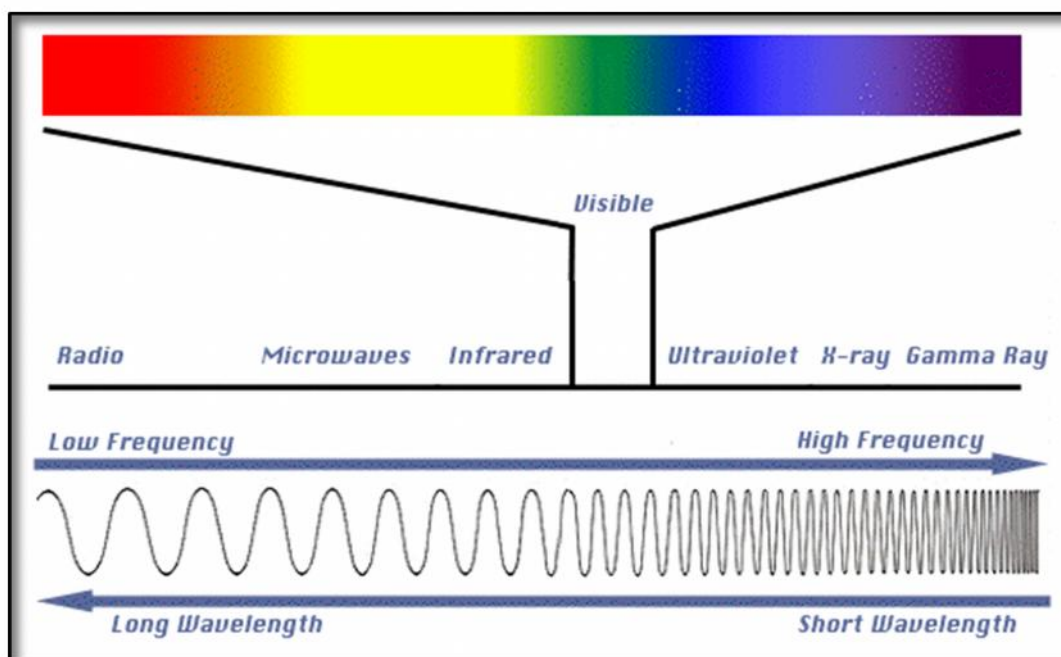


Figure 3: The electromagnetic spectrum⁽²³⁾

Frequency refers to the number of wave cycles that pass through a point in one second. It is measured in Hertz (Hz) where $1\text{Hz} = 1 \text{ cycle sec}^{-1}$. Wavelength is the length of one complete wave cycle. It is measured in centimeters (cm). Wavelength and frequency are inversely related as indicated below: ⁽²¹⁾

$$\nu = c / \lambda \text{ and } \lambda = c / \nu \quad (8)$$

Where:

c = speed of light ($3 \times 10^{10} \text{ cm sec}^{-1}$)

ν = frequency in Hz

λ = wavelength in cm

Energy is related to wavelength and frequency as follows:

$$E = h\nu = hc / \lambda \quad (9)$$

Where: h = Planck's constant ($6.6 \times 10^{-34} \text{ joules sec}^{-1}$)

The infrared section of the electromagnetic spectrum is divided into three regions namely the near, mid and far infrared regions. Near-IR is a high energy region ($14000 - 4000 \text{ cm}^{-1}$ or $0.8 - 2.5 \mu\text{m}$ wavelength) which can excite overtone or harmonic vibrations. The mid-infrared ($4000 - 400 \text{ cm}^{-1}$ or $2.5 - 25 \mu\text{m}$) is used to study the fundamental vibrations and associated rotational-vibrational structure while the far-infrared ($400 - 10 \text{ cm}^{-1}$ or $25\text{-}1000 \mu\text{m}$) has low energy and is used for rotational spectroscopy. ⁽²⁴⁾

Theory of infrared absorption

All atoms that are in a bonded state tend to vibrate. The only time vibration does not occur is when an atom in the bonded state is at zero degrees Kelvin. These vibrations typically take place at 10^{-15} seconds. Infrared spectrometry analyzes the number of infrared photons as well as the

amount of energy present in infrared photons absorbed by the molecule.
(25)

Absorption of IR is only possible in compounds with small energy differences in the possible vibrational and rotational states. A molecule will only absorb IR if the vibrations or rotations within the molecule cause a net change in the dipole moment of the molecule. Electromagnetic radiation is made up of oscillating electrical and magnetic fields which are perpendicular to each other. The electrical field of the radiation interacts with fluctuations in the dipole moment of the molecule and if the frequency of the radiation matches the vibrational frequency of the molecule, then radiation is absorbed and the amplitude of molecular vibration changes.
(26)

Molecular vibrations are classified into two types, stretching and bending. A molecule made up of n atoms has a total of $3n$ degrees of freedom which corresponds to the Cartesian coordinates of each atom in the molecule. In a nonlinear molecule, 3 of these degrees are rotational and 3 are translational and the rest correspond to fundamental vibrations, while in a linear molecule, 2 degrees are rotational and 3 are translational. Therefore a nonlinear molecule has " $3n-6$ " degrees of freedom and a linear molecule has " $3n-5$ " degrees of freedom.⁽²¹⁾

Water is a nonlinear molecule and has three fundamental vibrations indicated below in Figure 4.

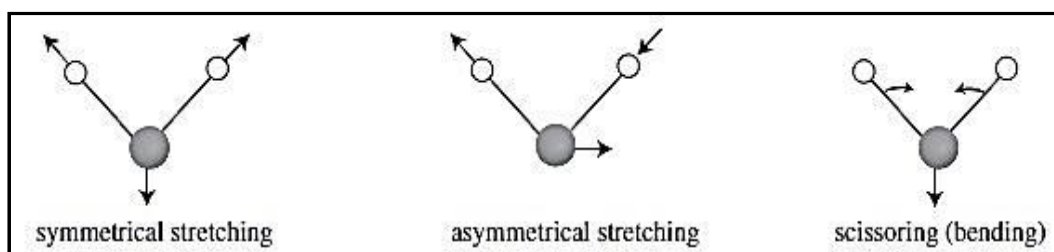


Figure 4: Stretching and bending vibrational modes for H_2O ⁽²¹⁾

Carbon Dioxide is a linear molecule and therefore will have four fundamental vibrations as seen in Figure 5 below.

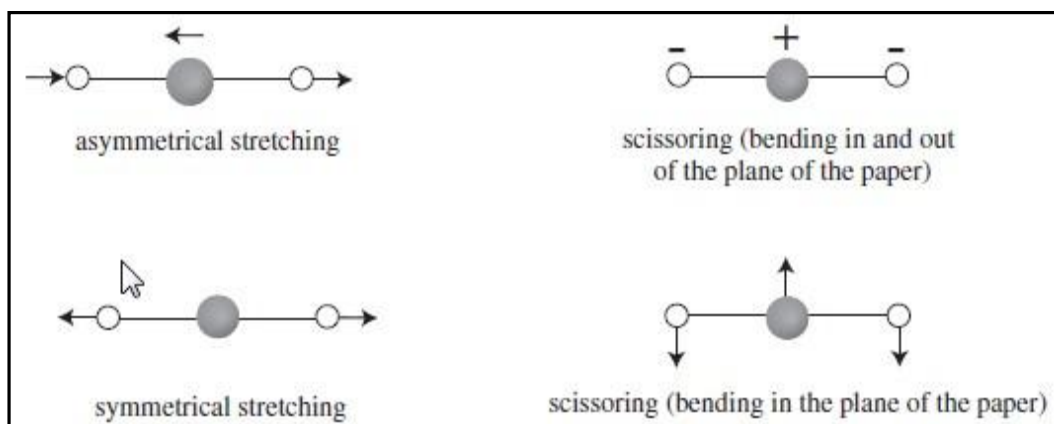


Figure 5: Stretching and bending vibrational modes for CO₂ ⁽²¹⁾

A molecule has a number of vibrational energy states, the lowest being the ground vibrational state and anything above that is referred to as an excited vibrational state. When a molecule absorbs a photon of light, it gains energy and moves from ground state to an excited state. This is not a physical movement as such but rather an increase in the average bond length of the molecule. Atoms in a molecule undergoing stretching will move further apart while atoms in a molecule that is bending will undergo a change in the bending angle when photon absorption occurs.

Since vibrational state energies are quantized, a molecule can only absorb specific photons with specific energies in an attempt to change its vibrational energy state. The following equation is used to calculate the change in energy between two vibrational states: ⁽²⁵⁾

$$\Delta E = h\nu \quad (10)$$

Where:

ΔE = change in energy between two vibrational states

ν = frequency of the photon (cm⁻¹)

h = Planck's constant (6.626×10^{-34} Hz)

IR stretching frequencies are controlled by the functional group and for this reason IR spectrometry can be used to determine which functional groups are present or absent in a molecule. The stretching frequency can be explained by Hooks Law which relates to the manner in which masses on a spring behave. The atoms in a molecule can be regarded as mass pieces and the bond between the atoms as a spring, and the greater the number of electrons shared between the atoms, the greater the resistance of the atoms to being pulled apart. Thus the higher the bond order, the higher the spring stiffness and the higher the stretching frequency. ⁽²⁵⁾

The energy change between molecular vibrational states is based on the bond order and the masses of the bonded atoms. Functional groups are described by the bond order and the masses of the bonded atoms. Functional groups in a molecule can therefore be predicted by recognizing common patterns of IR absorption i.e. the amount and wave number of photons. ⁽²⁵⁾

The general regions of the infrared spectrum in which various kinds of vibrational bands are observed are outlined in Figure 6 below. The blue colored sections refer to stretching vibrations and the green colored bands indicate bending vibrations. The infrared spectra in region of 1450 to 600 cm^{-1} is generally very complex making it difficult to assign all absorption bands but due to the unique patterns found in this region, it is often referred to as the fingerprint region. Absorption bands in the 4000 to 1450 cm^{-1} are usually due to stretching vibrations of diatomic units and this is often referred to as the group frequency region. ⁽²⁷⁾

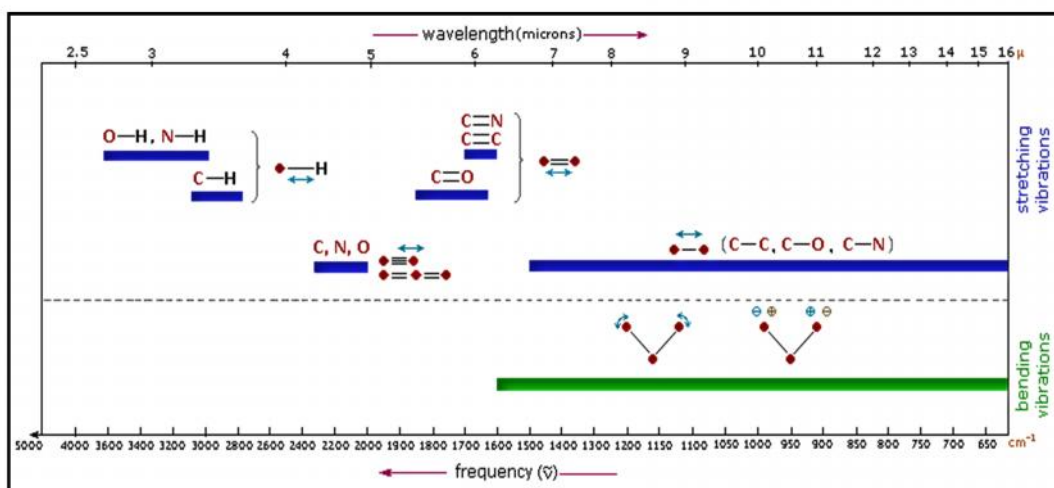


Figure 6: General regions of the IR spectrum ⁽²⁷⁾

Instrumentation

Dispersive spectrometers were introduced in the mid 1940's and were later followed by FTIR spectrometers. A FTIR spectrometer is able to collect all wavelengths simultaneously unlike the dispersive instrument which collects each wavelength sequentially. ⁽²⁸⁾ FTIR spectrometry is a technique based on the interference of radiation between two beams, to provide an interferogram. An interferogram is defined as the signal produced as a function of the change of path length between the two beams. ⁽²⁹⁾

A FTIR system is made up of three basic components, a radiation source, an interferometer and a detector as per Figure 7.

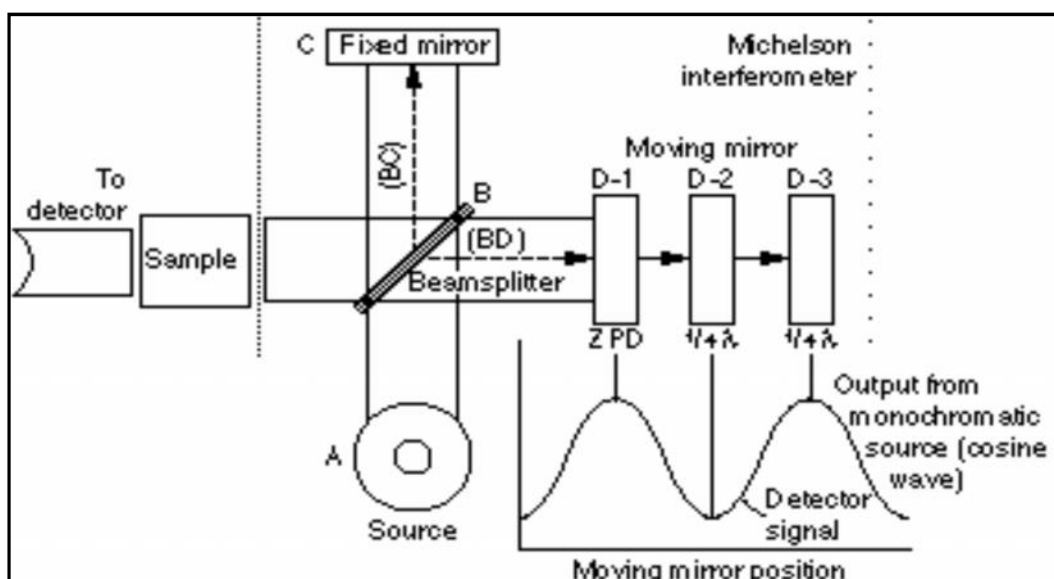


Figure 7: Simplified optical layout of a typical FTIR spectrometer. ⁽²⁸⁾

Interferometer

The most commonly used interferometer is the Michelson interferometer (See Figure 8). The interferometer consists of a beam splitter, a fixed mirror and a moving mirror. ⁽³⁰⁾ The mirrors are perpendicular to each other. ⁽²⁸⁾ The beam splitter is made of a material which transmits half the radiation striking it and reflects the other half. Typically a beam splitter is made by depositing a thin film of germanium onto a flat potassium bromide (KBr) substrate. ⁽²⁸⁾ Radiation from the source strikes the beam splitter and separates into two beams. One beam is transmitted through the beam splitter to the fixed mirror and the second is reflected off the beam splitter to the moving mirror. ⁽³⁰⁾ A path difference between the beams is introduced and the beams are then recombined. In this way, interference between the beams is obtained and the intensity of the output beam from the interferometer can be monitored as a function of path difference using an appropriate detector. ⁽³¹⁾

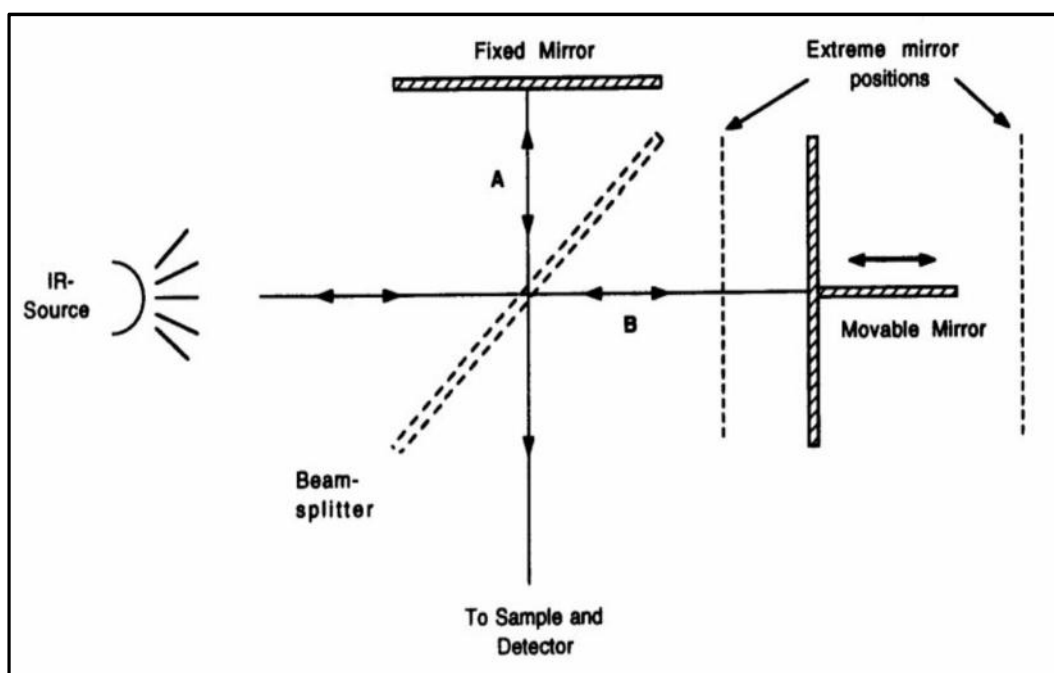


Figure 8: Schematic diagram of the optical layout of a Michelson interferometer⁽³¹⁾

Radiation source

FTIR spectrometers make use of a Globar or Nernst source for the mid-infrared region. A high pressure mercury lamp is used for the far-infrared region and tungsten-halogen lamps are used as sources for the near-infrared regions.⁽²⁹⁾

The Nernst glower is able to reach temperatures of up to 1500°C. It is made up of a fused mixture of oxides of zirconium, yttrium and thorium, molded into hollow rod shapes, approximately 1 - 3 mm in diameter and 2 - 5 cm in length. The rod ends are cemented to short ceramic tubes for easy mounting and short platinum leads provide power connections. Nernst glowers must be preheated to be conductive as they have a negative coefficient of resistance. They therefore require auxiliary heaters as well as a ballast system to prevent overheating. The energy output is predominantly concentrated between 1 and 10 μm , with relatively low

energy beyond 10 μm . Radiation intensity is double that of a Globar source with the exception of the near-infrared region.⁽³²⁾

A Globar typically has intermediate characteristics between heated wire coils and the Nernst glower. In comparison to the Nernst glower, the Globar is a less intense source below 10 μm , comparable between 10 to 15 μm and superior beyond 15 μm . It is made up of a silicon carbide rod, 6 - 8 mm in diameter, is self-starting and has an operating temperature of approximately 1300°C. In contrast to the Nernst glower, the Globar has a positive temperature coefficient of resistance and can be controlled with a variable transformer. The resistance of a Globar increases with time and provision must therefore be made for increasing the voltage across the unit. The spectral output of the Globar is roughly 80% that of a blackbody radiator.⁽³²⁾

Detector

Infrared detectors are classified into two types namely thermal and photon detectors. With photon detectors, radiation is absorbed within the material by interaction with electrons. The changed electronic energy distribution results in an electrical output signal which can be detected. Photon detectors are advantageous in that they show a selective wavelength dependence of the response per unit incident radiation power, have perfect signal to noise performance and a very quick response. The disadvantages of these detectors are that they require cryogenic cooling making them bulky and tedious to use.⁽³³⁾

Thermal detectors, in contrast to photon detectors, absorb incident radiation to change the temperature of the material, resulting in changes in physical properties which generate an electrical output. Thermal effects are generally independent of wavelength and depend on the radiant power and not on spectral content. Thermal detectors typically operate at room temperatures and are usually characterized by modest sensitivity and a response slower than that of the photon detectors.⁽³³⁾

The photon type detector of choice for this project was the Mercury cadmium telluride (MCT) detector so named for the mercury/telerium and cadmium/telerium detection element it contains. Because of its high response speed, there is no change in sensitivity with the standard mirror speed making this detector suitable for applications that require measurement over a short period of time. In addition, an MCT detector has a D^* value at least ten times larger than that obtained by a thermal detector. The D value is an indicator of performance and is defined as follows: ⁽³⁴⁾

$$D = 1/NEP \quad [\text{Hz}^{1/2}/\text{W}] \quad \text{and} \quad (11)$$

$$D^* = D/A^{1/2} \quad [\text{cm Hz}^{1/2}/\text{W}] \quad (12)$$

Where NEP is defined as *noise equivalent power* and is the incident power that gives signals for which the S/N ratio is 1. Signals smaller than 1 cannot be detected indicating that the lower the NEP of a detector, the more efficient its S/N characteristics are. Because the D^* value of the MCT detector is larger than that of a thermal detector, it's suitable for measurements associated with low levels of intensity such as measurements performed with long-path gas cells. High levels of light intensity on the other hand, may cause false peaks in the region below 650 cm^{-1} as there will be a nonlinear relationship created between the light incident on the detector and the output voltage. In this case, the light intensity will need to be reduced by for example, changing the aperture settings. ⁽³⁴⁾

Windows

The flow path of the sample in a FTIR system is fairly simple up to the point where the sample gas comes into contact with such parts as the O-rings, gas cell, optical windows and mirrors. The material for the windows and its transmission range determines the output for the detector. See

Figure 9. The correct window for the required application must be able to withstand the chemical environment while simultaneously having a wide enough transmission range for the selected analysis. ⁽²⁾

There are many types of infrared window materials to choose from and each type has its own characteristics. The most pertinent points to consider when choosing infrared windows are the following: spectral range, chemical properties of the sample versus that of the window, physical properties of the window and costs. ⁽³⁵⁾

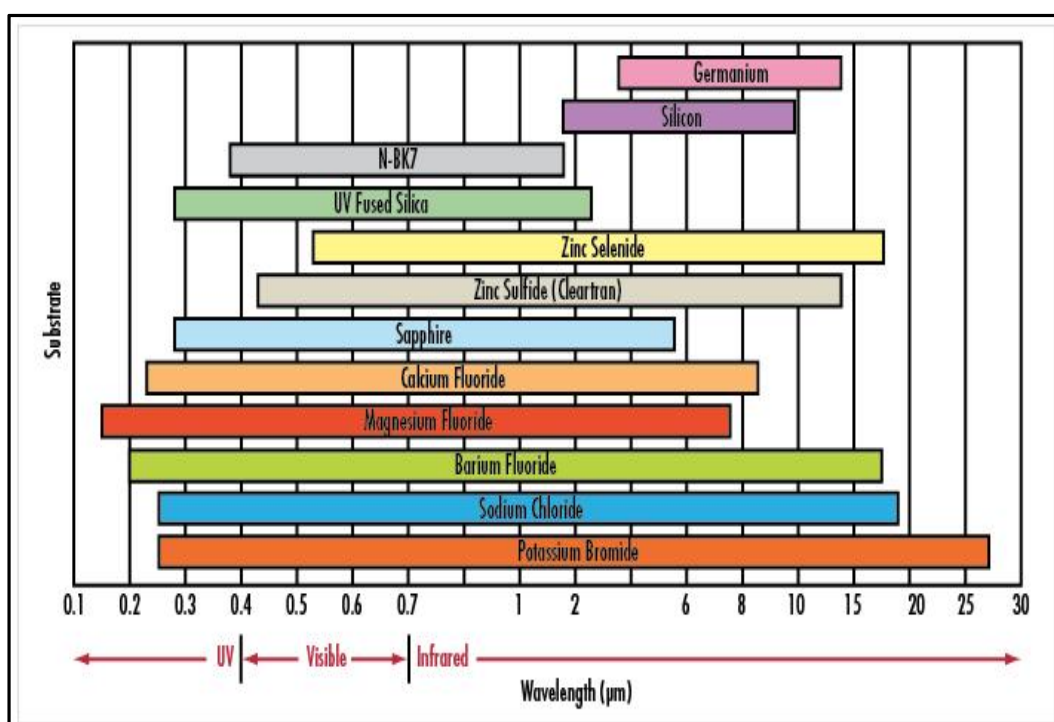


Figure 9: Infrared Substrate Comparison (Wavelength Range for N-BK7 is Representative for the Majority of Substrates Used for Visible Wavelengths such as B270, N-SF11, BOROFLOAT®, etc.) ⁽³⁶⁾

Table 1: FTIR window materials and properties ⁽²⁾

Material Description	Chemical Name	Transmission range (cm ⁻¹)	Refraction Index	Description
AMTIR-1	Ge-As-Se	13,333-714	2.606	Insoluble in H ₂ O; Expensive
Barium Fluoride	BaF ₂	50,000-869	1.46	Sensitive to thermal shock; insoluble H ₂ O; resistant to fluorine and fluorides
Calcium Fluoride	CaF ₂	66,667-1,111	1.40	Low solubility; insoluble in H ₂ O; resistant to most acids and alkalides; not to be used with NH ₃ salts
Cesium Iodide	CsI	6,667-200	1.74	Hygroscopic; easily scratched
Germanium	Ge	5,000-869	4.0	Chemically inert; hard and brittle and tends to fracture
Magnesium Fluoride	MgF ₂	90,909-1,333	1.37-1.38	More soluble than CaF ₂ ; sensitive to thermal shock
Potassium Bromide	KBr	40,000-400	1.53	Low cost; extended transmission range; withstands thermal and mechanical
Potassium Chloride	KCl	55,555-500	1.46	Less hygroscopic and more resistant to thermal shock than NaCl
Silicon dioxide	SiO ₂	25,000-2,500	1.5 ^a	Insoluble in water; birefringent
Silver Bromide	AgBr	20,000-300	2.2	Insoluble; will cold flow; darkens less than AgCl in UV light
Silver Chloride	AgCl	25,000-434	2.0	Soluble in H ₂ O; corrosive to metals
Sodium Chloride	NaCl	40,000-667	1.52	Low cost; rugged; hygroscopic
Thallium bromiodide (KRS-5)	TlBr-TlI	20,000-285	2.37	Soluble in bases; insoluble in acids; slightly H ₂ O soluble
Zinc Selenide	ZnSe	10,000-556	2.40	Insoluble in H ₂ O; resistant to most solvents; brittle; handle with caution
Zinc Sulfide	ZnS	10,000-714	2.20	Insoluble in H ₂ O; slightly soluble in nitric acid, sulfuric acid and potassium hydroxide

^a At 333 cm⁻¹

Long Path Gas Cell

Gas cells used for gas analyses in FTIR analytical systems generally have path lengths ranging from 2 to 10 m. High sensitivity is the greatest

advantage provided by a 10 m cell but this is offset against the very large sample volumes, generally about 2 liters, required for analyses.⁽³⁷⁾

Short path gas cells are generally used to measure gases at high concentrations while long path gas cells are used to measure gas concentrations down to the part per billion levels. For the purpose of this study, a long path gas cell was used to obtain the ppm levels of moisture required. See Figure 10 below.



Figure 10: A136 Variable gas cell 0.8-8 m.

A gas cell having a 10 or 20 m path length contains at least three mirrors and the long light path is achieved by repeated reflections of the light along the mirrors within the gas cell. The three mirrors shown in figure 11 each have an identical radius of curvature which provides the base light path length of the gas cell. Infrared light from the light source is focused on the inlet port of the gas cell. It is then reflected from mirror M_1 and focuses

on mirror M_2 . The infrared light from M_2 is then reflected from mirror M_3 and focuses back onto mirror M_2 .⁽³⁸⁾

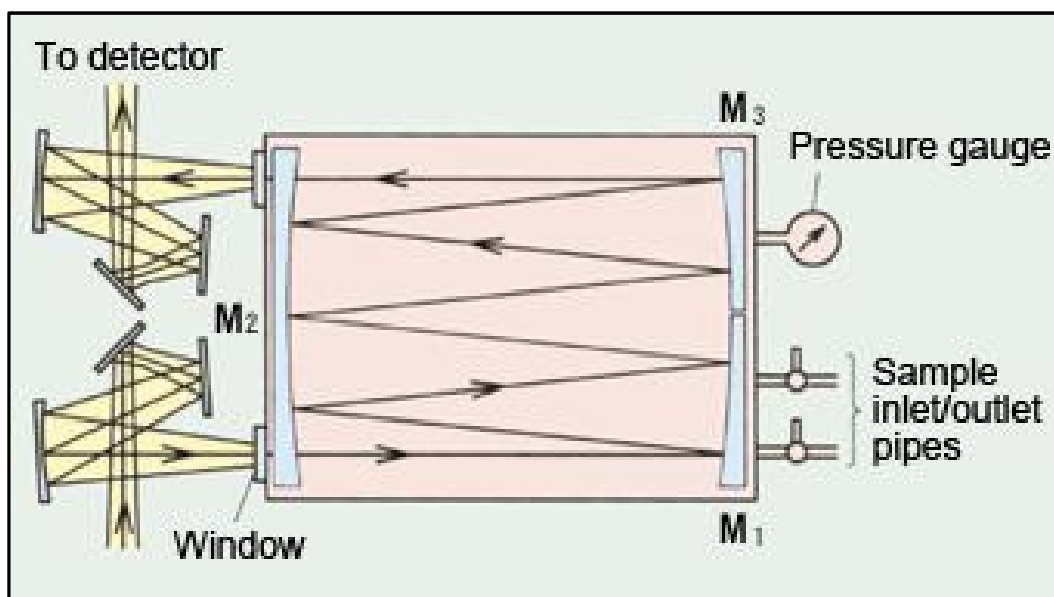


Figure 11: Optics for a Long path gas cell⁽³⁸⁾

Figure 12 indicates the images formed on mirror M_2 . It is made up of two levels namely $4n-2$ and $4n$ (where n is a natural number) which show the sequence numbers of the images formed on mirror M_2 . The infrared red light is reflected multiple times between mirrors M_1 , M_2 and M_3 and is finally reflected from mirror M_3 to be focused on the exit port before reaching the detector.

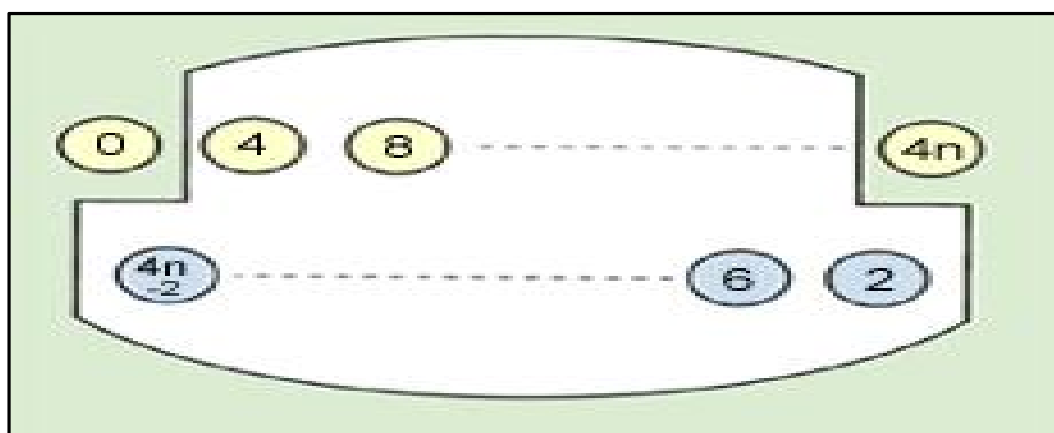


Figure 12: Images on mirror M_2 ⁽³⁸⁾

To determine trace amounts of analyte Beers-Lambert-Bouguer's Law is put into practice. It states that the absorbance is directly proportional to the absorptivity of the analyte, its concentration and the path length of the cell,

$$A = \alpha \cdot b \cdot C \quad (13)$$

Where:

A = Absorbance

α = absorptivity in units of length⁻¹ concentration⁻¹ (e.g. m⁻¹ M⁻¹)

b = Path length of the cell in units of length

C = Concentration in Molarity or g mol⁻¹

Each absorption, seen within a spectrum, may be assigned to a vibrational mode within the molecule and each has its own contribution to the absorptivity term α . Absorbance is then determined from the primary measurement as follows: ⁽³⁹⁾

$$A = \log(1/T) = -\log_{10} T \quad (14)$$

Where: A = Absorbance

T = Transmittance

The longer the path length at a fixed concentration, the greater the number of molecules the IR beam will pass through. In practice however, there is the competing process of increasing noise as the IR signal is reduced by mirror reflection losses as well as losses due to scattering. An acceptable number of reflections in a multi pass gas cell is approximately 40 reflections with a standard white cell and approximately 80 using a modified Horn Pimentel gas cell design. The purpose is to increase the path length at a rate which is quicker than that with which the noise increases. ⁽⁴⁰⁾

Measurement of gas samples on FTIR

In a solid or liquid sample, the molecules are in an associated state and there are no major differences between their spectral resolutions measured at 0.5 cm^{-1} high resolution and at normal 4 cm^{-1} resolution except at very low temperatures. The spectral resolution of gas samples differ significantly according to the FTIR resolution. This is due to the fact that in a gaseous state, many absorption peaks, having detailed structures, appear due to the transition between rotational energy levels as well as the transition between energy levels caused by molecular vibrations. A high resolution is therefore required to clarify the detailed structure inherent to gas samples. ⁽³⁸⁾

The cell internal pressure must be adjusted for quantitative analyses of the gas sample. The pressure broadening effect must also be taken into account. Even if the gas sample partial pressures are the same, the absorption band width and absorbance coefficient may change according to differences in total pressure. In addition the shape of the absorption band width and absorbance coefficient may change if the coexisting gas has a small or a large molecular radius. ⁽³⁸⁾

Measurement parameters for FTIR

There are various parameters to consider when setting up an experiment for FTIR. These include spectral resolution, number of co-added spectra, scan time and apodization function. Increasing the resolution enables the absorption peaks of interest to have better resolution from possible interfering molecules but also results in increased noise levels and longer scan times. Since the signal-to-noise ratio of a spectrum increases with the square root of the number of spectral scans, the co-addition of a large number of spectra increases sensitivity but simultaneously offsets the benefits of lower noise levels ⁽²⁾. In addition, higher resolution requires the use of a smaller aperture opening, referred to as the J-stop, and that means significant amounts of IR energy will be blocked by the J-stop

resulting in even poorer signal to noise ratios of the spectrum results. ⁽⁴¹⁾
As a result, for online water vapor analyses of flowing gas streams, a compromise has to be reached between sensitivity and data acquisition rate. Typically for low ppbv detection of water vapor, each infrared data point is obtained from the co-addition of anywhere between 200 and 400 spectral scans collected in less than 5 minutes. ⁽²⁾

2.5. Gas chromatography

Introduction

The following introduction, taken from “Principles of Instrumental Analysis” summarizes the basic idea of gas chromatography. “In gas chromatography, the components of a vaporized sample are separated as a consequence of being partitioned between a mobile gaseous phase and a liquid or stationary phase held in a column. In performing a gas chromatographic separation, the sample is vaporized and injected onto the head of a chromatographic column. Elution is brought about by the flow of an inert gaseous mobile phase. In contrast to most other types of chromatography, the mobile phase does not interact with molecules of the analyte; it's only function being to transport the analyte through the column” ⁽⁴²⁾

The first scientist to recognize chromatography as an efficient method of separation was the Russian botanist Tswett ⁽⁴³⁾ who used a simple form of liquid-solid chromatography to separate a number plant pigments. The term “chromatography”, meaning “colour writing”, was initiated as a result of the coloured bands that were produced on the adsorbent bed. Despite the fact that colour has very little to do with chromatography, the name has persisted and is still used today for all separation techniques employing the essential requisites for a chromatographic separation, namely both a mobile and stationary phase ⁽⁴³⁾.

Chromatography is an analytical technique based on separation of molecules according to the differences in their structures and compositions. In short, chromatography involves the movement of a test sample through a system whereby it is separated into its various components by use of a stationary phase. The molecules in the sample will interact with the stationary support resulting in separation of similar molecules. Chromatographic separation is divided into several categories based on the mobile and stationary phases used. These include thin layer chromatography, gas chromatography, paper chromatography and high performance liquid chromatography (HPLC). GC is a physical separation technique in which the components of a mixture are separated using an inert carrier gas as the mobile phase and the solid phase is in the form of a column. ⁽⁴⁴⁾

Theory of gas chromatography

In order to understand GC, it is necessary to have a grasp of a number of basic concepts relating to this technique. These include chromatographic principles such as retention time, retention factors, resolution and sensitivity to name but a few.

Partition coefficient

A solute entering a chromatographic system is immediately distributed between the stationary and mobile phase. The equilibrium reached by the solute, between the stationary and mobile phase, can be described quantitatively by using a temperature dependant constant called the partition ratio or partition coefficient K described by the following equation:

$$K = C_s/C_m \quad (15)$$

where C_s and C_m are the analytical concentrations of a solute in the stationary phase and mobile phase respectively. ⁽⁴⁵⁾ When $K = 1$, it is an indication that the solute is distributed evenly between the two phases. The partition coefficient determines the average velocity of each solute

zone and more specifically, the zone centre as the mobile phase moves down the column. When the first peak maximum appears at the column exit, half of the solute has eluted in the retention volume, V_R , and the other half remains in one of two phases, either the volume of the mobile phase, V_M , or the volume of the stationary liquid phase V_S . This leads to the following equation:

$$V_R C_M = V_M C_M + V_S C_S \quad (16)$$

Which, when rearranged and the partition coefficient added, gives a fundamental chromatography equation which relates the retention volume of a component to the column dead volume as well as the product of the partition coefficient and the volume of the stationary phase. ⁽⁴⁶⁾

$$V_R = V_M + K V_S \quad (17)$$

It can be noted that K is the fundamental quantity that affects distribution of components between phases and therefore between separations. By selecting the correct mobile phase, stationary phase or both, K can be manipulated within limits and by adjusting the volume of a phase, the molar ratio can be altered in the two phases. ⁽⁴²⁾

Retention time (t_R)

Despite K being a fundamental part of chromatography, it is not measured easily. For this reason we select a measurable parameter called *retention time* which is a function of K . Figure 13 below depicts a simple chromatogram consisting of two peaks.

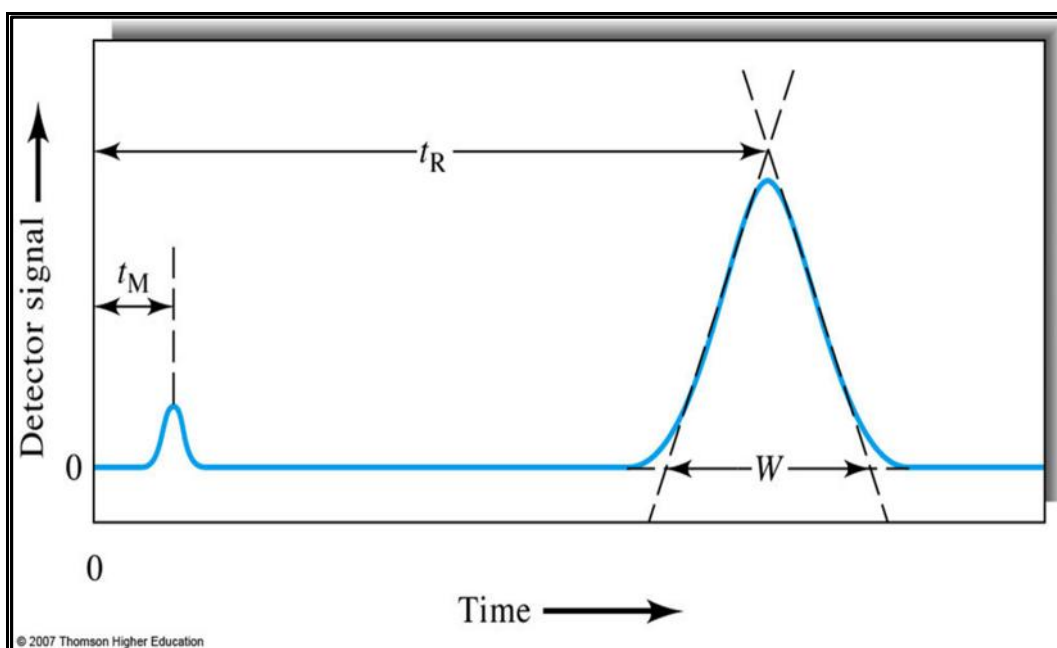


Figure 13: A typical chromatogram for a two component mixture. ⁽⁴²⁾

The initial, smaller peak on the left is regarded as an unretained peak and the time taken for this unretained species to reach the detector is called the dead or void time, t_M . The dead time gives an indication of the average rate of migration of the mobile phase and is an important parameter for identifying the analyte peaks. The larger peak on the right is the analyte species. The time required for this analyte to reach the detector after injection is called the retention time and is termed t_R . This analyte has been retained as it has spent time t_S on the stationary phase and this is summarized into the following equation: ⁽⁴²⁾

$$t_R = t_S + t_M \quad (18)$$

Additionally the average linear rate of solute migration V (cm s^{-1}) through a column of length L is given by the following equation:

$$V = L/t_M \quad (19)$$

And similarly the average linear velocity u of the mobile phase molecules is given by:

$$u = L/t_M \quad (20)$$

Resolution (Rs)

Resolution is a measure of the extent of the overlap between two adjacent peaks. It is defined as the measure of success of a given separation.⁽⁴⁷⁾ The higher the resolution, the smaller is the overlap between two peaks. Resolution takes into consideration both alpha (α) and the width of the peak.

Van Deemter Equation

For any particular GC column, the van Deemter theory is used to determine the flow rate which will give the optimum efficiency at a given column temperature for a specific compound⁽⁴⁸⁾. The van Deemter equation is set out below:

$$H = A + \frac{B}{u} + C_s u + C_m u \quad (21)$$

Where H is the plate height measured in centimeters, A, B, C_s and C_m are constants and u is the carrier gas flow rate measured in centimeters per second.

The first term, A, accounts for the multiple pathways that an analyte molecule may take through a column. These pathways may differ in length. B accounts for longitudinal diffusion and C_s and C_m , referred to as the mass transfer coefficients, account for the finite time required to reach equilibrium in the stationary and mobile phase respectively. For a particular column at a constant temperature, HETP varies with the flow rate of the carrier gas.⁽⁴²⁾

Instrumentation

Sampling system

Gas samples can be injected directly into a sample inlet connected to a column using a gas tight syringe or alternately an external gas sampling valve (GSV) connected directly to the column can be used. Using a six port valve, depicted in Figure 14 below, the principle behind the sample injection is described as follows.

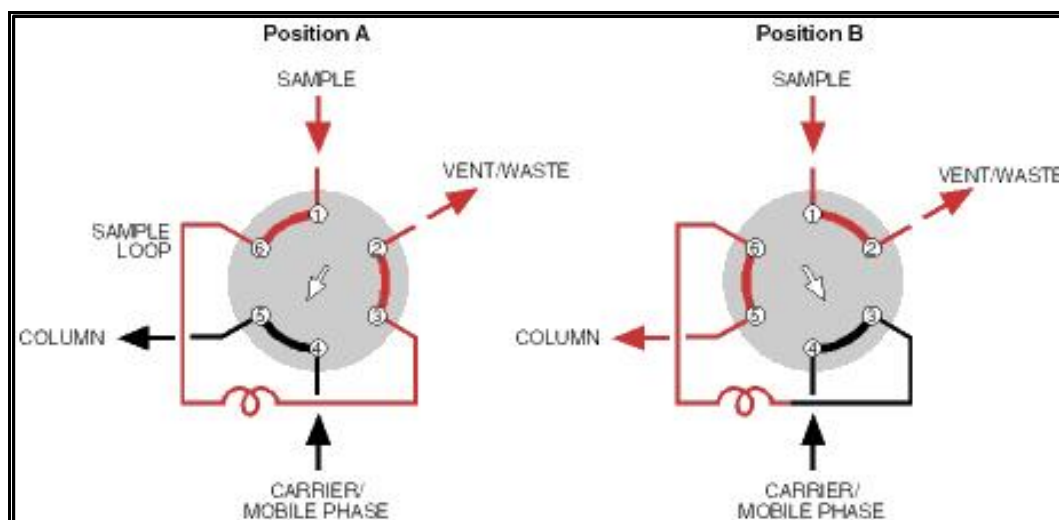


Figure 14: Sample injection-Valco 6 port valve. ⁽⁴⁹⁾

The external loop sample valve has three slots cut into the rotor and this allows for adjacent pairs of ports to be connected. In the loading position (A), the carrier gas is connected between port 4 and port 5 directly through to the column ensuring that carrier gas is running through the column at all times. In this position, the sample loop is connected across ports 3 and 6. Sample passes into port 1 through the rotor slot to the sample loop at port 6 and then to waste at port 2. When the valve is switched to position B, the sample caught in the sample loop is swept through to the column by the carrier gas which runs between ports 4 and 3 in position B. ⁽⁴³⁾

GSV's may or may not be heated. An unheated valve will allow vapor to condense, absorb or possibly deposit on the inside of the sample loop. In

the case where moist samples contain carbon dioxide for example, the deposited layer of water may dissolve some of the carbon dioxide. Upon injection of the sample, the gas will be flushed out of the loop quickly but the carbon dioxide trapped in the water layer will be released slowly causing the carbon dioxide peak to tail which in turn will affect any quantitative measurements. Heating the GSV to 60°C or higher will effectively remove this problem. The GSV may be heated by installing it in the GC oven itself.⁽⁵⁰⁾ Alternatively a heating block, in which the valve can be enclosed, can be purchased. The GC's auxiliary temperature zone controller is used to set and control the temperature.⁽⁵⁰⁾

The sample loop should be flushed thoroughly with at least 100 ml of sample prior to injection. If the sample quantity is limited, smaller flushing volumes may be used provided there is sufficient sample to remove all of the carrier gas or air previously contained in the loop. The alternative solution to small sample volumes is to evacuate the sample loop and associated gas lines. Vacuum and shut off valves should be installed as close to the GSV as possible to keep the volumes as small as possible. Samples injected at pressures below atmospheric create larger flow disturbances than samples injected at higher pressures and it has been noted that samples pressurized to the head pressure create almost no flow disturbance. It must be noted that if a larger quantity of sample is injected, the pressure must be known and this must be taken into account if the pressure differs from that of the calibration standards.⁽⁵⁰⁾

Pulsed discharge helium ionization detector

The advancement and versatility of gas chromatography as an analytical tool has been largely based on improvements in sample introduction inlets, column technology and detectors. There are two types of GC detectors, those which respond to a wide range of chemicals and are termed universal detectors and those which respond to a smaller range of chemicals and are termed selective detectors. There is however a small

group of detectors which are capable of both universal and selective modes of operation. These include the lesser known Pulsed Discharge Detector (PDD).⁽⁵¹⁾

First described in 1992⁽⁵¹⁾, the PDD is based on an ionization source resulting from a pulsed high voltage discharge between platinum electrodes. When the discharge occurs in pure helium, a photon emission results from the transition of diatomic helium to the dissociative 2He ground state as indicated below.



This transition is known as the Hopfield emission and occurs at very short wavelengths (60 – 100 nm) with energies ranging from approximately 13.5 to 17.5 Ev. The broad emission provides sufficient energy to ionize all elements and compounds excluding neon. The PDD can be configured as a universal, selective or elemental detector.⁽⁵¹⁾

For universal detection, the GC column eluents are photoionized directly by the Hopfield emission with the resulting electrons producing a measured current. This type of configuration is referred to as the helium pulsed discharge photoionization detector (He-PDPID). By adding small amounts of an additional gas, called dopant, into the detector, selective detection of electron capturing compounds can be achieved as the dopant gas is ionized to establish a standing current. Electron capturing compounds eluting from the GC lower this standing current. This configuration is termed the pulsed discharge electron capture detector (PDECD). Finally elemental detection is possible if the PDD is configured with a monochromator and photomultiplier tube to measure the emission lines which result from the analytes passing through the helium discharge. This configuration is termed the pulsed discharge emission detector (PDED).⁽⁵¹⁾

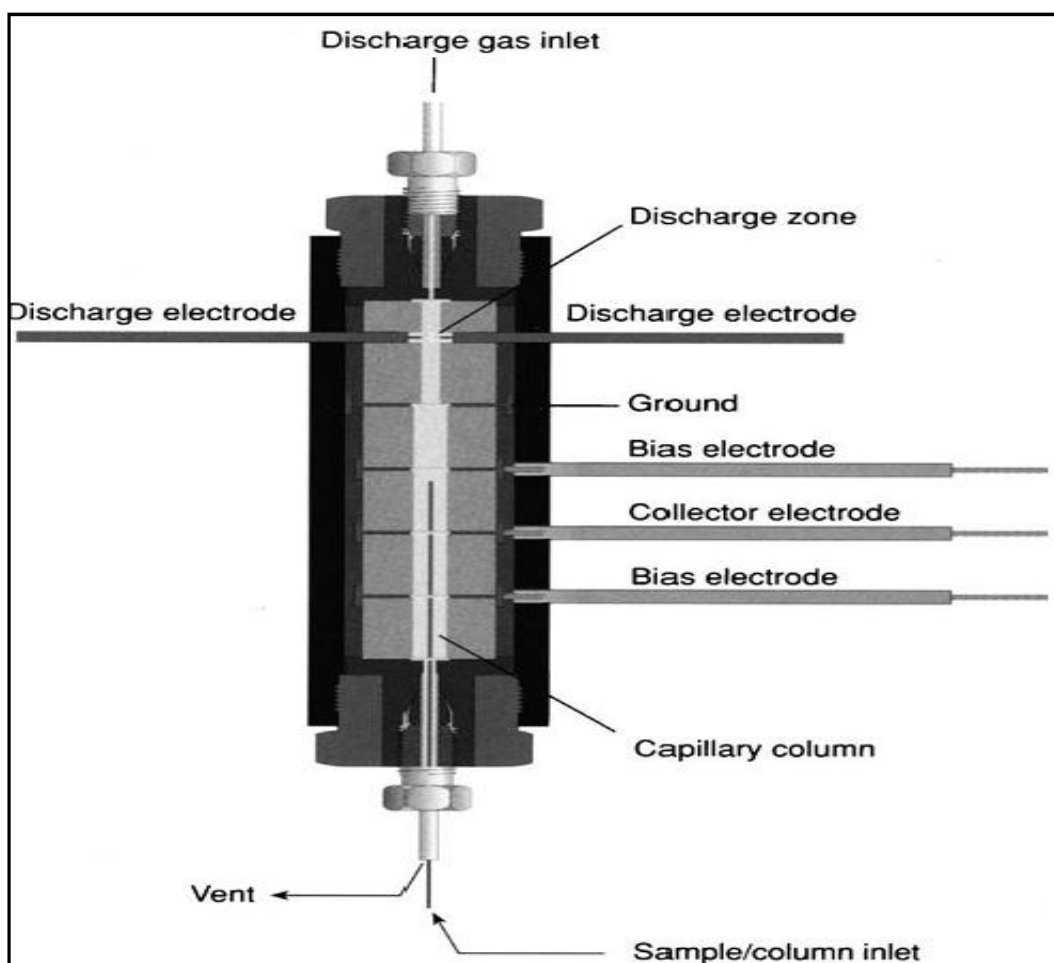


Figure 15: Cross section of the PDHID. ⁽⁵¹⁾

The high voltage pulsed discharge is a simple ionization source. The actual discharge occurs between two platinum electrodes which are spaced approximately 2 mm apart. The platinum electrodes are made up of a 0.25 – 0.05 mm diameter wire, tapered to points. The discharge between the sharp platinum tips is fine with a thread like appearance and the volume of the discharge region is small. The discharge is stable resulting in a highly sensitive ionization detector. As the frequency of the discharge is low and the intervals between the discharges are long, the platinum electrodes are allowed to cool between pulses resulting in less deterioration of the platinum electrodes over the long term. Since the

analyte signal presents an increase in ionization above that of the helium carrier gas, stability of the discharge is absolutely critical. ⁽⁶⁾

Compounds eluting from the column are ionized by high energy photons originating from the helium discharge zone (Figure 15). Electrons generated by this process are focused by the bias electrodes, towards the collector electrode. The detector response arises as a result of changes in the measured current. The separation of the discharge zone from the ionization zone along with the counter helium gas flow configuration ensures that only pure helium passes through the discharge region thus minimizing the possibility of contamination of the discharge electrode. ⁽⁵¹⁾

Ionization occurs by two processes. The first involves direct ionization of the analyte by the electrons that have been accelerated by the high voltage pulse:



In the second ionization process, ionization occurs by reaction of the analyte with the relatively long-lived helium metastables. The helium metastable state, 2^3S , is 19.7eV above the ground state and is capable of ionizing any compound excluding neon which has an ionization potential of 21.5eV ⁽⁶⁾



Factors affecting the detector signal include gas purity, temperature, flow rate, pressure, chromatographic column and geometry of the cell. ⁽⁵²⁾

2.6. Using a permeation tube to create a range of moisture standards for calibration

Several methods have been developed for making up trace moisture standards. The most absolute method involves saturating a gas stream under known conditions. This method establishes an absolute reference point. To create trace concentrations of moisture, cryogenic saturation

temperatures are needed and this method requires cumbersome equipment which is not well suited for field applications. It is also limited to gases which do not condense at the temperatures required to obtain very low concentrations⁽⁵³⁾.

Because environmental moisture is so pervasive, there is no effective way to predetermine the concentration of a final mixture. Part of this problem is related to the storage of such a mixture. While it might be possible to add a known quantity of moisture to a known volume of a gas matrix in a container, the contribution of the container to the final concentration cannot be determined. In addition the concentration may change over the life of the mixture due to variations in temperature and pressure of the contents. An additional uncertainty is introduced with the gas matrix which may itself contain residual moisture and additional moisture may be introduced in the process of transferring the matrix to the container.⁽⁵³⁾

The permeation device is made up of a length of Teflon tubing into which water has been sealed. Water vapor passes slowly through the tube wall and into the surrounding atmosphere. By passing a flow of a clean, dry gas over the tube (dilution gas), a known amount of moisture is added to the gas flow. By keeping the tube at a constant temperature in a stream of the dry gas for an extended period of time, and periodically weighing the tube to measure the rate of weight loss, the rate of flow of moisture emitted from the tube can be measured.⁽⁵³⁾ Figure 16 shows a diagram of a basic permeation tube device.

The dilution flow and the permeating moisture combine to form a mixture. This mixture now contains a known amount of moisture and the concentration of this moisture is given by the following formula:⁽⁵³⁾

$$C = (f / f + F) 10^6 \quad (25)$$

Where:

C = concentration in ppm

f = permeation flow of moisture

F = flow of the dilution gas

Since the flow of moisture from the permeation tube itself is miniscule (nL min^{-1}) compared to the dilution flow from the dry gas (L min^{-1}), the above equation reduces to the following: ⁽⁵³⁾

$$C = (f / F) 10^6 \quad (26)$$

The flow of moisture from the tube is described by the following equation:

$$F = k A \Delta p / t \quad (27)$$

Where:

f = permeation flow

K = permeability of the membrane to water

A = surface area of the permeation

Δp = partial pressure difference of water across the membrane

t = thickness of the membrane

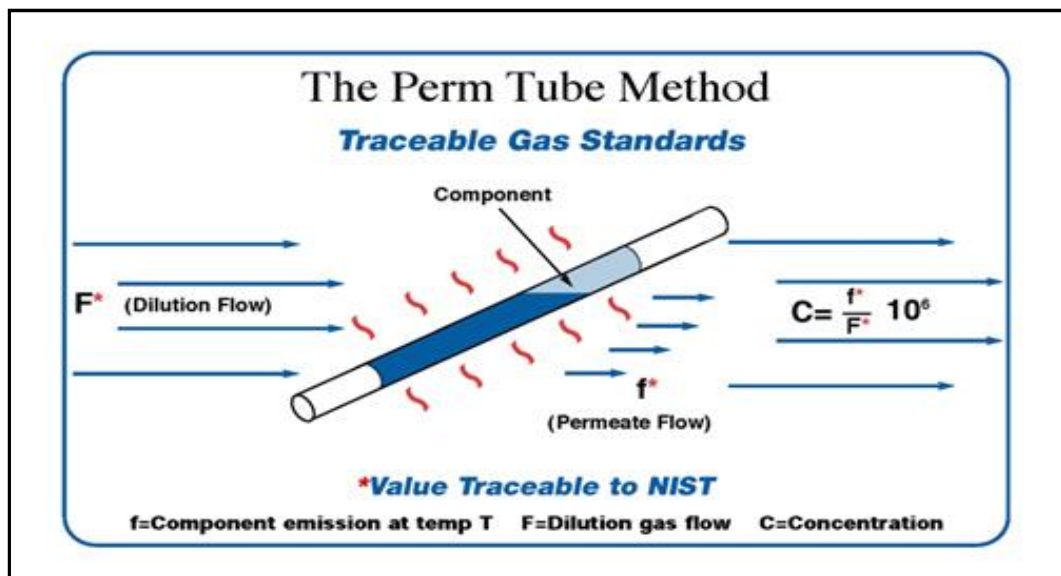


Figure 16: A basic permeation tube device ⁽⁵⁴⁾

The rate of addition of moisture to the gas stream can be set by selecting permeation tubes that have different areas or thicknesses. It is also possible to change the emission rate of a tube by changing the temperature at which it permeates. There are two factors that affect the temperature dependence of the permeation. The vapor pressure of water varies as the temperature is varied and therefore Δp will vary exponentially with inverse temperature. In addition, the permeability of the membrane varies exponentially with inverse pressure. ⁽⁵³⁾

$$K = k_0 \text{ Exp } (-B / T) \quad (28)$$

Where:

K_0 , B = equal constants

T = absolute temperature

The flow of moisture from a permeation tube is therefore strongly dependent on the temperature of the tube and it is necessary to carefully control temperature in order to make accurately known standard. ⁽⁵³⁾ The emission rate from a liquid fed permeation tube varies approximately 10% per °C and a stable temperature is essential for attaining an accurate, stable mixture. A system able to control the temperature to within $\pm 0.1^\circ\text{C}$ will ensure emission accuracy within $\pm 1\%$. ⁽⁵⁵⁾

The flow path is provided by a fixed, continuous, uninterrupted carrier flow over the permeation tube. A fixed carrier flow ensures that the component concentration is constant and surfaces in the system equilibrate ensuring rapid response while minimizing bias in the system. If a carrier flow is not available, the permeation chamber and surrounding components are quickly contaminated with a high concentration of the component compound. ⁽⁵⁵⁾

Permeation tubes are useful in the preparation of very low concentration standards. A tube emitting 50 nl min^{-1} of moisture mixed with a 1 l min^{-1}

carrier flow generates a 50 ppbv mixture. If the carrier flow is changed to 5 l min⁻¹, the same emission generates a 100 ppbv standard. Theoretically a tube with an emission of 1 nl min⁻¹, diluted in a 10 l min⁻¹ carrier gas flow should be able to generate a 100 pptv standard in a single dilution step but there are practical limitations to be considered. With permeation tubes, the basic limit is the minimum emission rate that can actually be measured. Emission rates are determined by measuring the rate of weight loss. A typical permeation tube weighs 10 to 15 g which is well within the range of a semi micro balance. The minimum readable mass change is 0.01 mg and a weight change of 1mg is needed to assure the possibility of measuring weight loss at $\pm 1\%$ accuracy. For a 100 ng min⁻¹ emission rate, the smallest interval between weighing is 7 days. At 10 ng min⁻¹, the smallest interval is over two months thus making the minimum time for emission certification approximately 8 months. ⁽⁵⁵⁾

An additional problem in the weighing process is that the Teflon membrane develops a static charge which attracts any particles in the sweep gas flowing over the tube during the emission measurement process. The practical limit for a single stage dilution using a permeation tube is 10⁸:1. A solution to these problems is to use a secondary dilution step for lower concentrations as indicated in Figure 17.

In this setup, a small portion of the primary mixture from the permeation tube is split off and diluted into an additional flow of matrix gas. This method can give 10³: 1 to 10⁵:1 additional dilutions meaning that a single digit pptv mixture can be prepared with only 2 dilution stages and total matrix gas consumption in the 2 - 10 l min⁻¹ range. As concentrations decrease, the purity of the gas matrix starts to have an effect. Unknown background contamination may introduce large random errors. ⁽⁵⁵⁾

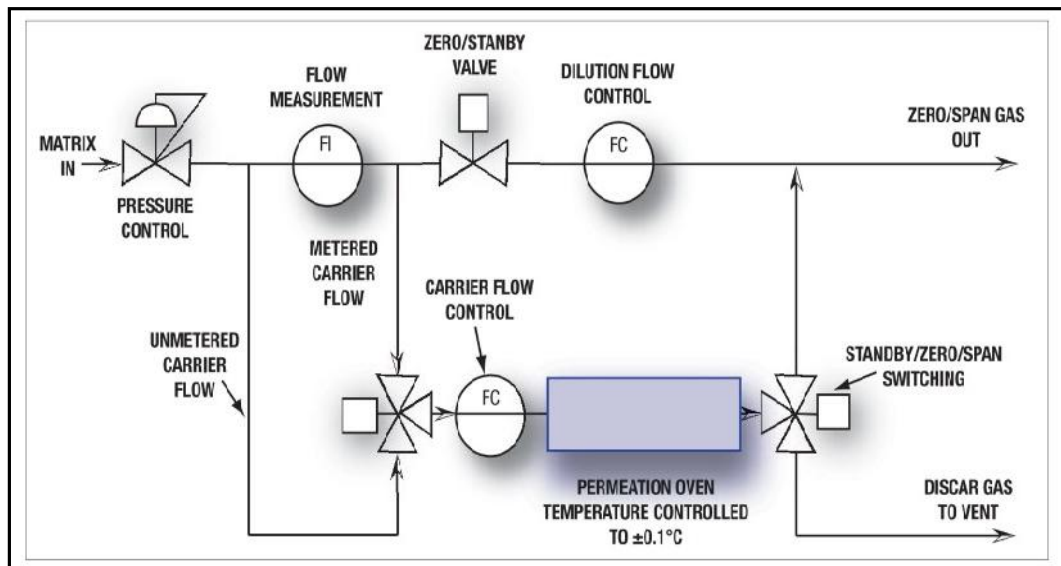


Figure 17: A typical permeation system flow ⁽⁵⁵⁾

CHAPTER 3: RESEARCH METHODOLOGY

3.1. Introduction

The methodology used in this research project, employed a combination of analytical techniques for the measurement of the moisture content in various gas samples. The techniques included GC/PDHID and FTIR. The FTIR was initially set up as a control system as this is a known and accepted method for moisture analyses, albeit for higher levels than were attempted in this research. The FTIR was optimized initially for moisture analyses using a moisture permeation reference standard and this was followed by optimization for acetylene using a selection of acetylene reference standards. Calibration curves were drawn up for both components. The GC/PDHID was initially optimized and calibrated for both moisture and acetylene analyses. A decision was taken not to risk the PDHID filaments by directly injecting moisture into the system and hence the system was only optimized and calibrated for acetylene. Following the instrument setups, the conversion of moisture to acetylene was tested by the addition of known amounts of moisture to excess amounts of calcium carbide in 2 ml sealed vials. The experimental work involved adding known amounts of moisture to the calcium carbide and injecting the gas formed into the GC/PDHID. The GC/PDHID was initially used to test the conversion process as the acetylene gas generated in this manner produced volumes that were too small to analyze using the long path glass gas cell which required at least 2000 ml of sample. Following these experiments, a sample container was designed that fitted directly onto the GC/PDHID and FTIR. The design of this sample holder was such that it enabled the flow of a known amount of a gas, containing moisture, directly into the sample container, allowed the reaction to occur and then by addition of a carrier gas through the container, directly sweep the acetylene formed into either the GC/PDHID or FTIR.

3.2. Section 1: FTIR experimental work

Commercial instrumentation

Bruker Tensor 27 Fourier Transform Infrared spectrophotometer with a RockSolid, permanently aligned, high stability interferometer and spectral range from 6000 to 500 cm^{-1} with “High Humidity” Zinc Selenide optics. [Bruker Optik GmbH, Ettlingen, Germany]

Liquid nitrogen cooled *MCT detector* supplied by Bruker [Bruker Optik GmbH, Ettlingen, Germany]

Bruker: Gas Cell 0.8 – 8 meters QL Gold mirror: P/N I10772.08, Type A1366/3Q. Description: Variable path length 0.8 to 8 meters. External path length control and cell volume approximately 2 liters. Glass cell body with 2 stainless steel valves for inlet and outlet as well as a safety valve. Maximum pressure of 1.05 bars.

Low Volume Steel 2 m long path gas cell: Supplied by Axiom

Instrument control and data processing were done with a HP Compaq personal computer (PC) utilizing the OPUS software, version 7.0, supplied by Bruker. Bruker Optik GmbH, Ettlingen, Germany]

Consumables

Dessicant Cartridge for FTIR: Supplied by Bruker

Laser module: Supplied by Bruker

Gases

The following *cylinder gases* were obtained from Air Products South Africa (Pty) Ltd. [Kempton Park, Gauteng]: Helium (5.0), Nitrogen (5.0) and Synthetic air (4.0).

Note: The figures indicated in brackets behind the gas type are an indication of the purity of that specific gas. For example, 5.0 indicates a 99.999% purity gas.

Liquid nitrogen was supplied by African Oxygen Limited (AFROX) [Alrode, Gauteng]

Reference standards

Standard 1: *Multicomponent Matheson reference standard 0.15% mixture in nitrogen*: Lot nr: 1059614693. Supplied by Puregas (Pty) LTD [Alrode, South Africa]

Standard 2: *Acetylene (100% by volume)*: Supplied by Air Products South Africa (Pty) Ltd. [Kempton Park, Gauteng]

Standard 3: *Acetylene (4835 ppm C₂H₂ in nitrogen)*: Certificate nr: 2258349: Supplied by Air Liquide South Africa Pty (Ltd) [Alrode, South Africa]

Internal Standard: *Methane 102 ppm in helium. Single component, Matheson reference standard*: Lot nr: 1023610432. Supplied by Puregas (Pty) LTD [Alrode, South Africa]

Kintek Trace Source Disposable Permeation Tube, 159 ng min⁻¹ at 30°C: Lot nr: 47884. Supplied by Kintek [Strada Goretta, Caselle Torinese TO]

FTIR Instrument set up and optimization

General

The purpose of this section of the experimental work was to draw up a calibration curve for moisture. From literature studies⁽⁹⁾ and work done at PAL it was deemed imperative to flush all the FTIR instrument compartments with dry nitrogen to remove atmospheric moisture found to be continuously present upon running scans on the evacuated glass cell.

Nitrogen obtained from a standard gas cylinder proved to be too costly as almost a cylinder per day was required for the process. Liquid nitrogen, boiled off from the building supply tank, was therefore put through a domnick hunter CO2RP280 free air generator where CO₂ was removed to levels below 1 ppm and moisture to a pressure dew point of -70°C or better. From the drier, the nitrogen gas was then piped into the laboratory where it was used to flush out the FTIR instrument compartments which included the electronics compartment, detector compartment, sample compartment, source/laser compartment and interferometer compartment. See Figure 18 below.

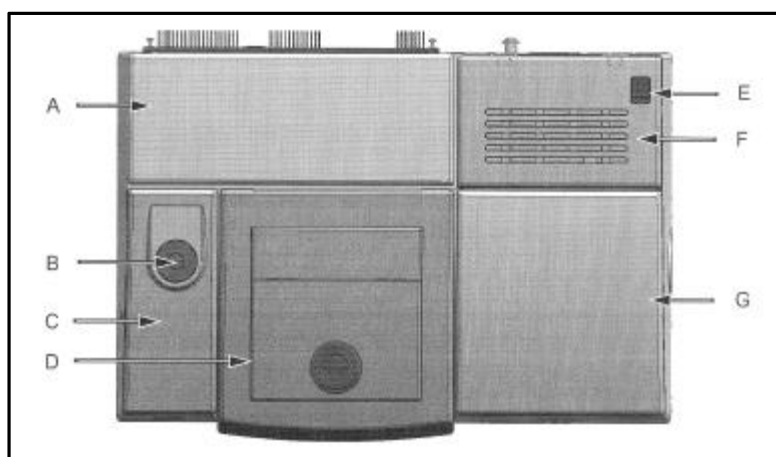


Figure 18: Top view of Bruker Tensor 27 FTIR showing various compartments ⁽⁵⁶⁾

Table 2: Label descriptions for Figure 18

Label	Compartment / External components
A	Electronics compartment
B	Filler inlet for MCT detector
C	Detector compartment
D	Sample compartment
E	Spectrometer display
F	Source/laser compartment
G	Interferometer compartment

Flushing of all the compartments was achieved by drilling small holes into each of the compartments and attaching swage lock fittings to each hole.

These fittings were then connected to a central plastic pipe by which nitrogen was flushed into each compartment. A rotameter was put in place after the nitrogen inlet from the nitrogen tank and drier to ensure flow control through the various compartments.

Detectors

The Bruker FTIR system was purchased by PAL in 2011. Both a DTGS and MCT detector were included in the purchase. It was decided to use the more sensitive MCT detector for the experimental work. The MCT detector had to be filled with liquid nitrogen at the start of each day and then replenished at least every three to four hours. It also required a stabilization period of at least twenty minutes after each fill.

Gas cell

A variable long path, high volume glass gas cell, 0.8 m to 8.0 m (See Figure 10) with calcium fluoride windows was used.

The recommended gas pressure range for the glass cell was 0 to 1 atm and to ensure that the maximum pressure in the cell was never exceeded, a pressure sensor and readout were connected to the outlet of the glass cell. In addition, a back pressure regulator was added to the glass cell exit, enabling control of flow and pressure through the glass cell at all times.

At the inlet of the gas cell, a three way valve was connected. This allowed for a vacuum with which to evacuate the cell or upon rotation of the valve handle, nitrogen could be selected to flush the cell or standards/samples could be sent through to the glass cell for analyses. See Figure 19 for instrument set up.

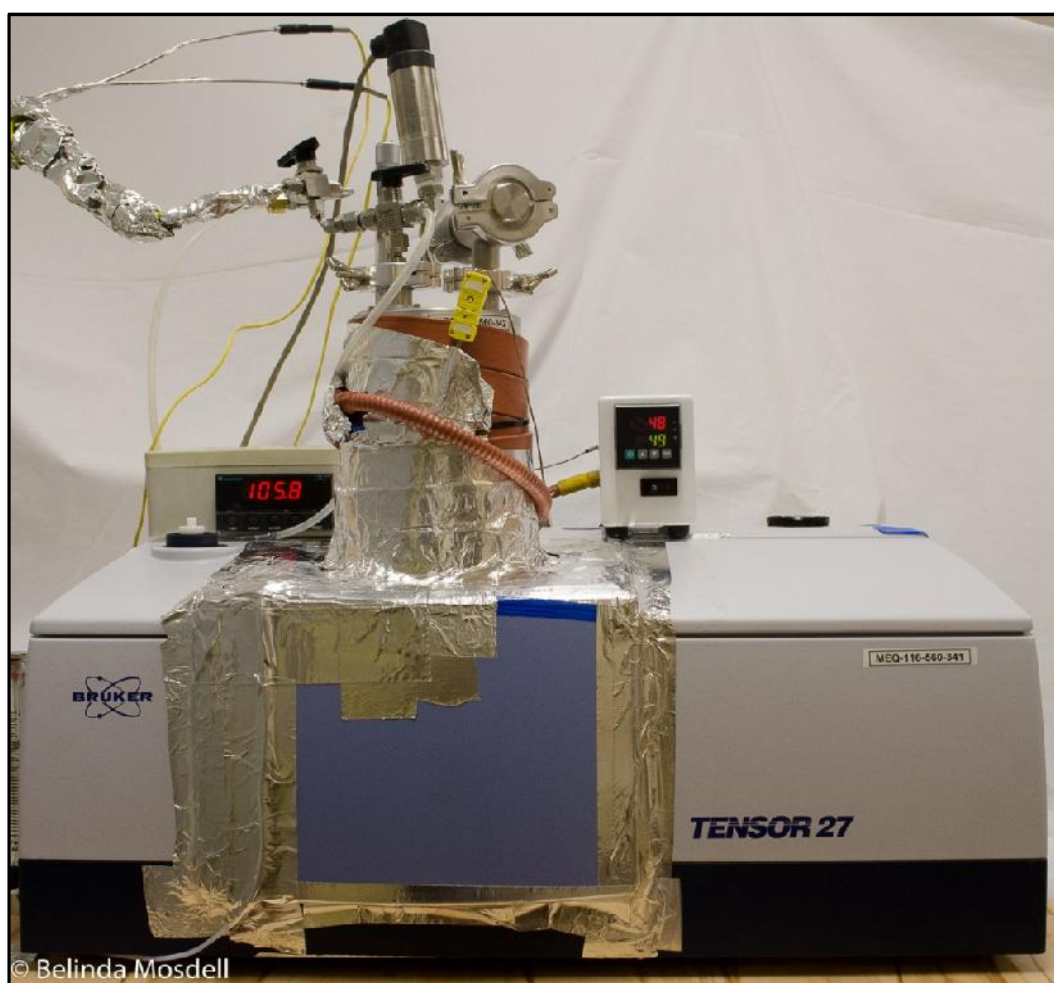


Figure 19: Schematic of FTIR set up for experimental work

Moisture is a highly pervasive component of air, and had to be thoroughly removed from the glass cell before any analyses could be performed. Despite drawing a vacuum on the cell over two days and attempting to flush out the cell with both nitrogen and then helium for a similar period, moisture was still present and could be clearly seen upon running a scan. Heating tape was then wrapped around both the glass cell as well as all the steel pipe lines running through to the glass cell ⁽⁹⁾. A controller with which to control the temperature was designed and installed in order to prevent the glass cell from overheating. Initial tests were run keeping the glass cell at 50°C.

As it appeared from early experimental work that the glass cell retained a certain amount of moisture despite heating and flushing processes implemented, a second single pass, folded Axiom steel gas cell was set up in exactly the same manner as the glass cell. It was expected that the concentration range obtained using the low volume steel cell would be higher than that obtained for the glass cell due to the shorter path length of the low volume cell. The advantage of the low volume cell was that it could be heated at much higher temperatures than the glass cell and also required much less sample due to its smaller internal volume. Unfortunately upon setting up this low volume cell, it was found that it could not be sufficiently sealed, due to its design, from atmospheric moisture ingress and thus could not be tested for this project.

Background

A background was drawn using the same nitrogen used for dilutions of the moisture permeation standard. The purpose of the background is to detect the influence of the ambient conditions i.e. air humidity, temperature and the spectrometer itself on the spectroscopic measurement results. OPUS automatically calculates the results sample spectrum by dividing the sample spectrum by the background spectrum. This ensures that the spectral bands resulting from ambient conditions and from the spectrophotometer are eliminated from the sample spectrum. ⁽⁵⁶⁾

Dilution system

In order to obtain a range of standards for both the moisture and acetylene calibration curves, the initial reference standards had to be diluted down to the desired concentration levels. A dilution system, designed and built at PAL, was available from a previous project. The system has four Bronkhorst High Tech mass flow controllers (MFC) in the following ranges:

0 – 50 ml min⁻¹

0 – 100 ml min⁻¹

0 – 250 ml min⁻¹

0 – 1000 ml min⁻¹

Additionally provision was made for two permeation ovens, originally targeted at hydrogen fluoride analyses at both a high and a low concentration, but for this project only one of the permeation ovens was put to use for moisture permeation.

Nitrogen was used as the carrier for the moisture permeation standard and a flow of 40 ml min⁻¹ was selected through the 0-100 ml min⁻¹ MFC and taken to the permeation oven which was set at 40°C. From the permeation oven, the 40 ml min⁻¹ flow was further diluted using either the 0 - 250 or 0 - 1000 ml min⁻¹ MFC as required.

For the C₂H₂ standards, the C₂H₂ was set at the required flow using the 0 - 50 ml min⁻¹ MFC and the dilutions were made using the 0 - 250 or 0 - 1000 ml min⁻¹ MFC and using nitrogen or the methane standard as the diluent.

The diluted standard, moisture or C₂H₂, could then be directed to either the gas cell on the FTIR system for analyses or it could be vented to atmosphere, depending on the process.

Table 3: FTIR Settings

Parameter	Value
Resolution	2
Number of Scans	100
Results Spectrum	Absorbance
Source Setting	MIR
Beam splitter	ZnSe
Aperture	4mm
Scanner Velocity	20KHz
Acquisition Mode	Double Sided, Forward Back
Phase Correction Mode	Power Spectrum
Apodization	Blackman Harris 3-Term

3.3. Method 1: H₂O analysis on FTIR

General

The purpose of this section of the experimental work was to draw up a calibration curve for moisture using a permeation standard.

Variation of gases used for dilutions

At the start of the experimental work, various gases were tested as both diluents for the permeation standard and for flushing the FTIR compartments. These included both helium and argon as both were found to contain less moisture than the nitrogen boiled of from the building supply. Due to the expensive nature of these two gases, it was decided to return to the original choice and to compensate for any additional moisture by heating the glass cell.

Optimizing the glass gas cell temperature

In order to determine the optimum temperature at which to run the glass cell for moisture analyses, a moisture calibration curve was initially drawn up at 50°C using the permeation standard, to obtain a rough estimate of the moisture content of the glass cell. The cell temperature was then systematically increased by 10°C from 40°C up to 110°C while flushing continuously with nitrogen and five moisture readings taken at every temperature change. The cell was allowed to stabilize at each temperature for at least 4 hours. The moisture results obtained in ppmv were plotted against the temperature changes as indicated in Figure 20. Based on these results, it was decided to recalibrate the FTIR for moisture keeping the cell temperature and stainless steel lines at a temperature of 40°C.

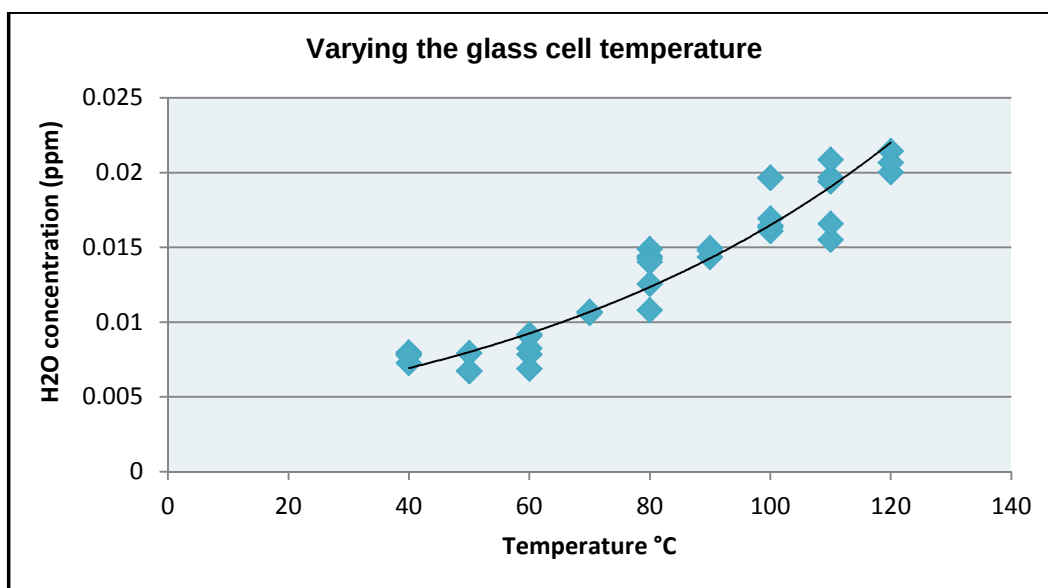


Figure 20: Plot of H₂O concentration versus cell temperature for glass cell

Moisture permeation reference standard: KINTEK

A Kintek Trace Source Disposable Moisture Permeation Tube, with an emission rate of 159 ng min⁻¹ at 30°C, was selected as a reference standard. The disposable permeation tube was placed in a steel holder designed with an inlet for the nitrogen carrier gas and an outlet for the diluted moisture mixture (see Figure 21). This steel holder was sealed and inserted into a permeation oven designed and built at PAL. The permeation oven was set to 40°C and a flow of 40 ml min⁻¹ of nitrogen, controlled by a mass flow controller with a range of 0 to 50ml min⁻¹, was used to carry the moisture permeation standard through to the FTIR gas cell. The permeation rate of 159 ng min⁻¹ is based on a temperature of 30°C as per the certificate of analysis ([See Appendix 1](#)) but due to the permeation oven design; the lowest temperature that could be set was 40°C. A The following calculation was used to calculate the rate change with temperature change ⁽⁵⁷⁾

$$\text{Log } P_1 = \text{Log } P_0 + \alpha (T_1 - T_0) \quad (29)$$

Where:

P_0 = Rate at temperature T_0 ($^{\circ}\text{C}$)

P_1 = New rate at temperature T_1 ($^{\circ}\text{C}$)

α = the temperature coefficient (0.034 for standard emission tubes)

Using above calculation, where the emission rate (159 ng min^{-1} at 30°C) is calculated at 40°C , is as follows:

$$\text{Log } P_1 = \text{Log } 159 + 0.034 (40 - 30) = 318 \text{ ng min}^{-1}$$

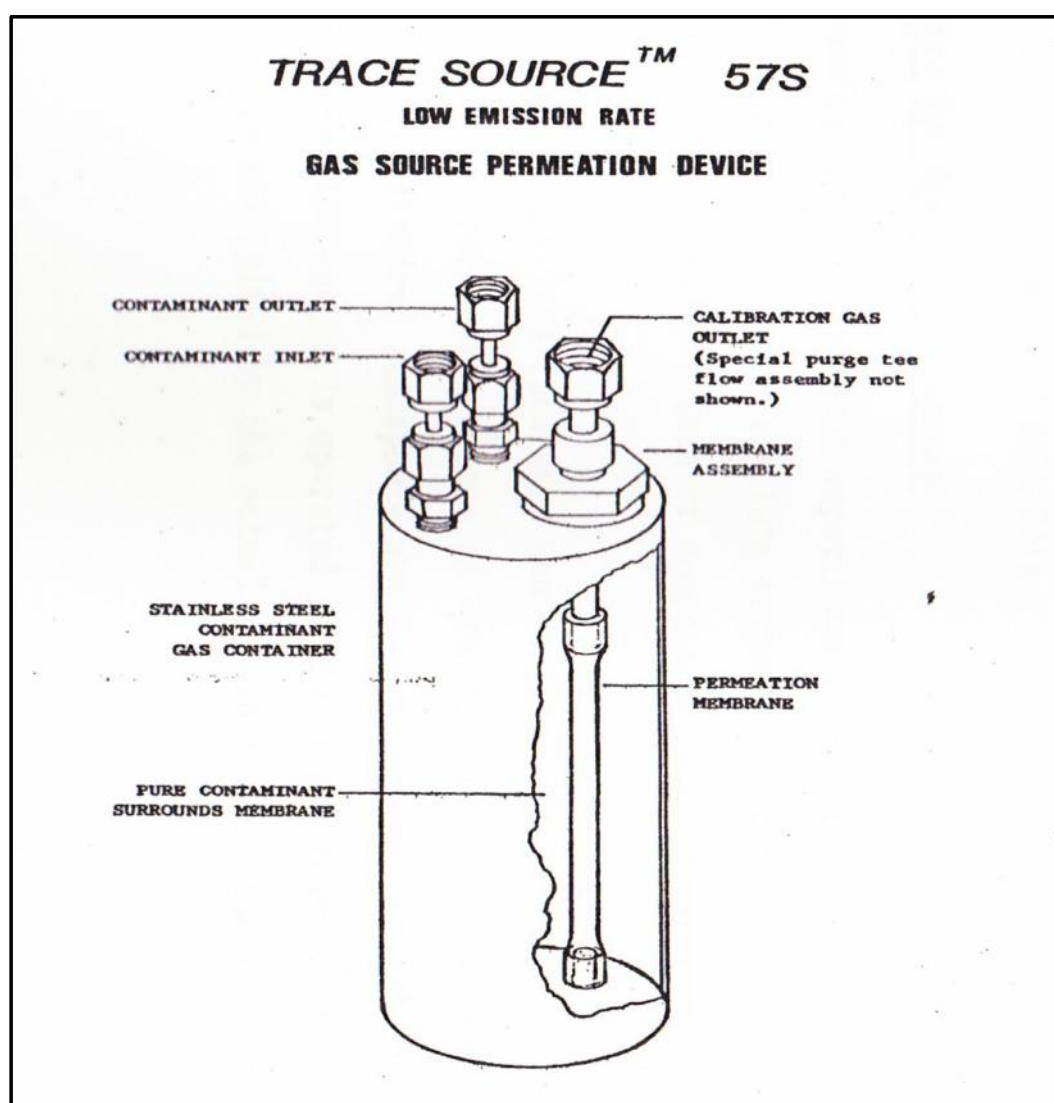


Figure 21: Typical permeation tube and permeation tube holder ⁽⁵⁸⁾

In order to draw up a calibration curve, the initial moisture mixture flowing from the permeation holder had to be further diluted to obtain a range of concentrations. This was achieved by adding additional volumes of nitrogen, regulated by mass flow controllers, to the flow of permeation standard flowing from the permeation holder and oven. A gas dilution system, designed and built in-house, was used to dilute the initial moisture permeation standard down to 8 different levels from which a calibration curve could be drawn up. The moisture, permeating at a fixed rate of 318 ng min⁻¹ (see equation 29), from the permeation tube sealed inside the permeation oven, was carried from the permeation oven to the FTIR using a Bronkhorst mass flow controller with a range of 0 to 50 ml min⁻¹ as indicated in the section above. This flow of 40 ml min⁻¹ was kept constant. The nitrogen diluent flow was controlled by an additional two Bronkhorst mass flow controllers, one ranging from 0 to 250 ml min⁻¹ and one ranging from 0 to 5000 ml min⁻¹. The diluent was added to the 40 ml min⁻¹ permeation flow prior to reaching the long path glass gas cell. Mixing of the diluent and standard took place in the dilution system and the resultant gas mixture was loaded directly from the dilution system into the long path gas cell at a 100 kPa. Table 4 summarizes the diluent and standard flows used to obtain a range of calibration levels from the moisture permeation standard at 318 ng min⁻¹.

Table 4: Dilution of moisture permeation standard to obtain calibration levels

Diluent flow (ml min⁻¹)	Permeation flow (ml min⁻¹)	Total Flow (ml min⁻¹)	[H₂O] (ppmv)
730	40	770	0.514
460	40	500	0.791
305	40	345	1.147
160	40	200	1.978
110	40	150	2.637
60	40	100	3.956
0	40	40	9.890

Calculations to obtain ppmv values from dilutions

The calculations performed to acquire the emission rate as ppmv after dilution was done as follows:

$$\text{ppmv} = K_0 \times \text{ng min}^{-1} / F$$

Where:

K_0 is the equal constant (from the suppliers COA)

ng min^{-1} is the permeation rate (calculated at 40°C: See equation 29) and

F is the total dilution flow in ml min^{-1} and includes permeation flow and dilution gas flow in ml min^{-1}

Peak selection

Moisture typically has two spectral ranges in which peaks can be selected for quantitation namely 3890 to 3560 cm^{-1} and 1840 to 1410 cm^{-1} . A total of eleven different peaks in both ranges were selected for quantitation, as indicated in Figure 22 below.

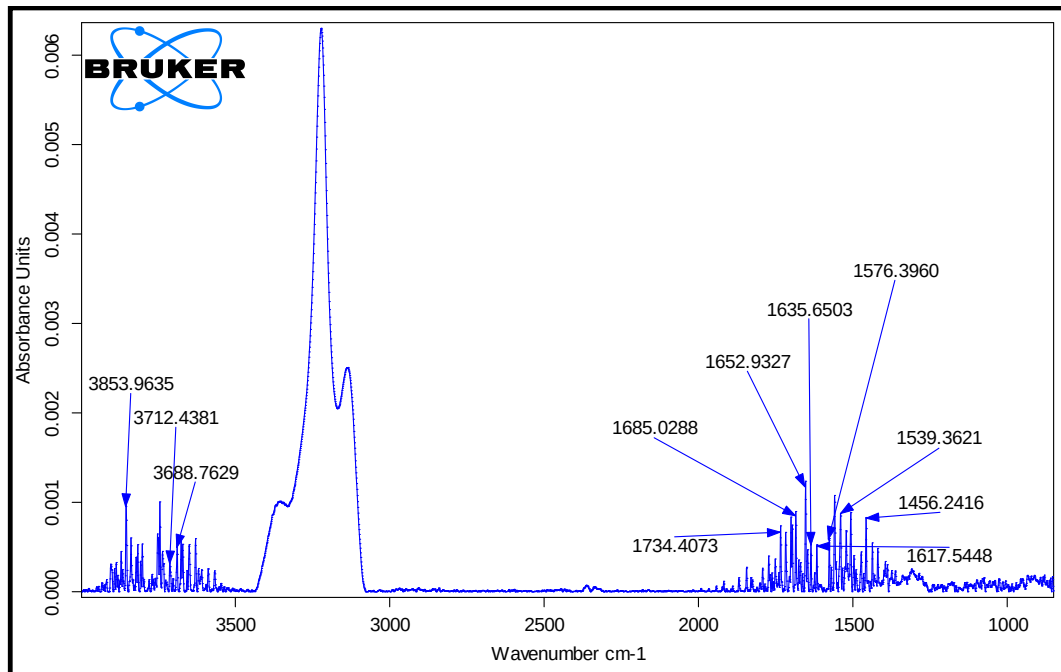


Figure 22: Typical FTIR spectra of H₂O indicating peaks selected for quantitation

The purpose of this selection was to determine which of the eleven peaks were most suited, statistically, for use. The large peak between 3000 and 3500 cm^{-1} , on all the H_2O graphs that follow, could not be identified and was subsequently not identified / labelled on the spectra.

Calibration for moisture

At the start of the project, a moisture calibration curve was drawn up with a concentration range from 0.404 ppmv to 9.890 ppmv moisture using the peak at wavenumber 3854 cm^{-1} (see Table 4) and the glass cell and stainless steel lines heated to and kept at 50°C. This calibration curve, although not optimum, was used to get rough values to determine the optimum cell temperature to use for the glass cell.

After stabilizing the glass gas cell at the selected temperature of 40°C, new calibration curves were drawn up at each of the previously selected wavenumbers and using the same dilution standards as discussed previously. The lowest calibration standard was run first and after each change in flow rate to obtain the next calibration level, 4 hours was allowed for stabilization of dilution flows and equilibration of the cell. Eleven different calibration curves were obtained, one for each selected wavenumber ([see Appendix 2](#)). Both linear and quadratic fits were applied to the calibration data and the results compared.

Use of methane to prove stability of FTIR system

From the calibration curve obtained for moisture in the previous experiment, it was clear that there was a wide spread of results around each calibration point specifically around the highest calibration level. This indicated instability in the moisture readings at each level, possibly due to adsorption of moisture on the glass cell walls or perhaps a problem with the instrument itself. In order to determine if this was a problem created by the instrument/cell or if it was only present for the moisture analysis, methane was selected as an additional component for FTIR analysis, a

reference standard being readily available in the laboratory. The following spectrum was obtained for methane at 3018 cm^{-1} :

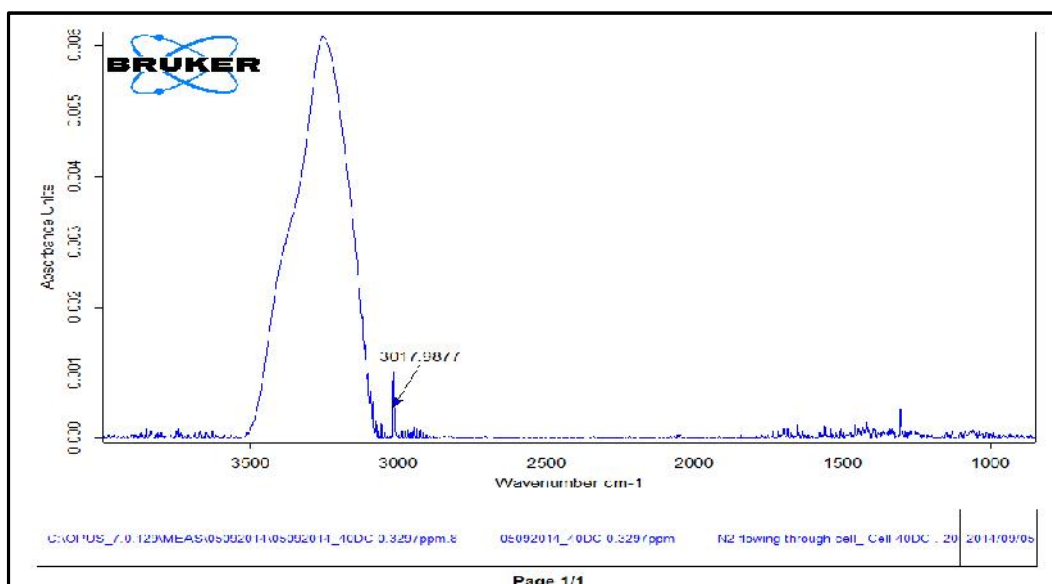


Figure 23: Typical FTIR spectra of CH_4 indicating peak selected for quantitation

Table 5 summarizes the diluent and standard flows used to obtain a range of calibration levels from the 9.93 ppmv CH_4 reference standard.

Table 5: Dilution of CH_4 reference standard to obtain calibration levels

Diluent flow (ml min^{-1})	CH_4 flow (ml min^{-1})	Total Flow (ml min^{-1})	$[\text{CH}_4]$ (ppmv)
2460	50	2510	0.198
2460	100	2560	0.388
1760	100	1860	0.534
960	100	1060	0.937
460	100	560	1.773
305	100	405	2.452
110	100	210	4.729

Visually the spread of results around each calibration point appeared to be smaller than that obtained for the moisture tests, indicating that the problem with the spread of results around the moisture calibration levels

was related to the moisture and possible adsorption to the glass walls of the cell and not the instrument.

CH₄ as internal standard for moisture analyses

In order to compensate for the spread of the results around each calibration point, it was decided to attempt to use methane as an internal standard for the moisture analyses in order to compensate/correct for loss of the analyte (moisture) during sample inlet. Calibration was obtained by plotting the ratio of the moisture signal to the CH₄ signal as a function of the analyte concentration of the standards. The CH₄ was initially tested for stability by using it to draw up a calibration curve in the same manner as was done for the moisture and by visually examining the spread of results around each calibration point.

3.4. Method 2: C₂H₂ analysis on FTIR

General

The purpose of this second section of the experimental work was to draw up a calibration curve for C₂H₂ using FTIR. The instrument set-up was identical to the set-up for experiment 1, the only difference being that the glass cell was not heated for the C₂H₂ experimental work.

Background

A background was run using the same nitrogen used for dilutions of the C₂H₂ standard dilutions.

Summary of acetylene reference standards tested:

Initially the certified 0.15% Matheson reference standard (Standard 1) containing 27 different components, including C₂H₂, was used to set up a calibration curve on the FTIR. Taking a spectrum from literature, four peaks were identified for quantitation purposes namely, a combination of 3313 / 3266 cm⁻¹ as well as 1350 cm⁻¹ and 1305 cm⁻¹. Problems were detected using Standard 1.

At this stage no further certified reference standards for C_2H_2 were available in the laboratory and a cylinder of, what was assumed to be predominantly C_2H_2 (Standard 2), used for the Atomic Absorption instrument, was selected as a replacement for Standard 1. Since no certificate of analysis was available for this standard and its purity was unknown, in-house certification using a Refinery Gas Analyser (RGA) as the analytical techniques was used to obtain the % purity. Good results were obtained upon using Standard 2 to create a calibration curve on the FTIR although large dilutions had to be made to bring the 94.8% standard down to the calibration levels required for the analyses.

It was at this point where funds became available and it was decided to purchase a NIST traceable certified C_2H_2 standard of 5000 ppm (Standard 3) made up in nitrogen.

Standard 1 (Matheson 0.15% reference standard)

The following dilutions were made to obtain the 6 calibration levels used to draw up a calibration curve for C_2H_2 using Standard 1:

Table 6: Dilution of Standard 1 using mass flow controllers and nitrogen as diluent

Diluent flow (ml min⁻¹)	C₂H₂ flow (ml min⁻¹)	Total flow (ml min⁻¹)	[C₂H₂] (ppmv)
2260	50	2310	33.550
1460	50	1510	51.235
960	50	1010	76.733
460	50	510	151.961
260	50	310	246.815
160	50	210	369.048

Overlaying the spectrum obtained from Standard 1 (Figure 24) with a spectrum obtained from a cylinder containing >94% C_2H_2 diluted down with nitrogen, figure 25 was obtained. Based on figure 25, the peaks that could be used for quantitation were a combination of 3313 / 3266 cm⁻¹ and possibly 1305 cm⁻¹ although the latter peak's shape in Standard 1 differed

from that in the >94% C₂H₂ indicating some form of interference from one of the other components in standard 1. The peak at 1350 cm⁻¹ appeared to be non-existent in Standard 1 and was therefore omitted from the calibration setup.

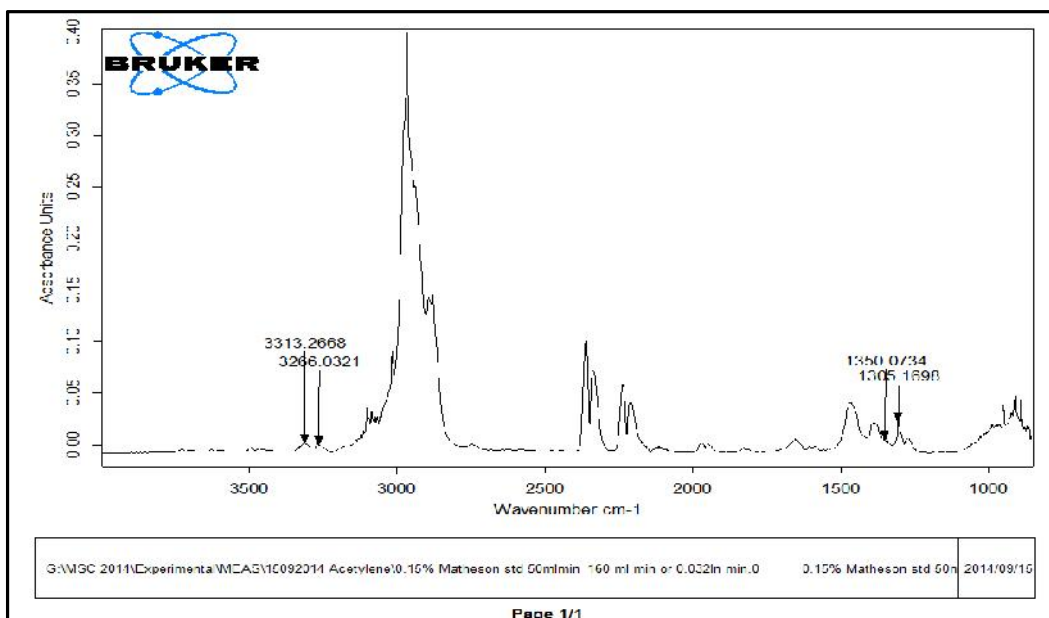


Figure 24: Spectrum obtained for Standard 1

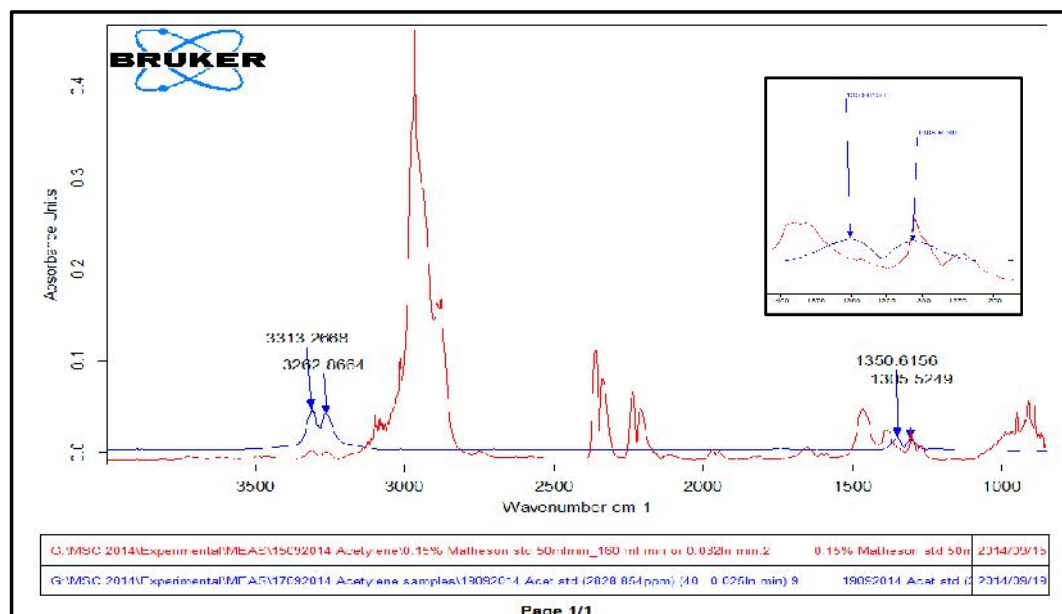


Figure 25: Overlay of Standard 1 with a >94% C₂H₂ standard. The insert shows a close up of the peaks at 1350 and 1305 cm⁻¹.

Standard 2 (C₂H₂ standard certified in-house)

The in-house C₂H₂ was certified using RGA and the concentration was determined to be 94.8%. Since this concentration was too high to be diluted directly down to the required calibration levels using the mass flow controllers available, as was done for the Matheson standard, a second dilution system was brought in. Standard 2 was put through the first dilution system and diluted down to 9384 ppm using a standard flow of 10 ml min⁻¹ and a nitrogen diluent flow of 1000 ml min⁻¹.

The following dilutions were then made from the 9384 ppm diluted standard to obtain the 7 calibration levels used to draw up a calibration curve for Standard 2:

Table 7: Dilution of Standard 2 using mass flow controllers and nitrogen as diluent

Diluent flow (ml min ⁻¹)	C ₂ H ₂ Flow (ml min ⁻¹)	Total Flow (ml min ⁻¹)	[C ₂ H ₂] (ppmv)
2500	40	2540	147.78
1500	40	1540	243.74
1000	40	1040	360.93
800	40	840	446.87
450	40	490	766.05
250	40	290	1294.37
100	40	140	2681.19

Figure 26 shows the spectrum obtained for Standard 2. From this spectrum it appeared that the 4 peaks originally selected, 3313 / 3266 cm⁻¹ as well as 1350 cm⁻¹ and 1305 cm⁻¹ were available for quantitation.

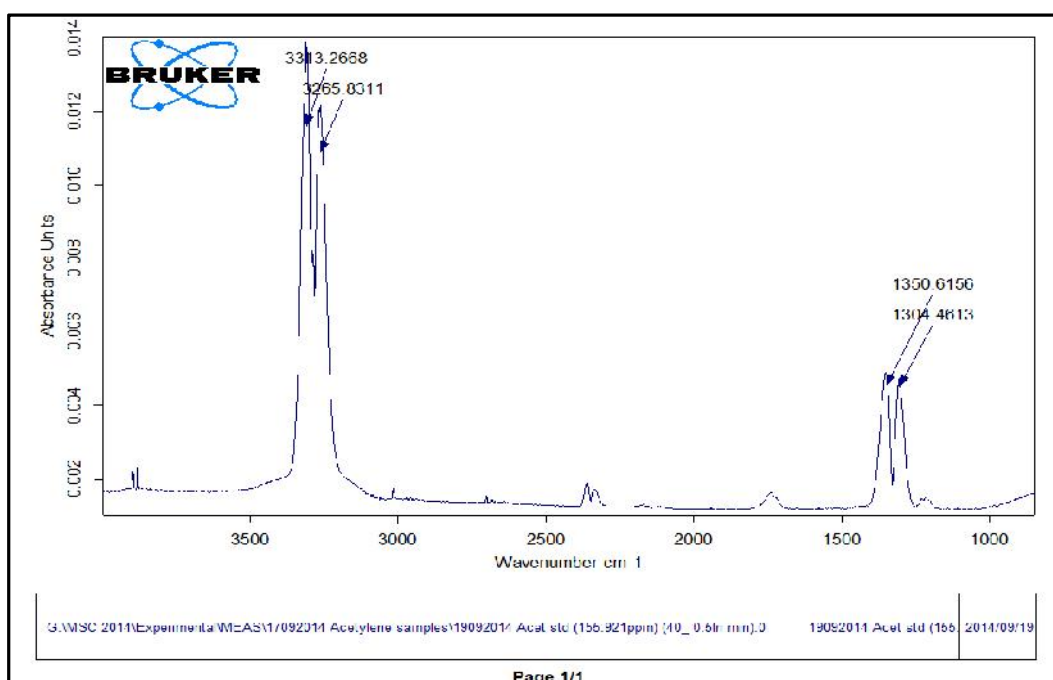


Figure 26: Spectrum obtained for Standard 2

Standard 2 with internal standard

For this experimental work, CH₄ was added as an internal standard to Standard 2. A CH₄ reference standard of concentration 9.9 ppm, balance of nitrogen, was used as the diluent in place of the nitrogen previously used. The following dilutions were made to obtain the 7 calibration levels used to draw up a calibration curve for Standard 2 with CH₄ as internal standard:

Table 8: Dilutions of Standard 2 using mass flow controllers and 9.9 ppm CH₄ standard in nitrogen as diluent

CH ₄ diluent flow (ml min ⁻¹)	C ₂ H ₂ flow (ml min ⁻¹)	Total flow (ml min ⁻¹)	[C ₂ H ₂] (ppmv)	[CH ₄] (ppmv)
2500	50	2550	184.00	9.71
1500	50	1550	302.71	9.58
800	30	830	339.19	9.54
1000	40	1040	360.93	9.52
450	20	470	399.33	9.48
450	20	490	507.25	9.36
390	25	415	565.31	9.32

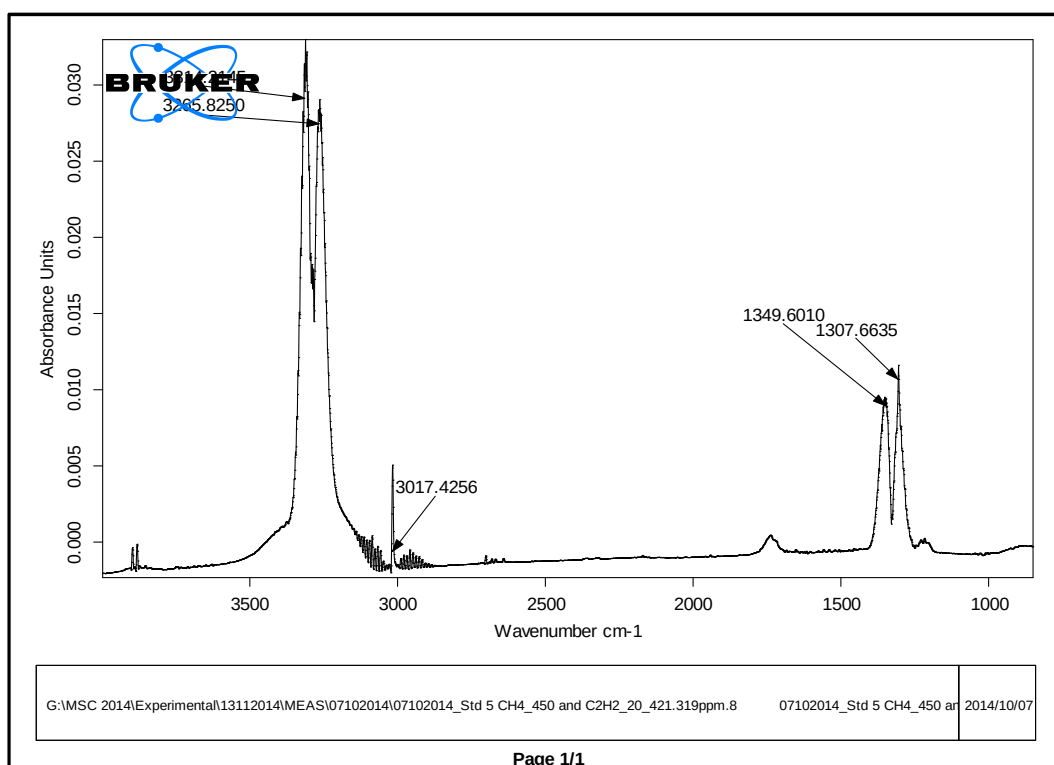


Figure 27: Spectrum obtained on analysing Standard 2 using CH_4 as internal standard at 3017 cm^{-1} .

Standard 3 (Air Liquide C_2H_2 reference standard)

The following dilutions were made to obtain the 7 calibration levels used to draw up a calibration curve for C_2H_2 using Standard 3:

Table 9: Dilution of Standard 3 using mass flow controllers and nitrogen as diluent

Diluent flow (ml min^{-1})	C_2H_2 flow (ml min^{-1})	Total flow (ml min^{-1})	$[\text{C}_2\text{H}_2]$ (ppmv)
2500	50	2550	94.804
1500	50	1550	155.968
1000	40	1040	185.962
450	20	470	205.745
800	40	840	230.238
350	20	370	261.351
390	25	415	291.265

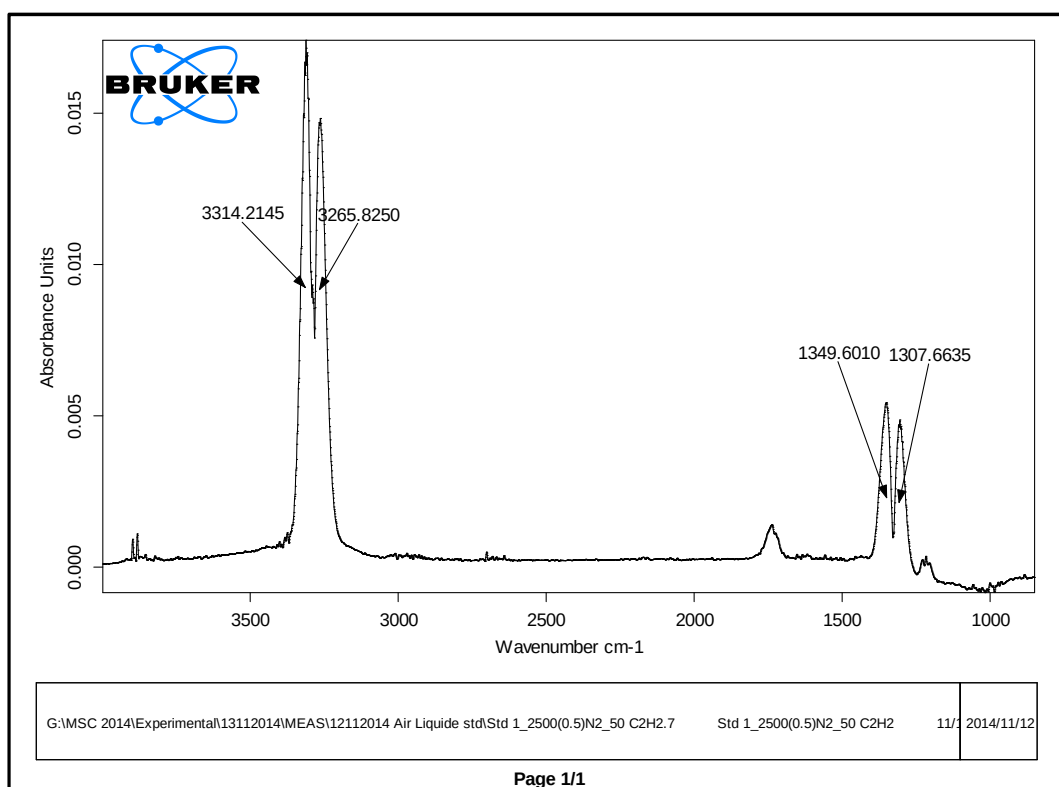


Figure 28: Spectrum obtained for Standard 3

Standard 3 with internal standard

For this experimental work, CH₄ was added as an internal standard to Standard 3. A CH₄ reference standard of concentration 102 ppm, made up in nitrogen, was used as the diluent replacing the nitrogen previously used. The following dilutions were made to obtain the 6 calibration levels:

Table 10: Dilutions of Standard 3 using mass flow controllers and 102 ppm CH₄ standard as diluent

CH ₄ diluent flow (ml min ⁻¹)	C ₂ H ₂ flow (ml min ⁻¹)	Total flow (ml min ⁻¹)	[C ₂ H ₂] (ppmv)	[CH ₄] (ppmv)
2000	25	2025	56.691	99.512
2500	50	2550	94.80	100.00
1500	50	1550	155.968	98.71
1000	40	1040	185.962	98.08
450	20	470	205.745	97.14
800	40	840	230.238	97.66

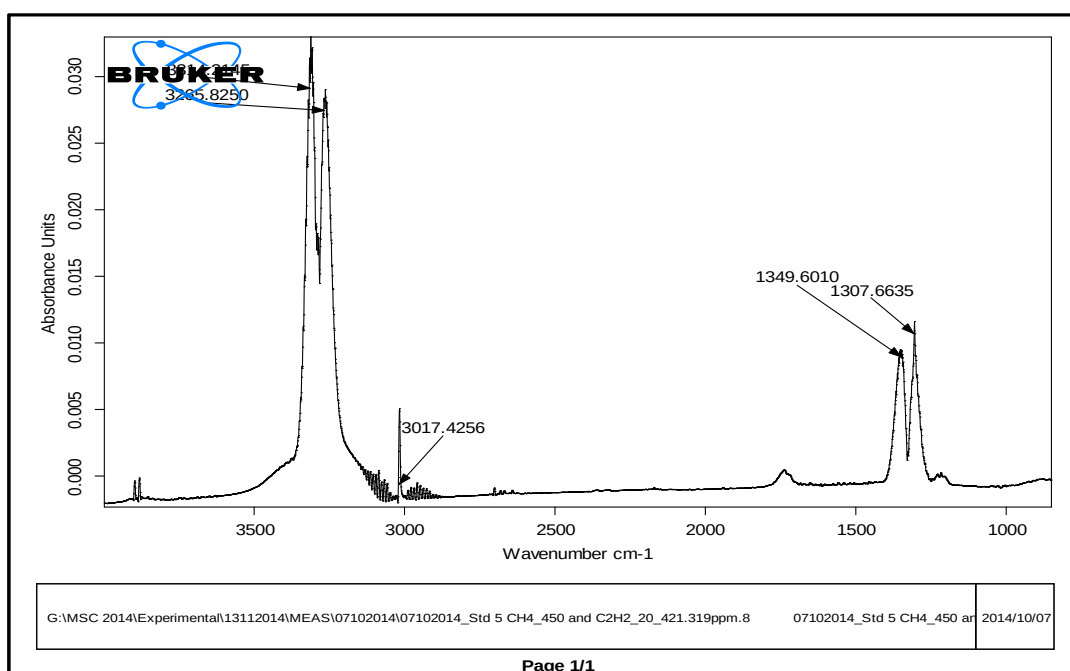


Figure 29: Spectrum obtained on analysing Standard 3 with CH₄ as internal standard at 3017 cm⁻¹.

3.5. Section 2: GC experimental work

Commercial instrumentation

Agilent 7890 Gas Chromatograph [Agilent Technologies, 5301 Stevens Creek Blvd, Santa Clara, CA, USA] equipped with a Valco 6 port valve and a VICI D-3 Pulsed Discharge Helium Ionization detector. [Valco Instruments Company Inc. Schenkon, Switzerland].

Agilent Software: OpenLAB CDS, Chemstation Edition, Rev. C. 01.03 (37)

Consumables

Haysep Q Silcosteel packed column: Mesh 80/100, ID 2.1 mm and length 5 m. Maximum temperature of 275°C.

Haysep N Nickel packed column: Mesh 80/100, ID 2.1 mm and length 4 m. Maximum temperature of 165°C.

Gases

The following *cylinder gases* were obtained from Air Products South Africa (Pty) Ltd. [Kempton Park, Gauteng]: Helium (5.0), Nitrogen (5.0) and Synthetic air (4.0).

Reference standards

Multicomponent Matheson reference standard 0.15% mixture in nitrogen:
Lot nr: 1059614693. Supplied by Puregas (Pty) LTD [Alrode, South Africa]

3.6. GC/PDHID set up and optimization

General

The performance of a PDHID detector is adversely affected by the presence of any impurities in the carrier or discharge gas streams. The GC system was therefore set up using helium (5.0) as carrier gas. The helium was connected directly to the GC, unlike the other instruments in the laboratory where a central source of helium is used for all the systems in the laboratory. The purpose of this was to keep air ingress to a minimum by limiting the length of the helium flow path. In addition the helium was put through heated purifiers to ensure the removal of water vapor and any fixed gas impurities that could be present. The purified helium was then split between the detectors and the columns using an electronic flow control device.

Valve configuration

The GC/PDHID was initially set by Scientific Supply Services cc who were contracted by Chemetrix upon PAL's purchase of the 7890 GC in 2011. Two six port Vici valves were installed together with two Vici PDHID's. The detectors and valves were set up as two independent systems with the possibility of linking them in future, depending on the type of analyses required. A sample inlet was designed in-house and linked to the GC. The sample inlet included a point whereby vacuum could be drawn to evacuate

the sample lines, a two way valve which could be switched between sample and calibration standards as required and a point connected to a helium source which could be used to flush the inlet with helium if required.

The system was initially setup such that in position A, the sample loop is filled and when the valve switches to position B, the contents of the loop are injected onto the column. This configuration is referred to as “Sample Injection”. See Figure 30 below.

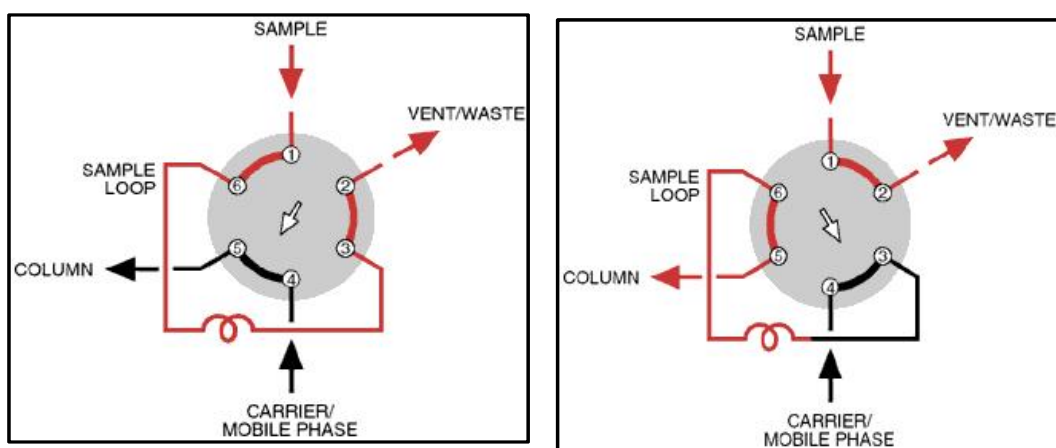


Figure 30: In position A on the left, the sample loop is filled and in position B on the right, the contents of the loop are injected onto the column. ⁽⁵⁹⁾

Subsequent to this setup, problems were encountered after injection of the first reference standard. Due to financial constraints at NECSA, no funds were available for the purchase of a single component acetylene reference standard and it was decided to use the available twenty seven component mix, one of the components being 0.155% C₂H₂. Acetylene elutes at approximately six minutes but the runtime had to be extended to thirty minutes in order to elute the remaining components. It was also found that the mixture of organic components caused the PDHID baseline to increase and additional time was required to stabilize the baseline after each run.

In a commercial laboratory, time is money and the quicker a sample can be analyzed, the greater the number of sample that can be run in a given period hence it was decided to re-plumb the system from a “Sample injection” configuration to a “Loop sampling with backflush of pre-column to vent” configuration. The “Loop sampling with backflush of pre-column to vent” plumbing scheme allows “heavy” eluting components with long retention times to be back flushed to waste. After the sample loop is loaded in position A, the valve is switched to position B to inject the sample onto column 1. Once all the components of interest have entered column 2, the valve is switched back to position A and column 1 is backflushed to vent during the analysis, reducing the total analysis time.⁽⁶⁰⁾ The “Loop sampling with backflush of pre-column to Vent” plumbing scheme is indicated in figure 31 below.

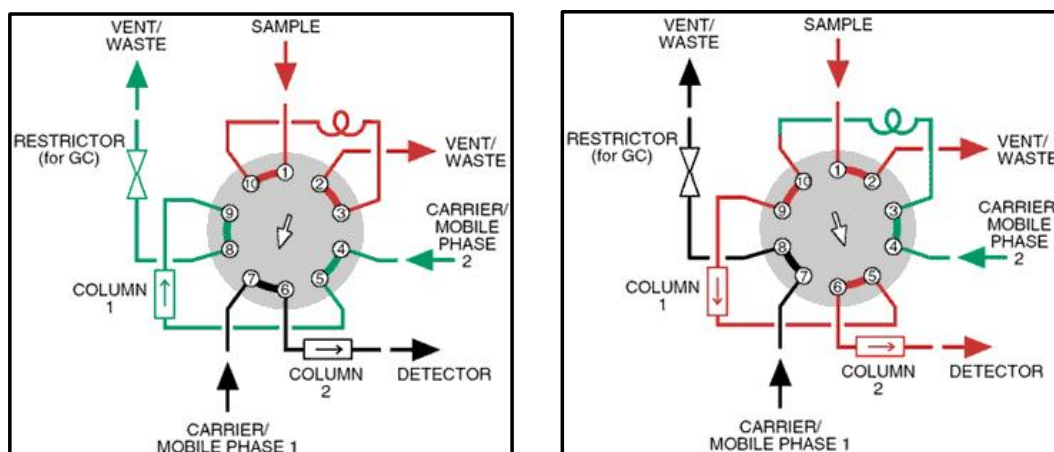


Figure 31: In position A on the left, the sample loop is loaded/column 1 is backflushed and in position B on the right, the sample is sent to the columns⁽⁶⁰⁾

Above configuration led to a modicum of success as all organic components eluting after the acetylene could be backflushed. However, the long term goal of the project is the analysis of high purity permanent gases such as nitrogen and oxygen in the 99, 9999% range. Since most of the permanent gases will elute prior to the acetylene and in much larger quantities than the acetylene, a massive disturbance in the PDHID baseline will be observed. In order to combat this problem, the major

component of the permanent gas being analysed must be eliminated from the analytical column before reaching the detector.

To address this problem, a valve configuration termed the “Sample injection and heart cut to detector” was setup. In this configuration the sample loop is loaded in position A. When the valve switches to position B, the loop contents are injected onto the analytical column and the front cut (containing the major permanent gas component being analysed) is eluted from the column and goes to vent. At this point the valve is switched back to position A, and the heart cut section containing the acetylene is backflushed to the detector. Once the acetylene has eluted, the valve is switched back to position B, sending the end cut to vent. ⁽⁶¹⁾ See Figure 32 below for the “Sample injection and heart cut to detector” configuration.

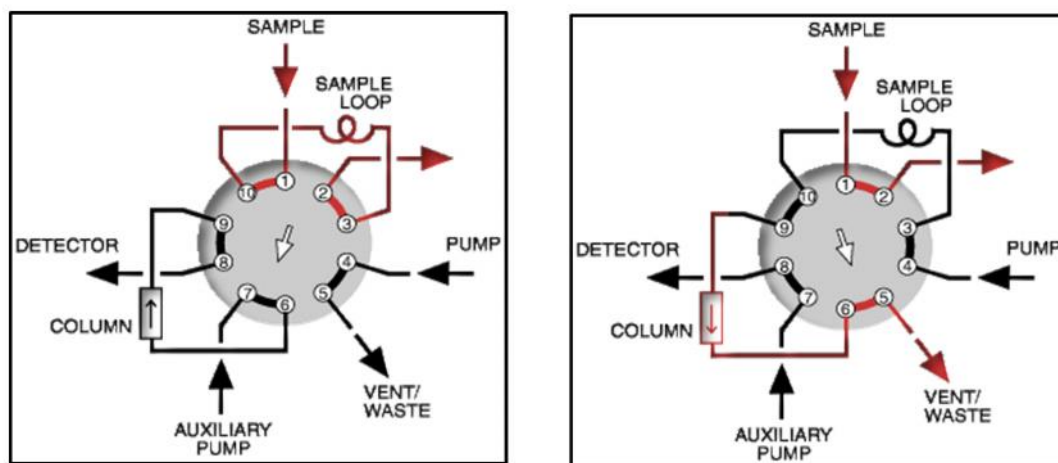


Figure 32: In position A on the left, the sample loop is loaded in the initial step and in the second step the heart cut is sent to the detector. In position B on the right, the loop contents are sent to the column in the initial step and in the second step the end cut is sent to waste. ⁽⁶¹⁾

According to Hayes Separations, INC ⁽⁶²⁾, the Haysep Q or HayesepT packed column would provide adequate analyses of acetylene. A Hayesep Q, five metre, 80/100 mesh was selected as the analytical column and a four meter Hayesep N, 80/100 mesh was selected as the pre-column.

The GC was configured such that a flow of thirty ml/min of Helium passed through the discharge region of the PDHID and a flow of twenty ml min⁻¹ through the column. The detector was kept at a temperature of 150°C. Grade 5 helium (99.999%) was used at all times and it was additionally purified using a VICI helium purifier, prior to entering the PDHID and the analytical column. The valve box was heated to 60°C and the column temperature was isothermal at 80°C throughout each run.

3.7. GC/PDHID experimental work

General

The purpose of this second section of the experimental work was to draw up a calibration curve for acetylene using the GC/PDHID and then analyze samples containing moisture and in which the moisture had been converted to C₂H₂ via reaction with calcium carbide.

Dilution of standards using mass flow controllers

A dilution system, designed and built in-house, was used to dilute the original 0.15% Matheson reference standard down to eight different levels from which a calibration curve could be drawn up. The nitrogen diluent flow was controlled by a mass flow controller with a range of 2500 to 50 ml min⁻¹ and the reference standard was controlled by a mass flow controller with a range of 1 to 20 ml min⁻¹. Mixing of the diluent and standard took place within the dilution system and the resultant gas mixture was loaded directly from the dilution system into the sample loop on the GC at a 100 kPa. Table 11 below summarizes the diluent and standard flows used to obtain a range of calibration levels.

Table 11: Dilution of C₂H₂ standard using mass flow controllers

Diluent flow (ml min⁻¹)	Standard flow (ml min⁻¹)	[C₂H₂] (ppmv)
2500	1.0	0.620
1800	1.0	0.861
1500	1.0	1.033
1000	1.0	1.584
800	1.0	1.935
600	1.0	2.579
400	1.0	3.865
300	1.0	5.150
250	1.0	6.175
200	1.0	7.711

Calculations to obtain ppmv values for dilutions

The calculations performed to acquire the concentration of C₂H₂ as ppmv after dilution was done as follows:

$$\text{ppmv} = F_s / (F_s + F_D) \times C_s$$

Where:

F_s = Flow of Reference standard in ml min⁻¹

F_D = Flow of Diluent gas in ml min⁻¹

C_s = Concentration of Reference standard in ppmv

3.8. Section 3: Conversion of moisture to C₂H₂

Consumables

Calcium Carbide (100g/0.3-1 mm): Supplied by Fluka: Purity >75%: Lot nr-437549/1

Agilent Technologies 2ml clear wide opening *glass crimp cap vial*: Lot nr-924-01-13/001: Supplied by Chemetrix

1µl SGE Type B Plunger needle syringe P/N:020705: Supplied by SGE

Optimization of the conversion process using vials

GC/PDHID was initially selected as the analytical method for the optimization of the conversion process primarily due to the low sample volumes generated in the initial testing processes. Conversion of moisture to C_2H_2 was initially undertaken in 2ml GC vials which were tightly sealed using crimp caps and a capper. The initial tests included the following:

- CaC_2 was added to 5 vials and the vials sealed. The headspace from each vial was analyzed using the headspace above the CaC_2 .
- CaC_2 was added to 5 vials and the vials then purged with a light flow of helium for 5 minutes. The vials were then sealed and the headspace from each vial was analyzed using the headspace above the CaC_2 .
- CaC_2 was added to 5 vials and the vials then purged with a light flow of helium for 5 minutes. The vials were then sealed. 1 µl of $H_2O_{(l)}$ was added to each vial, using a 1 µl syringe and inserting the liquid via the cap septum. The headspace of each vial was analyzed.
- CaC_2 was added to 5 vials and the vials then purged with a light flow of helium for 5 minutes. The vials were then sealed. Each vial was tared using a 5 decimal place balance and 1 µl of $H_2O_{(l)}$ was added to each vial, using a 1 µl syringe and inserting the liquid via the cap septum. The mass of $H_2O_{(l)}$ added was recorded. The headspace of each vial was analyzed.

Sample holder for conversion process

The crimp cap vials worked well for the optimization of the conversion process using $H_2O_{(l)}$ but a bigger container was required for gas sampling. A sample holder was put together using Swagelok fittings (See Figure 33). A digital pressure gauge was connected to the holder and provision was made to either evacuate, or fill the holder with helium as required. The central compartment was filled with CaC_2 , contained on either side by

glass wool. An inlet, sealed with a rubber septum, directly coupled to the CaC_2 in the holder was used to add moisture for the conversion reaction using H_2O (l). Alternately a quantity of gas sample, containing H_2O could be loaded into the holder, and once the reaction had occurred, the liberated acetylene could be swept through to the GC or FTIR using the helium inlet.



Figure 33: Sample holder for $\text{CaC}_2/\text{H}_2\text{O}$ reaction

The sample holder was initially flushed with helium to remove any atmospheric moisture which reacts with the calcium carbide giving higher results than expected. A known mass of water was added to the evacuated sample holder containing the calcium carbide. The holder was pressurized to 100 kPa with helium and allowed to stand for 2 to 3 minutes. Thereafter aliquots were transferred from the holder to the GC or FTIR and the acetylene concentrations (ppmv) calculated back to moisture values. An initial run with high % recovery indicated air ingress and the holder was then sealed and purged externally with helium. Results obtained for both GC and FTIR are discussed in Chapter 4.

CHAPTER 4: RESULTS AND DISCUSSION

4.1. Method 1: H₂O analysis on FTIR

Optimization of the glass cell temperature

From the plot of H₂O concentration versus cell temperature for the glass cell in Figure 20, it can be seen that an increase in the moisture concentration occurred as the temperature of the glass cell was systematically raised from 40°C to 120°C. The supplier of this particular glass cell indicated that the cell could be heated to 200°C using a standard heating mantle designed specifically for the cell. Unfortunately this was not available at PAL and an in-house system, utilizing heating tape and a sensor, was set up as an alternative to the heating mantle. It was decided not to increase the temperature beyond 120°C during the testing as there was a concern that the glass cell electronics risked overheating and possible damage. From the plot of H₂O concentration versus cell temperature for glass cell, 40°C was selected as the optimal temperature for the moisture analysis. No temperature optimization was done for the C₂H₂ tests as stabilization at different calibration levels was rapidly reached, unlike for the moisture tests where hours of stabilization was required between each level.

Calibration results for moisture

Calibration data was generated as per section 3.3. A typical linear calibration curve for wavenumber 3854 cm⁻¹, obtained from Excel, is shown in figure 34 below. All calculated parameters for the calibration curves at the selected wavelengths are indicated in Tables 12 through to 16 below. The concentration ranges are classified as follows: **Level 1:** 0.514 ppm to 9.890 ppm and **Level 2:** 0.514 to 3.956 ppm

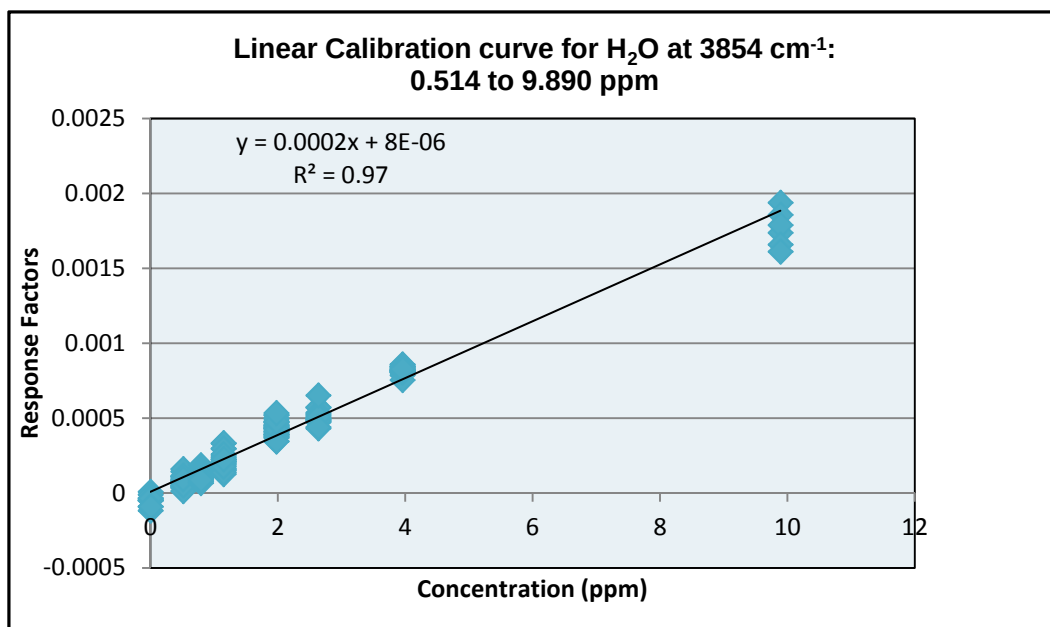


Figure 34: Linear calibration curve for moisture at 3854 cm⁻¹ with a working range between 0.514 and 9.890 ppm

Table 12: Summary of linear regression data for moisture standard: Confidence intervals for the intercept.

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3854	Level 1	-8.14938E-06	2.28403E-05
	Level 2	-4.87399E-05	-2.13524E-05
3712	Level 1	2.65291E-05	6.41903E-05
	Level 2	-3.03179E-05	-4.81437E-06
3689	Level 1	5.83273E-06	2.87751E-05
	Level 2	-2.49687E-05	-7.60199E-06
1734	Level 1	-8.43603E-06	1.16038E-05
	Level 2	-3.38966E-05	-1.74508E-05
1685	Level 1	-8.47766E-06	8.33048E-06
	Level 2	-2.98813E-05	-1.67029E-05
1653	Level 1	1.88803E-06	3.44341E-05
	Level 2	-4.31429E-05	-1.80523E-05
1635	Level 1	-4.1607E-06	2.1526E-05
	Level 2	-3.76559E-05	-1.83672E-05
1617	Level 1	-5.28292E-06	1.88789E-05
	Level 2	-3.74357E-05	-1.83628E-05
1576	Level 1	1.18962E-05	3.10726E-05
	Level 2	-1.21553E-05	1.00874E-06

Table 12 continued:

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
1539	Level 1	2.17066E-05	6.09913E-05
	Level 2	-3.2341E-05	-1.35222E-06
1456	Level 1	5.12543E-06	6.46051E-05
	Level 2	-6.99185E-05	-3.29746E-05

**Table 13: Summary of linear regression data for moisture standard:
Regression data for t test.**

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3854	Level 1	0.9853	0.9709	69.08	1.98	4771.9
	Level 2	0.9842	0.9687	65.17	1.98	4247.3
3712	Level 1	0.98587	0.97194	70.88	1.98	5023.8
	Level 2	0.99099	0.98205	86.90	1.98	7552.3
3689	Level 1	0.9899	0.9799	83.90	1.98	7039.7
	Level 2	0.9918	0.9837	91.18	1.98	8314.0
1734	Level 1	0.9896	0.9792	82.38	1.98	6786.9
	Level 2	0.9899	0.9799	82.07	1.98	6735.2
1685	Level 1	0.9893	0.9788	81.53	1.98	6647.8
	Level 2	0.9906	0.9814	85.26	1.98	7269.2
1653	Level 1	0.9900	0.9802	84.46	1.98	7133.4
	Level 2	0.9916	0.9833	90.30	1.98	8153.6
1635	Level 1	0.9915	0.9831	91.55	1.98	8381.8
	Level 2	0.9926	0.9853	95.71	1.98	9160.9
1617	Level 1	0.9874	0.9751	75.15	1.98	5647.8
	Level 2	0.9892	0.9785	79.18	1.98	6269.2
1576	Level 1	0.9823	0.9649	62.94	1.98	3961.8
	Level 2	0.9889	0.9778	77.91	1.98	6070.0
1539	Level 1	0.9893	0.9787	81.47	1.98	6638.0
	Level 2	0.9907	0.9814	85.38	1.98	7289.5
1456	Level 1	0.9839	0.9681	66.14	1.98	4374.5
	Level 2	0.9910	0.9822	86.94	1.98	7559.1

Table 14: Summary of linear regression data for moisture standard: LOD and LOQ values

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3854	Level 1	1.06	3.52
	Level 2	0.66	2.20
3712	Level 1	1.08	3.61
	Level 2	0.50	1.65
3689	Level 1	0.87	2.90
	Level 2	0.47	1.57
1734	Level 1	0.89	2.96
	Level 2	0.52	1.75
1685	Level 1	0.90	2.99
	Level 2	0.50	1.68
1653	Level 1	0.86	2.88
	Level 2	0.48	1.59
1635	Level 1	0.84	2.79
	Level 2	0.45	1.50
1617	Level 1	0.97	3.24
	Level 2	0.54	1.81
1576	Level 1	1.16	3.87
	Level 2	0.55	1.84
1539	Level 1	0.90	2.99
	Level 2	0.50	1.68
1456	Level 1	1.16	3.86
	Level 2	0.49	1.63

Table 15: Summary of linear regression data for moisture standard: P values

Wavenumber (cm ⁻¹)	Range (ppm)	P value (Slope)	P value (Intercept)
3854	Level 1	9.8370E-112	0.35030429
	Level 2	5.4229E-105	1.31899E-06
3712	Level 1	2.0165E-114	4.61999E-06
	Level 2	2.2725E-122	0.007287727
3689	Level 1	3.7270E-124	0.003367965
	Level 2	3.3564E-125	0.000301328
1734	Level 1	4.9135E-123	0.755155405
	Level 2	5.2867E-119	7.00000E-09
1685	Level 1	2.1160E-122	0.986215062
	Level 2	3.0247E-121	1.07707E-10

Table 15 continued:

Wavenumber (cm ⁻¹)	Range (ppm)	P value (Slope)	P value (Intercept)
1653	Level 1	1.4655E-124	0.028975813
	Level 2	1.2598E-124	3.69579E-06
1635	Level 1	1.6399E-129	0.183575588
	Level 2	2.3276E-127	5.73734E-08
1617	Level 1	2.0264E-117	0.26789414
	Level 2	6.7144E-117	4.65611E-08
1576	Level 1	1.1657E-106	1.86088E-05
	Level 2	5.9412E-116	0.096342857
1539	Level 1	2.3478E-122	5.42776E-05
	Level 2	2.5026E-121	0.033309235
1456	Level 1	1.1787E-109	0.021901266
	Level 2	9.8228E-122	1.74121E-07

The same data was taken for the selected wavenumbers for moisture and quadratic fits were tested in the same manner as for the linear fits. The data is summarized in Tables 16 through to 18 below. A typical quadratic calibration curve for wavenumber 3854 cm⁻¹, obtained from Excel, is shown in figure 35 below.

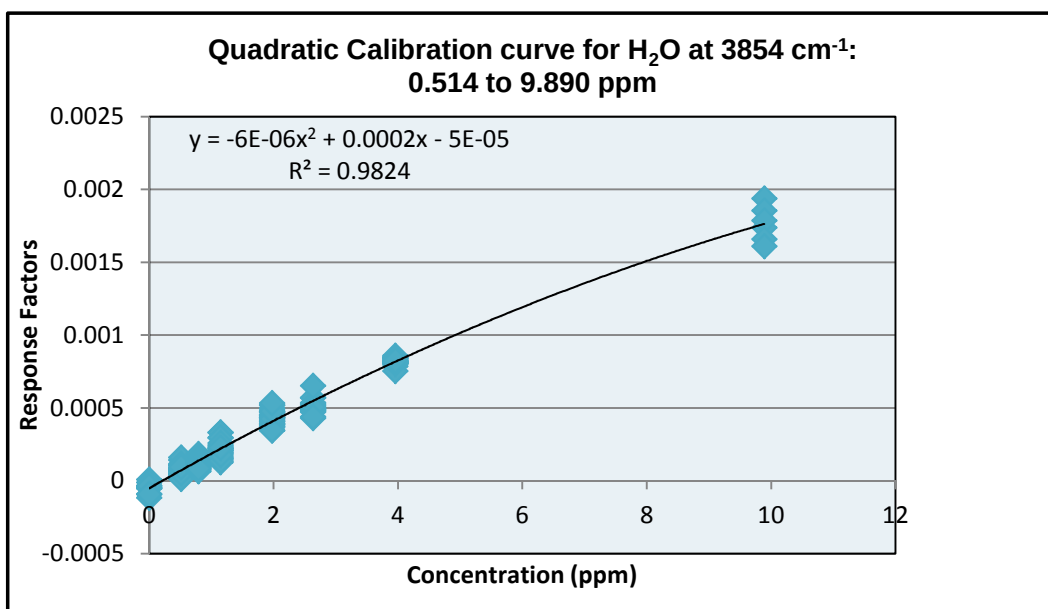


Figure 35: Quadratic calibration curve for moisture at 3854 cm⁻¹ with a working range 0.514 to 9.890 ppm.

**Table 16: Summary of quadratic regression data for moisture standard:
Regression data for t test**

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3854	Level 1	0.9914	0.9829	90.62	1.98	4077.3
	Level 2	0.9849	0.9700	66.59	1.98	2200.6
3712	Level 1	0.9938	0.9877	107.86	1.98	5776.6
	Level 2	0.9919	0.9840	92.04	1.98	4205.3
3689	Level 1	0.9947	0.9895	116.39	1.98	6726.6
	Level 2	0.9926	0.9852	95.91	1.98	4565.7
1734	Level 1	0.9941	0.9882	109.99	1.98	6007.2
	Level 2	0.9916	0.9832	89.93	1.98	4014.6
1685	Level 1	0.9938	0.9876	107.31	1.98	5717.8
	Level 2	0.9912	0.9825	87.99	1.98	3842.6
1653	Level 1	0.9951	0.9902	120.87	1.98	7254.2
	Level 2	0.9927	0.9855	96.99	1.98	4668.9
1635	Level 1	0.9951	0.9903	121.15	1.98	7288.1
	Level 2	0.9933	0.9868	101.05	1.98	5068.3
1617	Level 1	0.9933	0.9866	103.02	1.98	5269.4
	Level 2	0.9903	0.9806	85.52	1.98	3462.3
1576	Level 1	0.9899	0.9799	83.778	1.98	3484.9
	Level 2	0.9894	0.9789	79.97	1.98	3174.2
1539	Level 1	0.9946	0.9893	115.47	1.98	6619.9
	Level 2	0.9919	0.9838	91.529	1.98	4158.4
1456	Level 1	0.9908	0.9817	88.03	1.98	3848.1
	Level 2	0.9924	0.9848	94.18	1.98	4402.9

Table 17: Summary of quadratic regression data for moisture standard: LOD and LOQ values.

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3854	Level 1	0.64	2.12
	Level 2	0.57	1.91
3712	Level 1	0.54	1.79
	Level 2	0.41	1.36
3689	Level 1	0.51	1.69
	Level 2	0.40	1.32
1734	Level 1	0.54	1.80
	Level 2	0.40	1.33
1685	Level 1	0.55	1.85
	Level 2	0.44	1.46
1653	Level 1	0.49	1.62
	Level 2	0.38	1.27
1635	Level 1	0.52	1.73
	Level 2	0.38	1.25
1617	Level 1	0.56	1.87
	Level 2	0.44	1.48
1576	Level 1	0.67	2.24
	Level 2	0.48	1.61
1539	Level 1	0.51	1.69
	Level 2	0.40	1.34
1456	Level 1	0.67	2.22
	Level 2	0.38	1.28

Table 18: Summary of quadratic regression data for moisture standard: P values.

Wavenumber (cm ⁻¹)	Range (ppm)	P value (X ²)
3854	Level 1	4.4941E-18
	Level 2	0.01756596
3712	Level 1	1.55181E-27
	Level 2	8.60962E-05
3689	Level 1	9.01167E-22
	Level 2	0.000228788
1734	Level 1	2.16311E-19
	Level 2	7.34024E-07
1685	Level 1	1.69034E-18
	Level 2	0.003683124

Table 15 continued:

Wavenumber (cm ⁻¹)	Range (ppm)	P value (X ²)
1653	Level 1	1.05348E-23
	Level 2	1.17574E-05
1635	Level 1	6.80292E-19
	Level 2	0.000139987
1617	Level 1	5.81156E-21
	Level 2	0.000158626
1576	Level 1	5.30763E-19
	Level 2	0.008327421
1539	Level 1	4.46555E-23
	Level 2	1.56245E-05
1456	Level 1	4.7751E-19
	Level 2	3.88367E-06

4.2. Determining the suitability of methane as internal standard

A calibration curve with a regression of 0.997 was obtained for methane using a linear fit and 0.999 using a quadratic fit. See figures 36 and 37 below.

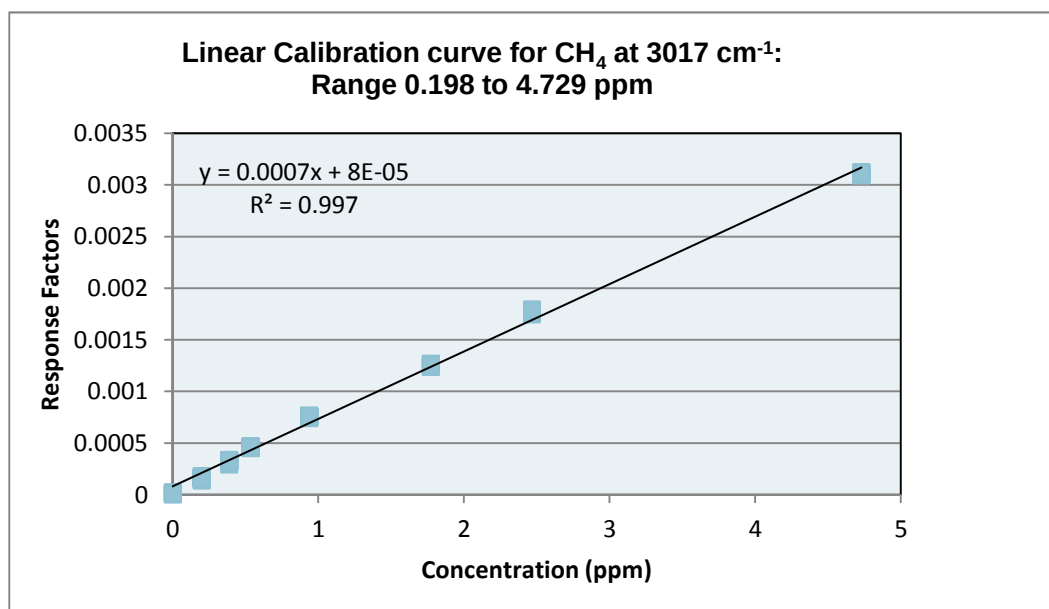


Figure 36: Linear calibration curve for CH₄ at 3017 cm⁻¹ with a working range between 0.198 and 4.729 ppm

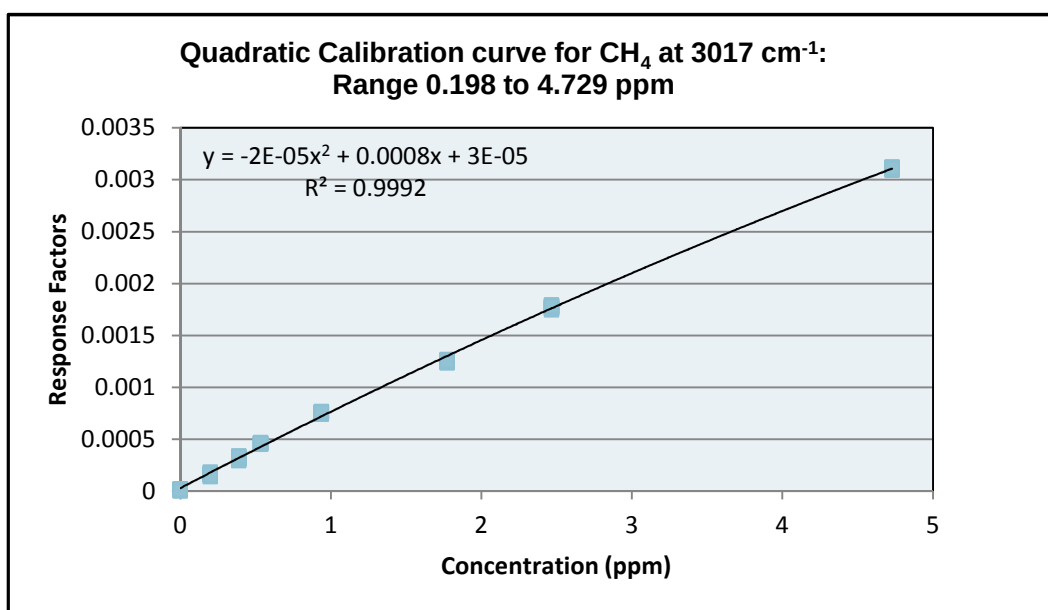


Figure 37: Quadratic calibration curve for CH₄ at 3017 cm⁻¹ with a working range between 0.198 and 4.729 ppm

Visually the spread of results around each calibration point appeared to be less than that obtained for the moisture tests indicating that the problem with the spread of results around the moisture calibration levels was related to the moisture itself and not the instrument. Moisture adheres to the side walls of the glass cell despite heating of the cell and this could be the cause of the spread of results around each calibration point for the moisture. The spread of results around each calibration point for methane was much less than the spread of results around each calibration point for moisture indicating that methane does not adhere to the side walls of the glass cell.

Methane as internal standard for moisture

The internal standard method allows the operating conditions to vary from sample to sample without affecting the end results. The internal standard must not be present in the unknown mixture and must not have any unknown matrix effects. A known quantity of this internal standard is added to the sample and any variation in sample size will be noticeable by comparison of the response factors in different runs. ⁽³²⁾

Unfortunately the idea of using methane as internal standard with the moisture permeation standard could not be implemented in this project. The Matheson CH₄ reference standard, imported from America, was very expensive and due to the long equilibration times required for the moisture, the scenario existed in which the CH₄ reference standard would be finished quite quickly. Since the CH₄ is required as an internal standard for ratio purposes, it does not have to be of as high a quality as the Matheson CH₄ reference standard. A more cost effective methane standard possibly from a South African supplier such as Afrox will be purchased and used to draw up a calibration curve for moisture using methane as an internal standard.

To test the internal standard theory however, it was possible to use the CH₄ Matheson reference standard as an internal standard for the C₂H₂ calibration curves as the stabilization/equilibration times for C₂H₂ were much less than those required for moisture.

4.3. Method 2: C₂H₂ analysis on FTIR

Calibration results for Standard 1: no internal standard

Calibration curves were set up using Standard 1 and the combination peak at 1313 / 3249 cm⁻¹ and the single peak at 1305 cm⁻¹. The linear calibration curves obtained from Excel for aforementioned wavenumbers are shown in figures 39 and 40. The following concentrations were used for both 3313/3266 and 1305 cm⁻¹ (ppm): 33.550, 51.235, 76.733, 151.961, 246.815 and 369.048 ppm. All calculated parameters for the calibration curves at the selected wavelengths are indicated in Tables 19 through to 22. The concentration ranges are classified as follows: **Level 1:** 33.550 ppm to 369.0480 ppm and **Level 2:** 33.550 ppm to 246.815 ppm.

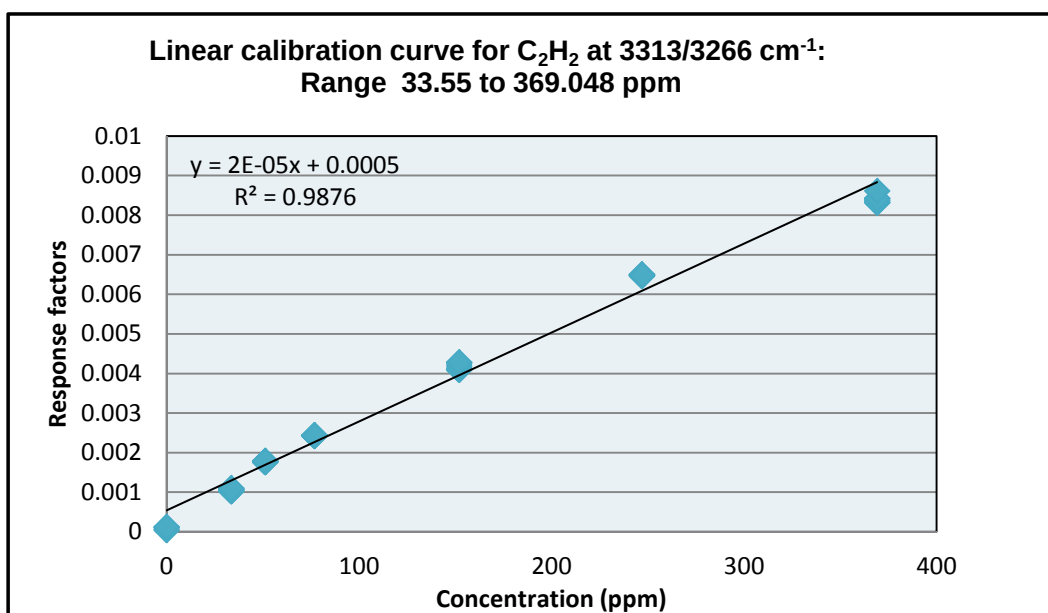


Figure 38: Linear calibration curve obtained for Standard 1 for C₂H₂ at 3313/3266 cm⁻¹

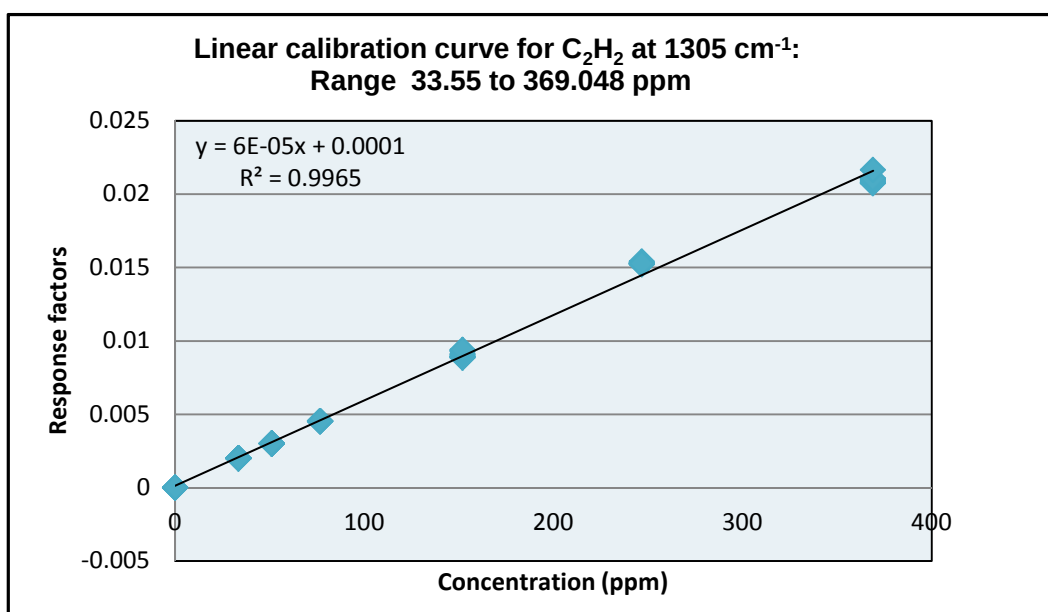


Figure 39: Linear calibration curve obtained for Standard 1 for C₂H₂ at 1305 cm⁻¹

Table 19: Summary of linear regression data for Standard 1 (C₂H₂): Confidence intervals of the intercept.

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266:	Level 1	0.000425408	0.000656938
	Level 2	0.000273578	0.000397811
1305	Level 1	-2.08504E-05	0.000294918
	Level 2	-0.000213869	-8.35493E-05

Table 20: Summary of linear regression data for Standard 1 (C₂H₂): Regression data for t test.

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9938	0.9876	69.09	2.0	4773.4
	Level 2	0.9976	0.9952	103.75	2.0	10727.3
1305	Level 1	0.9982	0.9965	131.09	2.0	17184.7
	Level 2	0.9995	0.9910	242.73	2.0	58919.9

Table 21: Summary of linear regression data for Standard 1 (C₂H₂): LOD and LOQ values.

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	40.07	133.58
	Level 2	17.00	56.65
1305	Level 1	21.12	70.40
	Level 2	7.25	24.17

Table 22: Summary of linear regression data for Standard 1 (C₂H₂): P values.

Wavenumber (cm ⁻¹)	Range (ppm)	P value (Slope)	P value (Intercept)
3313/3266	Level 1	6.76708E-59	2.54682E-13
	Level 2	6.47881E-62	5.8721E-15
1305	Level 1	1.80548E-75	0.087672483
	Level 2	4.18159E-81	2.94031E-05

The same data was taken for Standard 1 and quadratic fits were tested in the same manner as for the linear fits. The data is summarized in Tables 23 through to 26 below and the quadratic calibration curves obtained from Excel are shown in Figures 40 and 41 below.

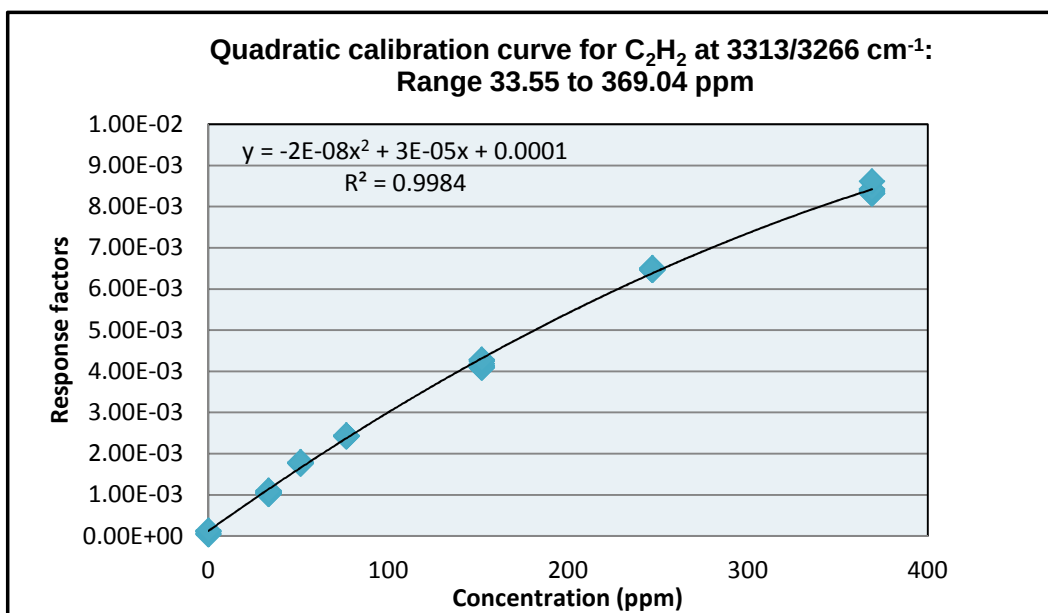


Figure 40: Quadratic calibration curve obtained for Standard 1 for C₂H₂ at 3313/3266 cm⁻¹.

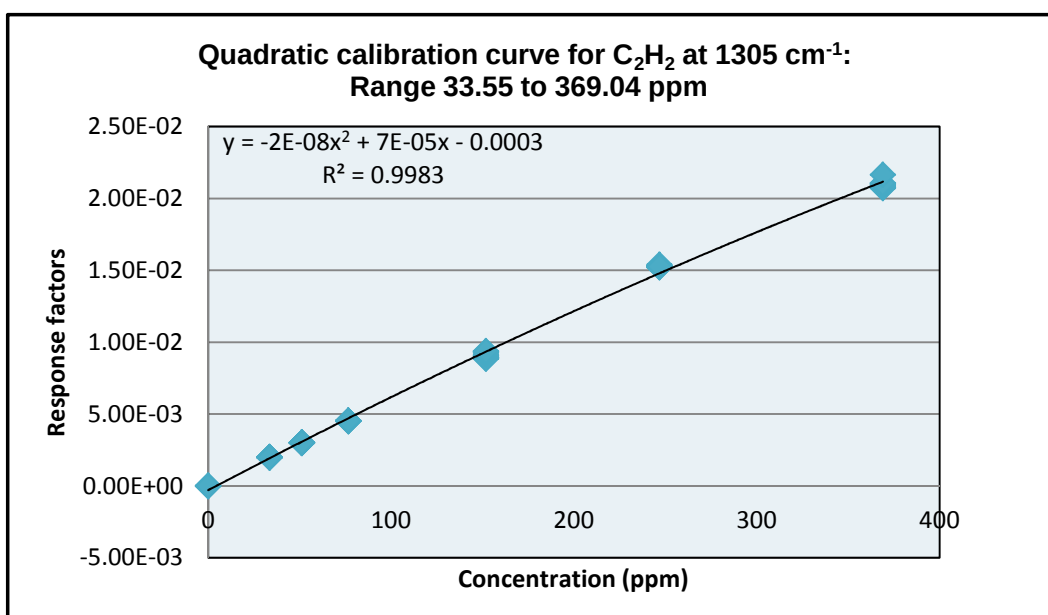


Figure 41: Quadratic calibration curve obtained for Standard 1 for C₂H₂ at 1305 cm⁻¹

The peak at 1350 cm⁻¹ could not be quantified, as previously indicated, due to interferences from other components in the reference standard.

Table 23: Summary of quadratic regression data for Standard 1 (C₂H₂): Confidence intervals of the intercept.

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	5.90035E-05	0.000179881
	Level 2	0.0004087	-0.000814349
1305	Level 1	-0.000459578	-0.000139254
	Level 2	-2.30221E-06	0.000121307

Table 24: Summary of quadratic regression data for Standard 1 (C₂H₂): Regression data for t test.

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9992	0.9984	190.78	2.0	17895.9
	Level 2	0.9971	0.9941	102.47	2.0	5165.81
1305	Level 1	0.9991	0.9983	185.45	2.0	16909.9
	Level 2	0.9998	0.9997	391.05	2.0	74989.5

Table 25: Summary of quadratic regression data for Standard 1 (C₂H₂): LOD and LOQ values.

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	10.60	35.34
	Level 2	13.60	45.34
1305	Level 1	13.04	43.48
	Level 2	5.00	16.67

Table 26: Summary of quadratic Excel regression data for Standard 1 (C₂H₂): P values.

Wavenumber (cm ⁻¹)	Range (ppm)	P value (X ²)
3313/3266	Level 1	1.43584E-27
	Level 2	3.54145E-11
1305	Level 1	1.95761E-10
	Level 2	3.89607E-12

Calibration results for Standard 2: no internal standard

Calibration curves were set up using the in-house certified standard and the combination peak at 3313 / 3266 cm⁻¹ and the single peaks at 1350

cm^{-1} and 1305 cm^{-1} used for quantitation. Both linear and quadratic selections were tested using Excel regression data. The results are summarized in Tables 28 to 31 and the calibration curves shown in Figures 42 to 44. The following concentrations (ppm) were used for both $3313/3266$, 1350 and 1305 cm^{-1} : 147.780, 243.740, 360.930, 446.870, 766.050, 1294.370 and 2681.190 ppm.

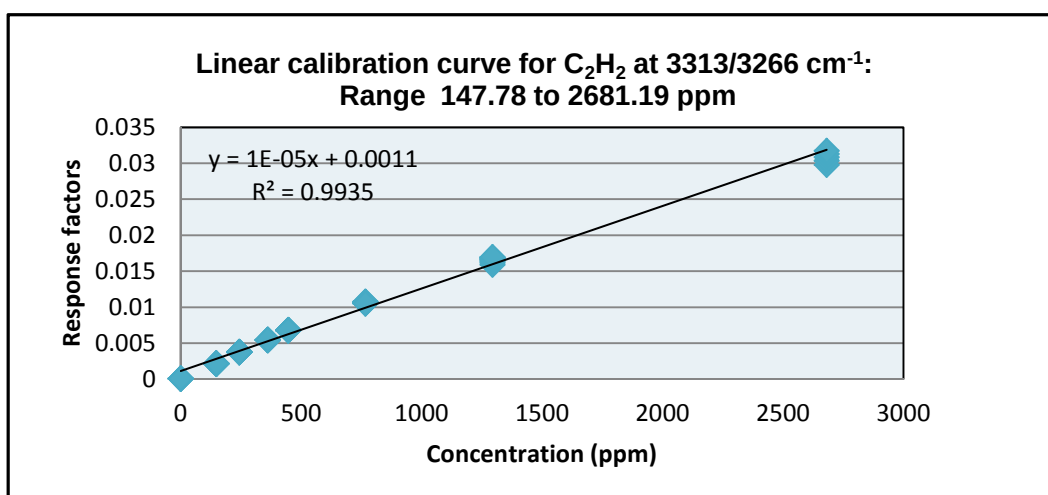


Figure 42: Linear calibration curve obtained for Standard 2 for C_2H_2 at $3313/3266 \text{ cm}^{-1}$

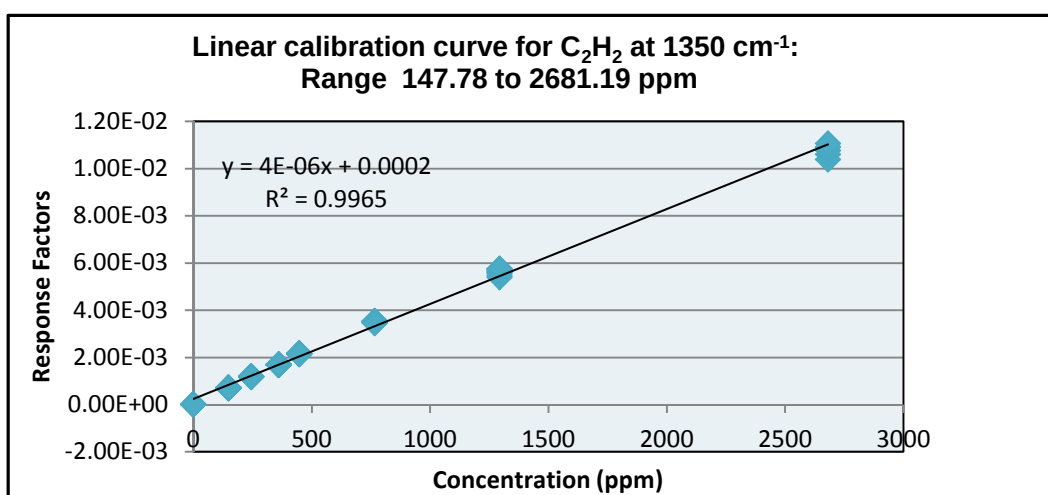


Figure 43: Linear calibration curve obtained for Standard 2 for C_2H_2 at 1350 cm^{-1}

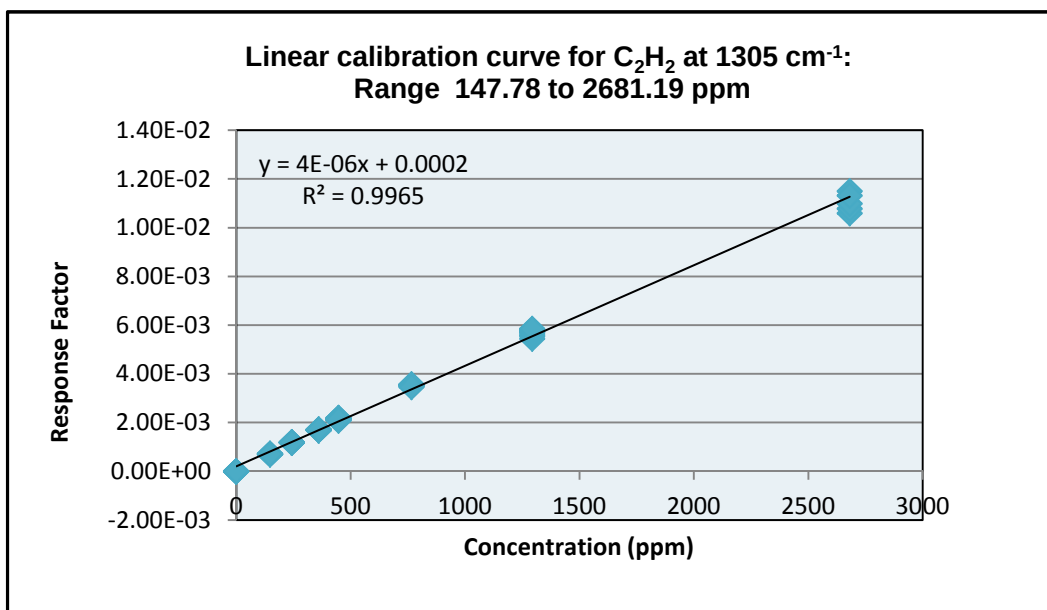


Figure 44: Linear calibration curve obtained for Standard 2 for C₂H₂ at 1305 cm⁻¹

All calculated parameters for the calibration curves at the selected wavelengths are indicated in Tables 27 through to 30 below. The concentration ranges are classified as follows: **Level 1:** 147.780 ppm to 2681.190 ppm and **Level 2:** 147.780 ppm to 1294.370 ppm

Table 27: Summary of linear regression data for Standard 2 (C₂H₂): Confidence intervals of the intercept.

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	0.00088442	0.001326591
	Level 2	0.000478288	0.000790794
1350	Level 1	0.000181354	0.000295743
	Level 2	8.4462E-05	0.000154231
1305	Level 1	0.000150379	0.000261357
	Level 2	7.11203E-05	0.000136962

Table 28: Summary of linear regression data for Standard 2 (C₂H₂): Regression data for t test.

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9967	0.9933	102.07	2.0	10418.47
	Level 2	0.9970	0.9940	102.58	2.0	10523.58
1350	Level 1	0.9982	0.9965	139.45	2.0	19445.75
	Level 2	0.9987	0.9975	158.30	2.0	25057.31
1305	Level 1	0.9984	0.9968	147.43	2.0	21734.92
	Level 2	0.9989	0.9978	170.17	2.0	28958.22

Table 29: Summary of linear regression data for Standard 2 (C₂H₂): LOD and LOQ values.

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	178.66	595.52
	Level 2	95.37	317.9
1350	Level 1	130.43	434.78
	Level 2	61.62	205.40
1305	Level 1	123.37	411.24
	Level 2	57.32	191.06

Table 30: Summary of linear regression data for Standard 2 (C₂H₂): P values.

Wavenumber (cm ⁻¹)	Range (ppm)	P value (Slope)	P value (Slope)
3313/3266	Level 1	6.80372E-78	4.4728E-15
	Level 2	1.00621E-72	2.04018E-11
1350	Level 1	2.5378E-86	5.18137E-12
	Level 2	1.20091E-83	3.84532E-09
1305	Level 1	5.52663E-88	2.47993E-10
	Level 2	1.27258E-85	3.06535E-08

The same data was taken for Standard 2 and quadratic fits were tested in as for the linear fits. The data is summarized in Tables 31 to 34 below and the quadratic calibration curves obtained from Excel are shown in Figures 45 to 47 below.

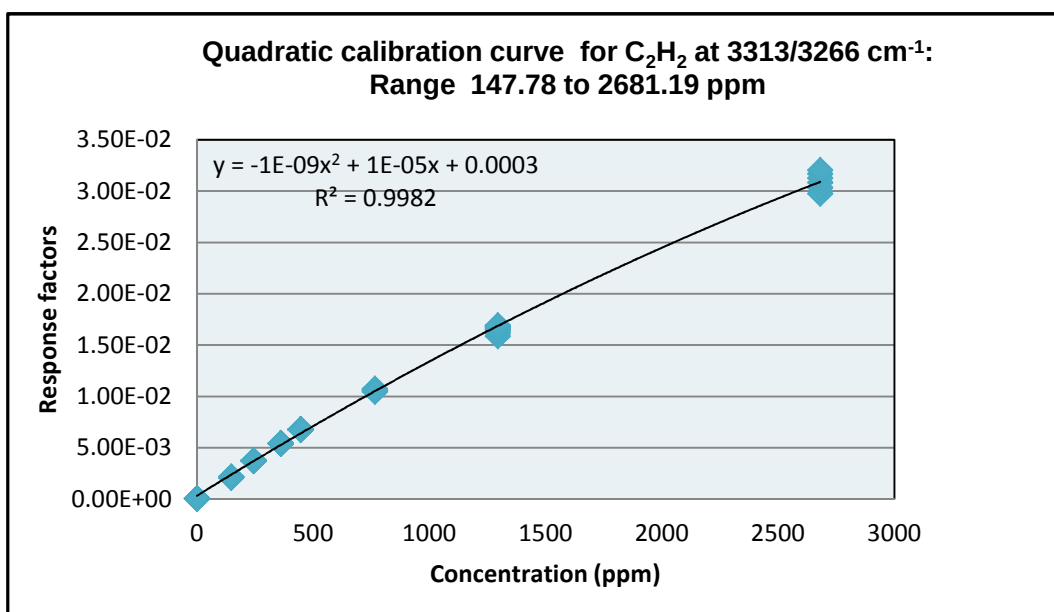


Figure 45: Quadratic calibration curve obtained for Standard 2 for C₂H₂ at 3313/3266 cm⁻¹

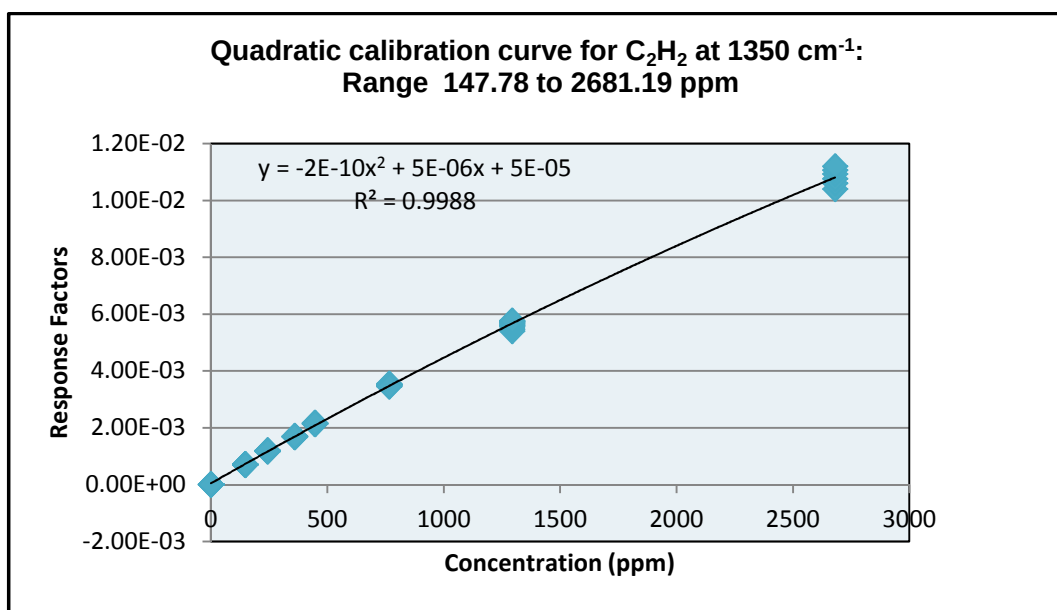


Figure 46: Quadratic calibration curve obtained for Standard 2 for C₂H₂ at 1350 cm⁻¹

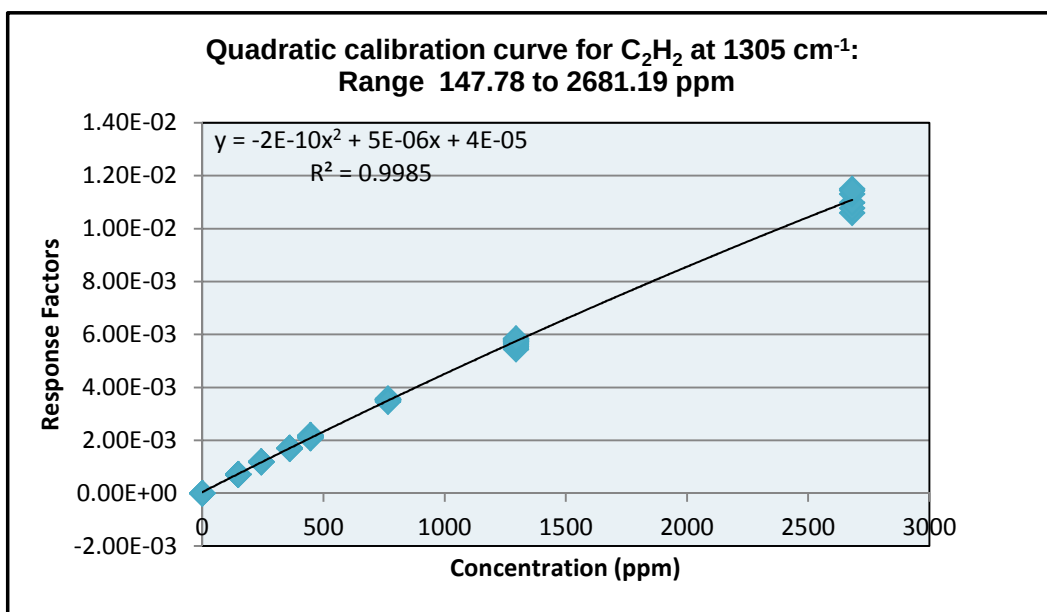


Figure 47: Quadratic calibration curve obtained for Standard 2 for C₂H₂ at 1305 cm⁻¹

Table 31: Summary of quadratic regression data for Standard 2 (C₂H₂): Confidence intervals (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	0.00015920	0.000480646
	Level 2	-0.0001090	9.59103E-05
1350	Level 1	2.2841E-07	9.34798E-05
	Level 2	-3.686E-05	2.67931E-05
1305	Level 1	-1.268E-05	9.59851E-05
	Level 2	-3.836E-05	2.86994E-05

Table 32: Summary of quadratic regression data for Standard 2 (C₂H₂): Regression data for t test (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9991	0.9982	199.26	2.0	19568.37
	Level 2	0.9994	0.9989	239.10	2.0	28137.30
1350	Level 1	0.9994	0.9988	242.22	2.0	28909.26
	Level 2	0.9995	0.9991	263.36	2.0	34127.96
1305	Level 1	0.9992	0.9985	213.11	2.0	22379.20
	Level 2	0.9995	0.9990	253.55	2.0	31633.92

Table 33: Summary of quadratic regression data for Standard 2 (C₂H₂): LOD and LOQ values (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	75.40	251.32
	Level 2	32.87	109.56
1350	Level 1	65.61	218.37
	Level 2	32.60	108.65
1305	Level 1	76.12	253.75
	Level 2	34.45	114.84

Table 34: Summary of quadratic regression data for Standard 2 (C₂H₂): P values (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	P value (X ²)
3313/3266	Level 1	1.18488E-21
	Level 2	9.09852E-25
1350	Level 1	6.27893E-18
	Level 2	2.58555E-15
1305	Level 1	1.8312E-12
	Level 2	2.55682E-12

Calibration results for Standard 2 using CH₄ as internal standard

Calibration curves were once again set up using the in-house certified standard and the combination peak at 13313 / 3266 cm⁻¹ and the single peaks at 1350 cm⁻¹ and 1305 cm⁻¹ used for quantitation. CH₄ was used as internal standard and the methane peak at 3017 cm⁻¹ used for quantitation. Both linear and quadratic selections were tested using Microsoft Excel software. The results are summarized in Tables 35 to 38 and the calibration curves shown in Figures 48 to 50. The following concentrations (ppm) were used for 3313/3266, 1350 and 1305 cm⁻¹: 194.137, 319.387, 380.807, 357.867, 421.319, 535.189 and 596.445 ppm. The concentration ranges are classified as follows: **Level 1**: 194.137 ppm to 596.445 ppm and **Level 2**: 194.137 ppm to 535.1890 ppm

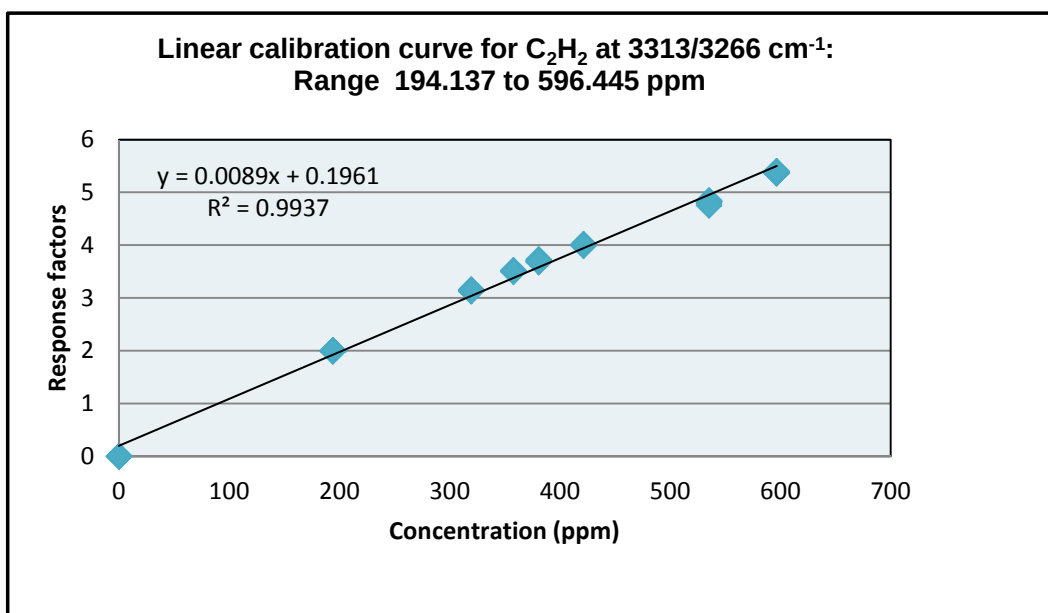


Figure 48: Linear calibration curve obtained for Standard 2 for C₂H₂ at 3313/3266 cm⁻¹ using CH₄ as internal standard.

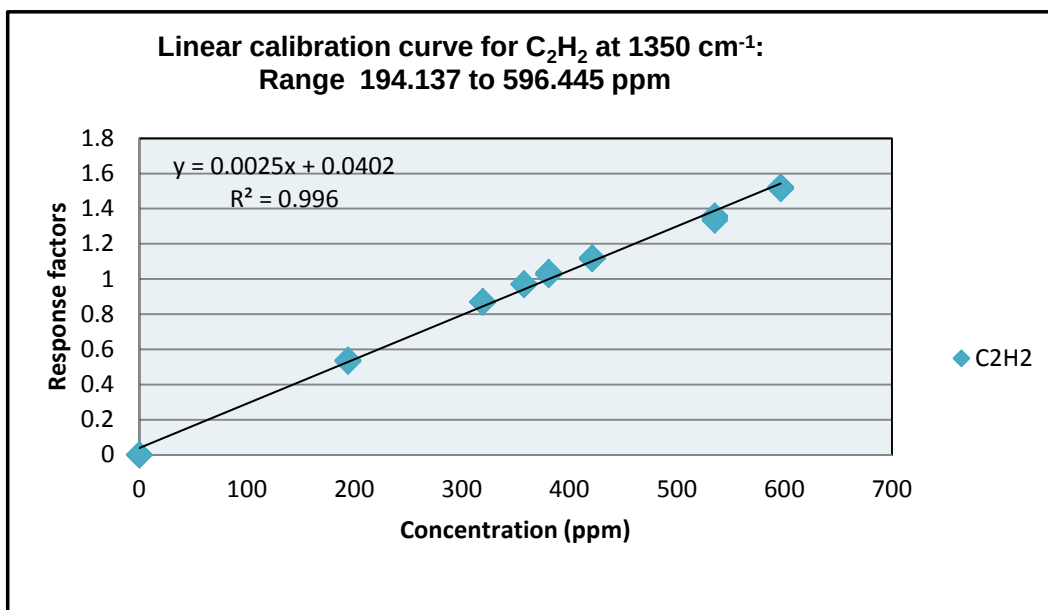


Figure 49: Linear calibration curve obtained for Standard 2 for C₂H₂ at 1350 cm⁻¹ using CH₄ as internal standard.

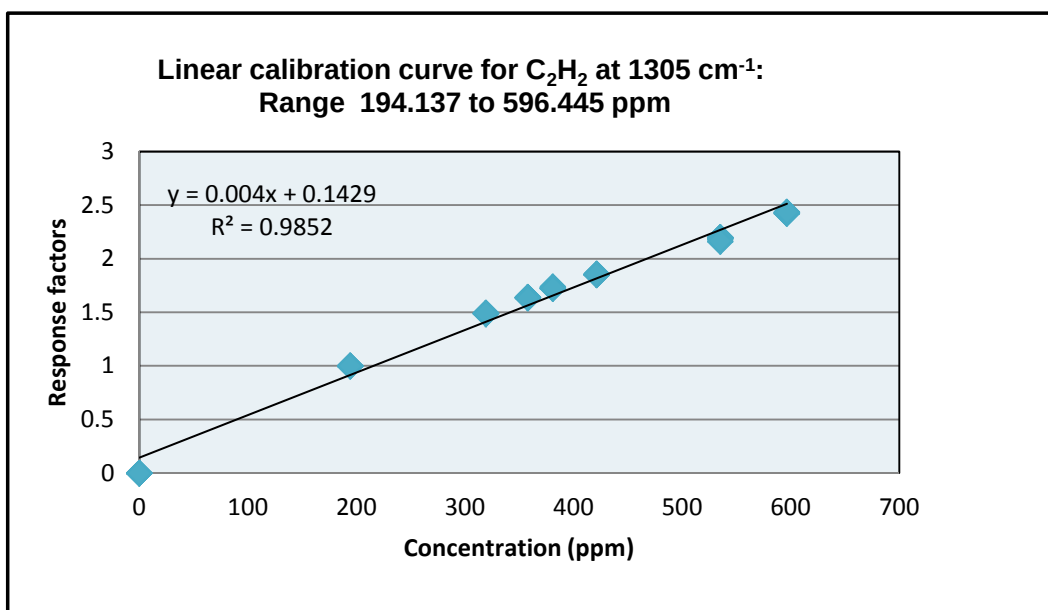


Figure 50: Linear calibration curve obtained for Standard 2 for C₂H₂ at 1305 cm⁻¹ using CH₄ as internal standard.

Table 35: Summary of linear regression data for Standard 2 (C₂H₂): Confidence intervals (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	0.12955472	0.262647993
	Level 2	0.08430639	0.220987003
1350	Level 1	0.02304273	0.052207036
	Level 2	0.01404659	0.044448757
1305	Level 1	0.09112652	0.179604735
	Level 2	0.06273288	0.152891778

Table 36: Summary of linear regression data for Standard 2 (C₂H₂): Regression data for t test (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9968	0.9937	107.07	2.0	11463.62
	Level 2	0.9966	0.9933	96.40	2.0	9292.582
1350	Level 1	0.9980	0.9961	137.74	2.0	18971.98
	Level 2	0.9978	0.9957	121.27	2.0	14707.64
1305	Level 1	0.9928	0.9858	72.08	2.0	5194.969
	Level 2	0.9927	0.9854	66.20	2.0	4382.004

Table 37: Summary of linear regression data for Standard 2 (C₂H₂): LOD and LOQ values (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	42.87	142.89
	Level 2	40.59	135.31
1350	Level 1	34.23	114.09
	Level 2	33.24	110.79
1305	Level 1	65.82	219.41
	Level 2	61.66	205.52

Table 38: Summary of linear regression data for Standard 2 (C₂H₂): P values (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	P value (slope)	P value (intercept)
3313/3266	Level 1	5.19447E-82	1.17521E-07
	Level 2	3.91259E-70	3.40448E-05
1350	Level 1	5.96385E-91	2.15446E-06
	Level 2	2.36646E-77	0.000281237
1305	Level 1	5.16399E-71	4.35106E-08
	Level 2	2.26153E-61	1.05569E-05

The same data was taken for Standard 2 and quadratic fits were tested in as for the linear fits. The data is summarized in Tables 39 to 42 below and the quadratic calibration curves obtained from Excel are shown in Figures 51 to 53 below.

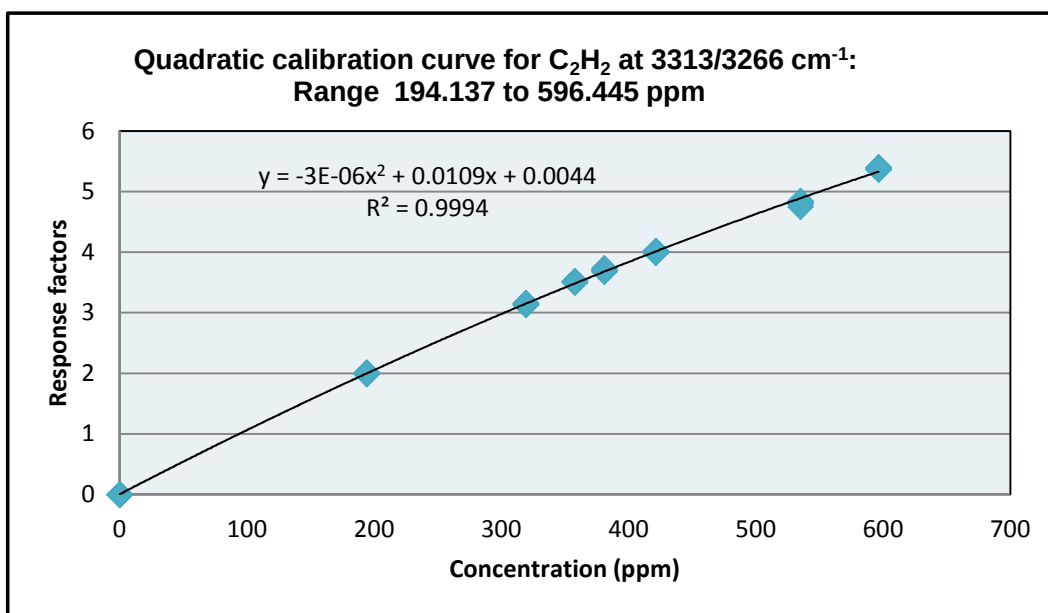


Figure 51: Quadratic calibration curve obtained for Standard 2 for C₂H₂ at 3313/3266 cm⁻¹ using CH₄ as internal standard.

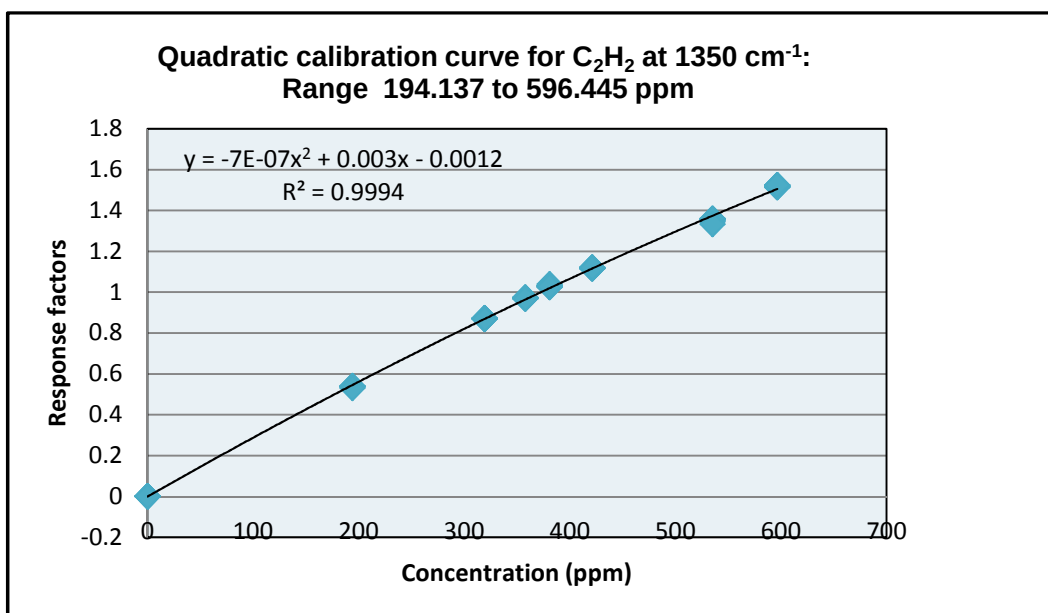


Figure 52: Quadratic calibration curve obtained for Standard 2 for C₂H₂ at 1350 cm⁻¹ using CH₄ as internal standard.

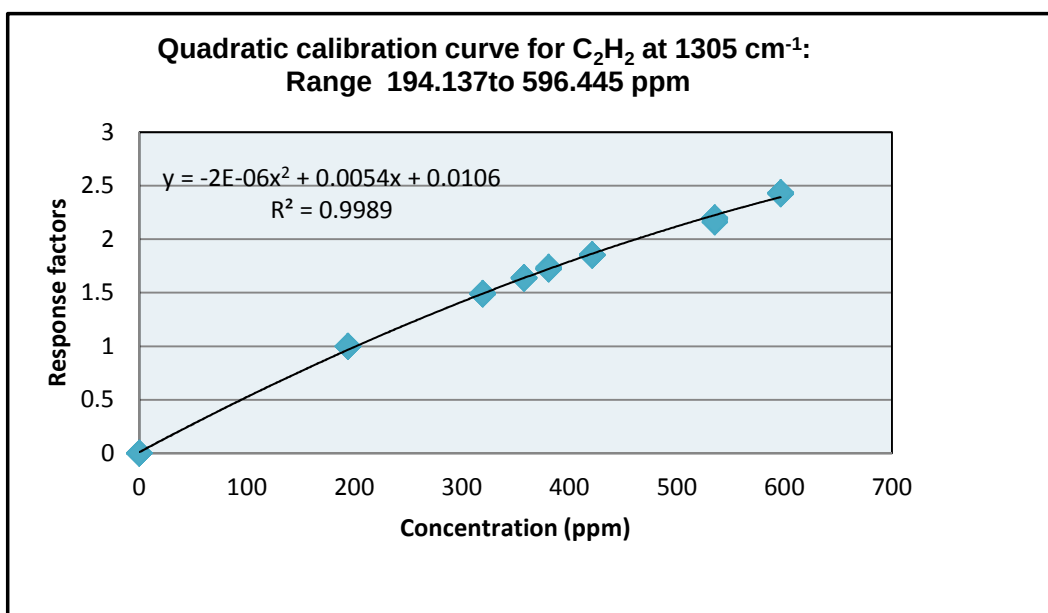


Figure 53: Quadratic calibration curve obtained for Standard 2 for C₂H₂ at 1305 cm⁻¹ using CH₄ as internal standard.

Table 39: Summary of quadratic regression data for Standard 2 (C₂H₂): Confidence intervals (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	-0.0207010	0.02947818
	Level 2	-0.0215348	0.006950984
1350	Level 1	3.8363E-05	0.00085136
	Level 2	-4.422E-05	0.000708285
1305	Level 1	-0.0041123	0.025320269
	Level 2	-0.0028631	0.009960539

Table 40: Summary of quadratic regression data for Standard 2 (C₂H₂): Regression data for t test (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9997	0.9994	351.09	2.0	60788.83
	Level 2	0.9999	0.9998	545.38	2.0	146359.9
1350	Level 1	0.9997	0.9993	347.51	2.0	59562.54
	Level 2	0.9998	0.9996	411.84	2.0	83481.32
1305	Level 1	0.9995	0.9989	264.92	2.0	34623.66
	Level 2	0.9999	0.9998	545.64	2.0	146569.3

Table 41: Summary of quadratic regression data for Standard 2 (C₂H₂): LOD and LOQ values (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	10.75	35.84
	Level 2	5.86	19.52
1350	Level 1	11.68	38.93
	Level 2	8.33	27.77
1305	Level 1	13.47	44.88
	Level 2	5.58	18.62

Table 42: Summary of quadratic regression data for Standard 2 (C₂H₂): P values (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	P value (X ²)
3313/3266	Level 1	8.86497E-39
	Level 2	2.72658E-48
1350	Level 1	5.22739E-31
	Level 2	4.2033E-35
1305	Level 1	2.29859E-43
	Level 2	3.74658E-60

Calibration results for Standard 3: no internal standard

Calibration curves were set up using Standard 3. The combination peak at 13313 / 3266 cm⁻¹ and the single peaks at 1350 cm⁻¹ and 1305 cm⁻¹ were used for quantitation. Both linear and quadratic selections were tested using Excel software. The results are summarized in Tables 43 to 46 and the calibration curves shown in Figures 55 to 56. The following concentrations (ppm) were used for 3313/3266, 1350 and 1305 cm⁻¹: 94.804, 155.968, 185.962, 205.745, 230.238, 261.35 and 291.265 ppm. The concentration ranges are classified as follows: **Level 1**: 94.804 ppm to 291.265 ppm and **Level 2**: 94.804 ppm to 261.265 ppm

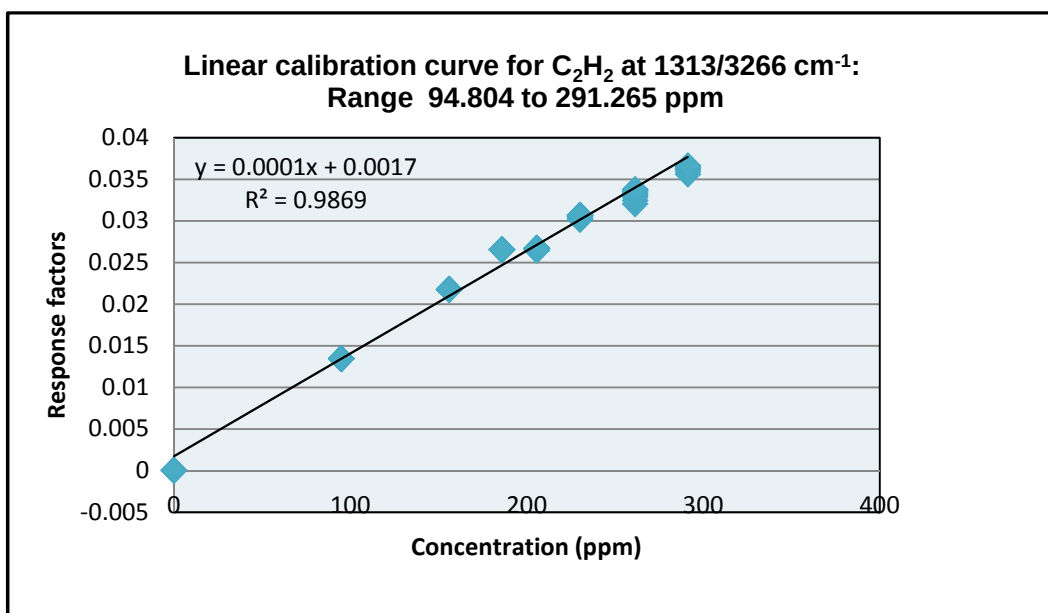


Figure 54: Linear calibration curve for Standard 3 for C₂H₂ at 1313/3266 cm⁻¹ with a working range between 94.804 and 291.265 ppm

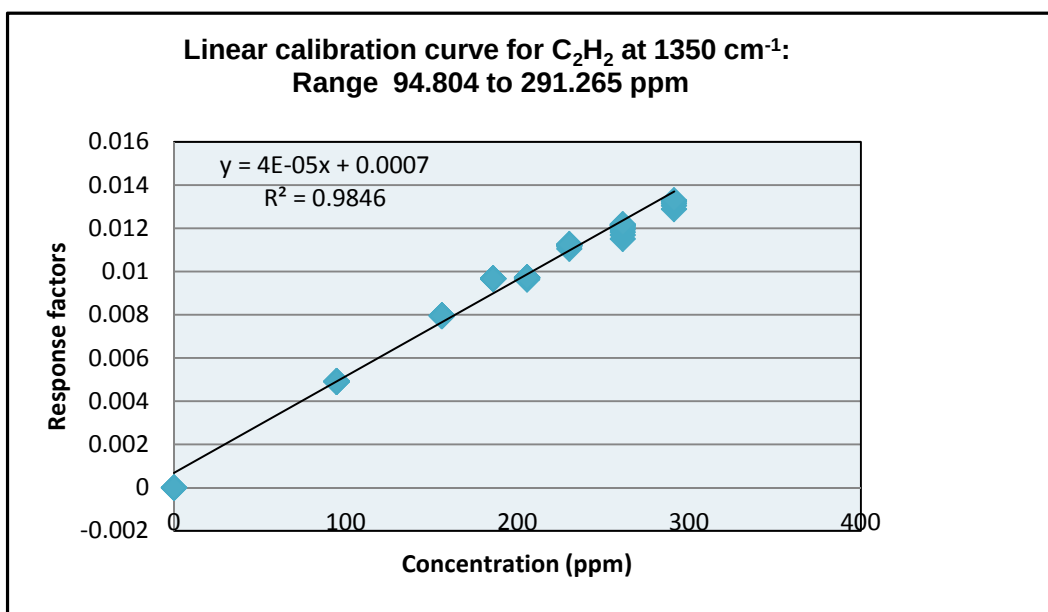


Figure 55: Linear calibration curve for Standard 3 for C₂H₂ at 1305 cm⁻¹ with a working range between 94.804 and 291.265 ppm

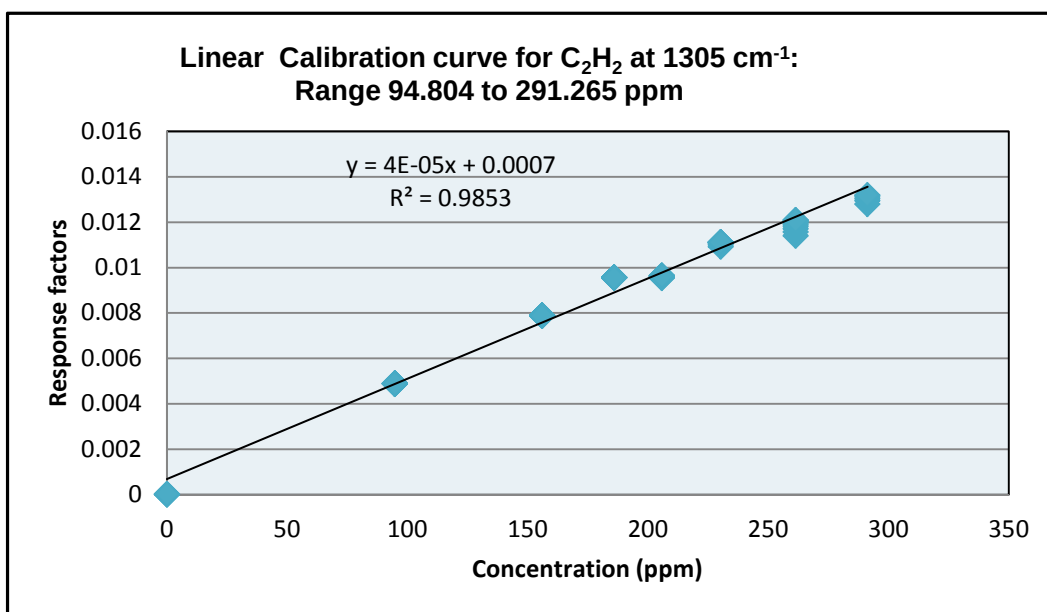


Figure 56: Linear calibration curve for Standard 3 for C₂H₂ at 1350 cm⁻¹ with a working range between 94.804 and 291.265 ppm

Table 43: Summary of linear regression data for Standard 3 (C₂H₂): Confidence intervals (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	0.00117620	0.002499126
	Level 2	0.00071569	0.002049139
1350	Level 1	0.00045900	0.000977111
	Level 2	0.00028313	0.000810735
1305	Level 1	0.00047042	0.000969695
	Level 2	0.00030628	0.000819745

Table 44: Summary of linear regression data for Standard 3 (C₂H₂): Regression data for t test (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9938	0.9876	75.26	2.0	5664.0
	Level 2	0.9939	0.9879	71.11	2.0	5056.7
1350	Level 1	0.9927	0.9856	28.69	2.0	4842.8
	Level 2	0.9928	0.9856	65.15	2.0	4244.9
1305	Level 1	0.9931	0.9863	71.43	2.0	5103.0
	Level 2	0.9930	0.9860	66.09	2.0	4367.4

Table 45: Summary of linear regression data for Standard 3 (C₂H₂): LOD and LOQ values (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	26.53	88.42
	Level 2	24.37	81.22
350	Level 1	28.69	95.63
	Level 2	26.60	88.65
1305	Level 1	27.95	93.16
	Level 2	26.22	87.40

Table 46: Summary of linear regression data for Standard 3 (C₂H₂): P values (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	P value (slope)	P value (intercept)
3313/3266	Level 1	1.85805E-69	4.82942E-07
	Level 2	3.85989E-61	0.000105007
1350	Level 1	4.4888E-67	5.07866E-07
	Level 2	8.16328E-59	0.000105123
1305	Level 1	7.18204E-68	2.06572E-07
	Level 2	3.42094E-59	4.59395E-05

The same data was taken for Standard 3 and quadratic fits were tested in as for the linear fits. The data is summarized in Tables 47 to 50 below and the quadratic calibration curves obtained from Excel are shown in Figures 57 to 59 below.

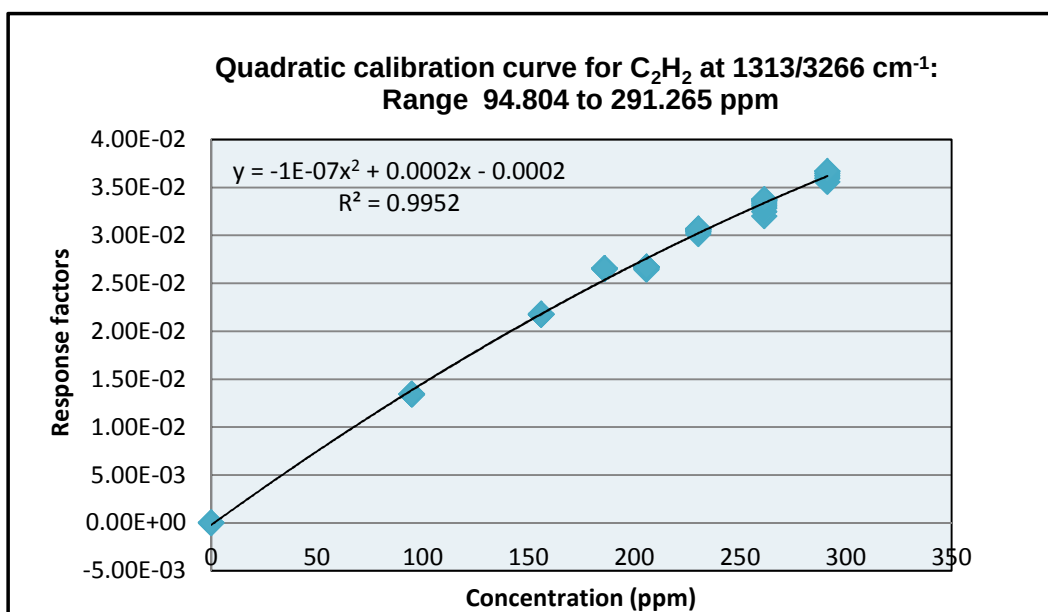


Figure 57: Quadratic calibration curve for Standard 3 for C₂H₂ at 1313/3266 cm⁻¹ with a working range between 94.804 and 291.265 ppm

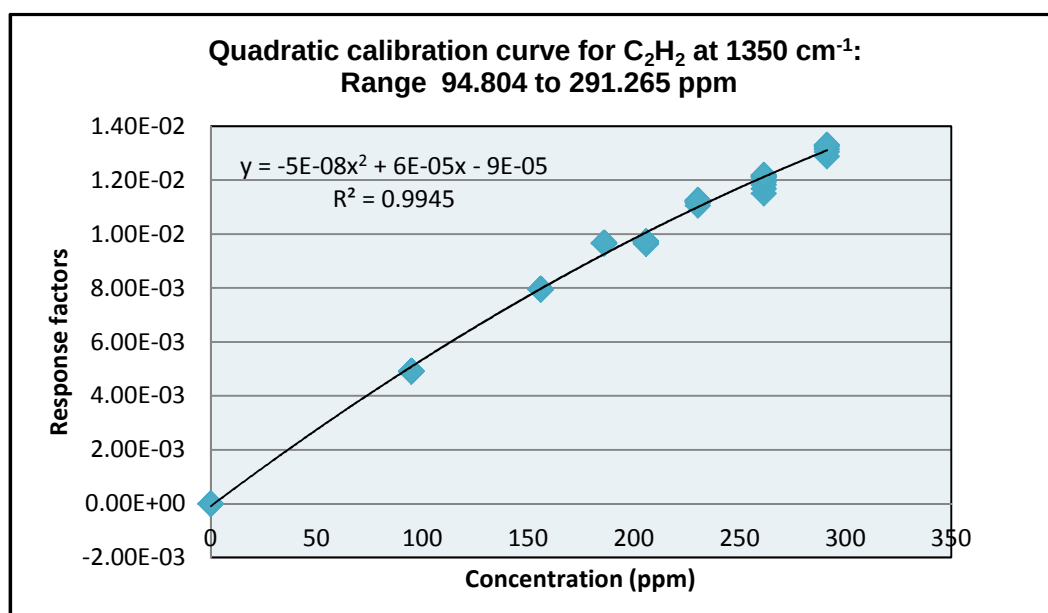


Figure 58: Quadratic calibration curve for Standard 3 for C₂H₂ at 1350 cm⁻¹ with a working range between 94.804 and 291.265 ppm

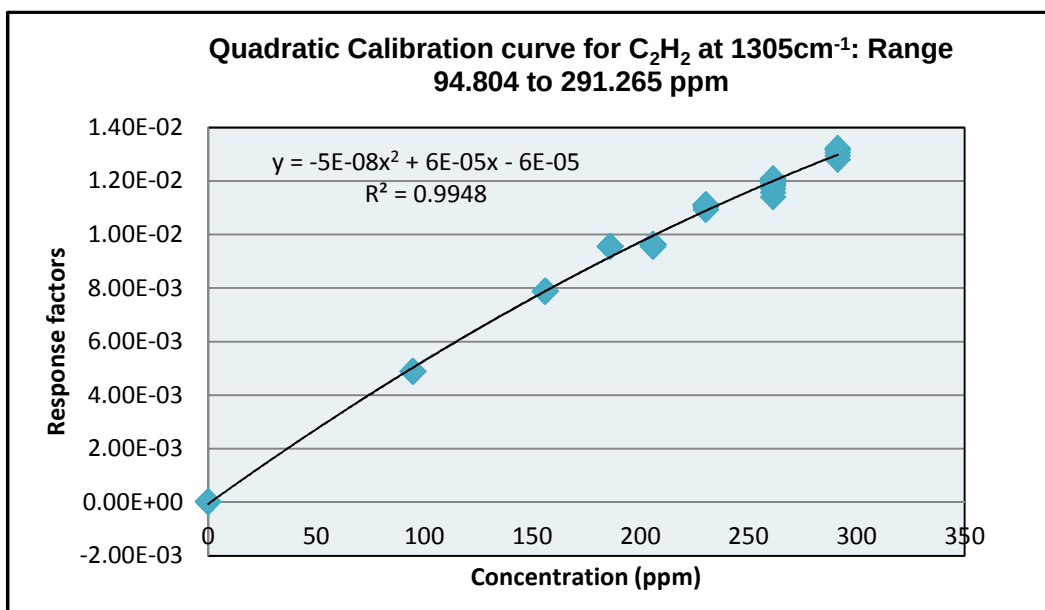


Figure 59: Quadratic calibration curve for Standard 3 for C₂H₂ at 1305 cm⁻¹ with a working range between 94.804 and 291.265 ppm

Table 47: Summary of quadratic regression data for Standard 3 (C₂H₂): Confidence intervals (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	-0.0007558	0.0003972
	Level 2	-0.0008143	0.0004087
1350	Level 1	-0.0002939	0.000137445
	Level 2	-0.0003358	0.000119124
1305	Level 1	-0.0004116	0.000163365
	Level 2	-0.0002999	0.000136153

Table 48: Summary of quadratic regression data for Standard 3 (C₂H₂): Regression data for t test (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9975	0.9950	117.90	2.0	6850.5
	Level 2	0.9971	0.9941	102.47	2.0	5165.8
1350	Level 1	0.9973	0.9946	114.77	2.0	6493.3
	Level 2	0.9969	0.9938	99.103	2.0	4890.8
1305	Level 1	0.9974	0.9949	117.29	2.0	6781.1
	Level 2	0.9970	0.9942	102.69	2.0	5187.2

Table 49: Summary of quadratic regression data for Standard 3 (C₂H₂): LOD and LOQ values (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	13.16	43.87
	Level 2	13.60	45.87
1350	Level 1	13.36	44.52
	Level 2	13.51	45.04
1305	Level 1	13.16	43.85
	Level 2	13.13	43.76

Table 50: Summary of quadratic regression data for Standard 3 (C₂H₂): P values (no internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	P value (X ²)
3313/3266	Level 1	2.01128E-15
	Level 2	3.54145E-11
1350	Level 1	1.01132E-16
	Level 2	9.15023E-13
1305	Level 1	1.36391E-16
	Level 2	3.58022E-13

Calibration results for Standard 3 using CH₄ as internal standard

Calibration curves were once again set up using the in-house certified standard and the combination peak at 13313 / 3266 cm⁻¹ and the single peaks at 1350 cm⁻¹ and 1305 cm⁻¹ used for quantitation. CH₄ was used as internal standard and the methane peak at 3017 cm⁻¹ used for quantitation. Both linear and quadratic selections were tested using Microsoft Excel software. The results are summarized Tables 52 to 54 and the calibration curves shown in Figures 60 to 61. The following concentrations (ppm) were used for 3313/3266, 1350 and 1305 cm⁻¹: 56.691, 94.804, 155.968, 185.962, 205.745 and 230.238 ppm.

The results for wavenumber 1305 cm⁻¹ could not be used due to erroneous data obtained, the reason for which could not be determined.

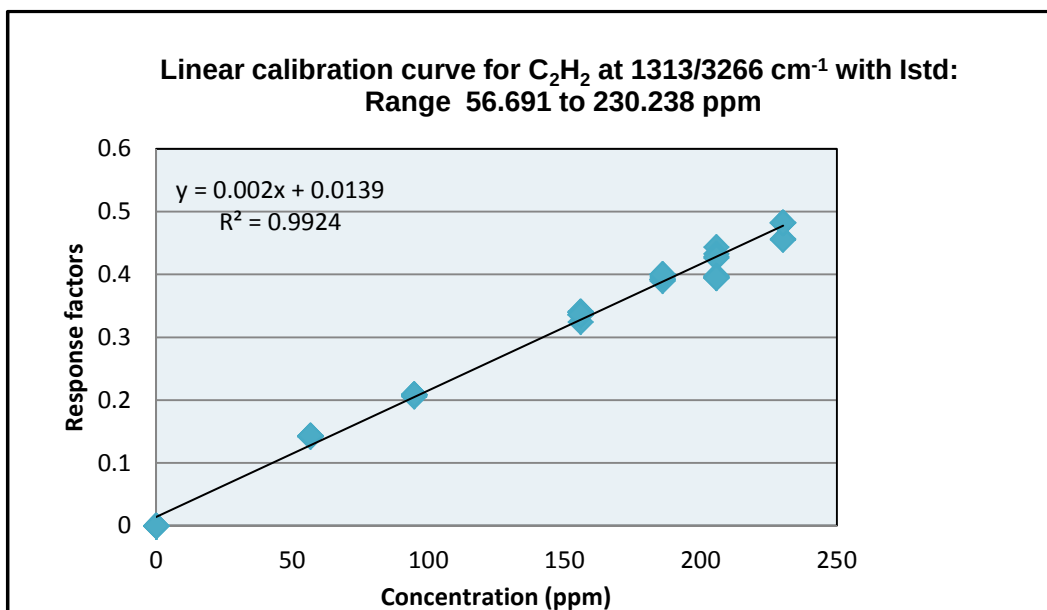


Figure 60: Linear calibration curve obtained for Standard 3 for C₂H₂ at 3313/3266 cm⁻¹ using CH₄ as internal standard.

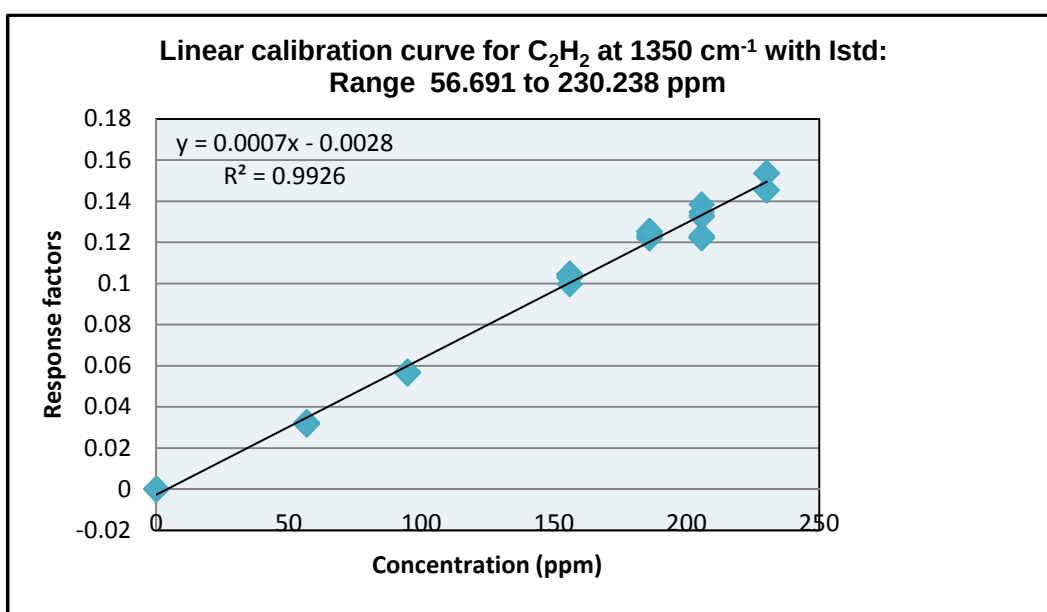


Figure 61: Linear calibration curve obtained for Standard 3 for C₂H₂ at 1350 cm⁻¹ using CH₄ as internal standard.

Table 51: Summary of linear regression data for Standard 3 (C₂H₂): Confidence intervals (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	0.00706656	0.02064528
	Level 2	0.00584642	0.020044992
1350	Level 1	-0.0047636	-0.00045907
	Level 2	-0.0045340	-3.8981E-05

Table 52: Summary of linear regression data for Standard 3 (C₂H₂): Regression data for t test (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9961	0.9924	91.18	2.0	8313.781
	Level 2	0.9956	0.9913	78.96	2.0	6235.102
1350	Level 1	0.9964	0.9929	94.30	2.0	8891.707
	Level 2	0.9958	0.9916	80.67	2.0	6508.163

Table 53: Summary of linear regression data for Standard 3 (C₂H₂): LOD and LOQ values (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	20.92	69.72
	Level 2	20.97	69.89
1350	Level 1	20.22	67.41
	Level 2	20.52	68.41

Table 54: Summary of Linear regression data for Standard 3 (C₂H₂): P values (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	P value (slope)	P value (intercept)
3313/3266	Level 1	1.80468E-69	0.000128463
	Level 2	2.68233E-58	0.000576734
1350	Level 1	2.13415E-70	0.018194373
	Level 2	8.33504E-59	0.046287699

The same data was taken for Standard 3 and quadratic fits were tested in as for the linear fits using internal standard. The data is summarized in

Tables 47 to 50 below and the quadratic calibration curves obtained from Excel are shown in Figures 62 to 63 below.

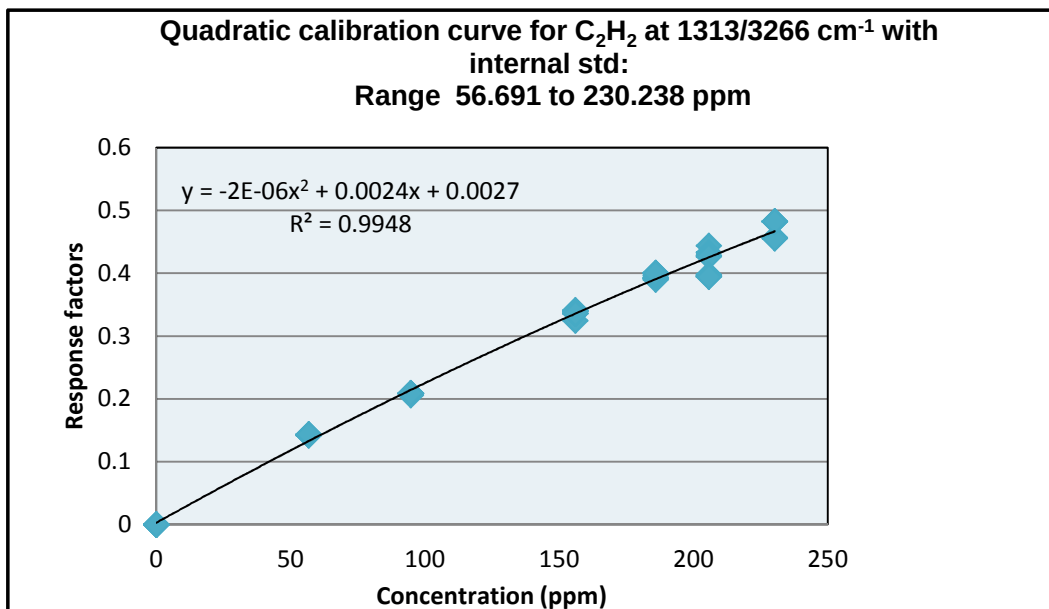


Figure 62: Quadratic calibration curve obtained for Standard 3 for C₂H₂ at 3313/3266 cm⁻¹ using CH₄ as internal standard.

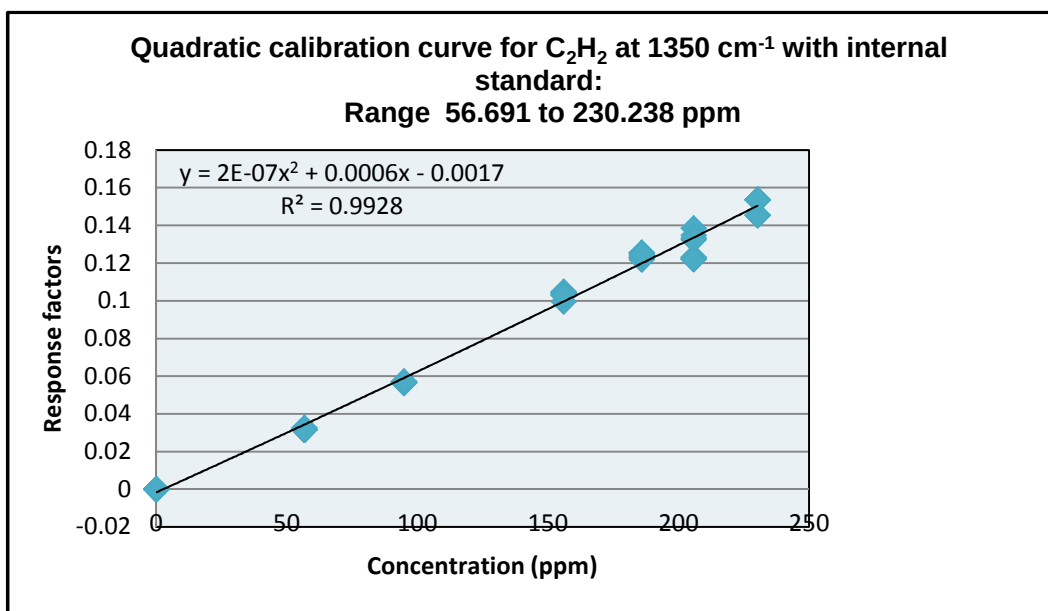


Figure 63: Quadratic calibration curve obtained for Standard 3 for C₂H₂ at 1350 cm⁻¹ using CH₄ as internal standard.

Table 55: Summary of quadratic regression data for Standard 3 (C₂H₂): Confidence intervals (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	Lower 95%	Upper 95%
3313/3266	Level 1	-0.0041941	0.009671629
	Level 2	-0.0056897	0.007244002
1350	Level 1	-0.0041349	0.001123955
	Level 2	-0.0043343	0.00114257

Table 56: Summary of quadratic regression data for Standard 3 (C₂H₂): Regression data for t test (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	r	r ²	t _{calc}	t _{crit}	F _{ANOVA}
3313/3266	Level 1	0.9974	0.9948	111.01	2.0	4273.733503
	Level 2	0.9975	0.9952	106.60	2.0	3242.106026
1350	Level 1	0.9965	0.9931	95.85	2.0	653.3079694
	Level 2	0.9959	0.9917	81.27	2.0	895.1266653

Table 57: Summary of quadratic regression data for Standard 3 (C₂H₂): LOD and LOQ values (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	LOD	LOQ
3313/3266	Level 1	14.65	48.82
	Level 2	12.74	42.45
1350	Level 1	21.24	70.80
	Level 2	21.44	71.46

Table 58: Summary of quadratic regression data for Standard 3 (C₂H₂): P values (with internal standard)

Wavenumber (cm ⁻¹)	Range (ppm)	P value (X ²)
3313/3266	Level 1	7.64412E-07
	Level 2	1.61015E-08
1350	Level 1	0.154811684
	Level 2	0.377772294

4.4. Statistics

Linear regression analyses

A linear regression line equation generally takes the form:

$$Y = b_0 + b_1x$$

Where Y = Dependent variable

b_0 = Intercept

b_1 = Slope

x = variable

The sample slope (b_1) is given in the “*Coefficients*” column and the “*X Variable/Slope*” row. The estimated change in y as a result of a one unit change in x is measured by b_1 .

The intercept b_0 is given in the “*Coefficients*” column and the “*Intercept (Y)*” row and b_0 is the estimated value of y when x is 0.

Evaluating the results of the regression analysis

Excel software was used to determine the linear regression parameters. The interpretations of each of the more common parameters are discussed below.

Plot of the residuals

A plot of the residuals can be used to determine possible problems with the calibration data that may not be immediately obvious from a simple scatter plot of the data.

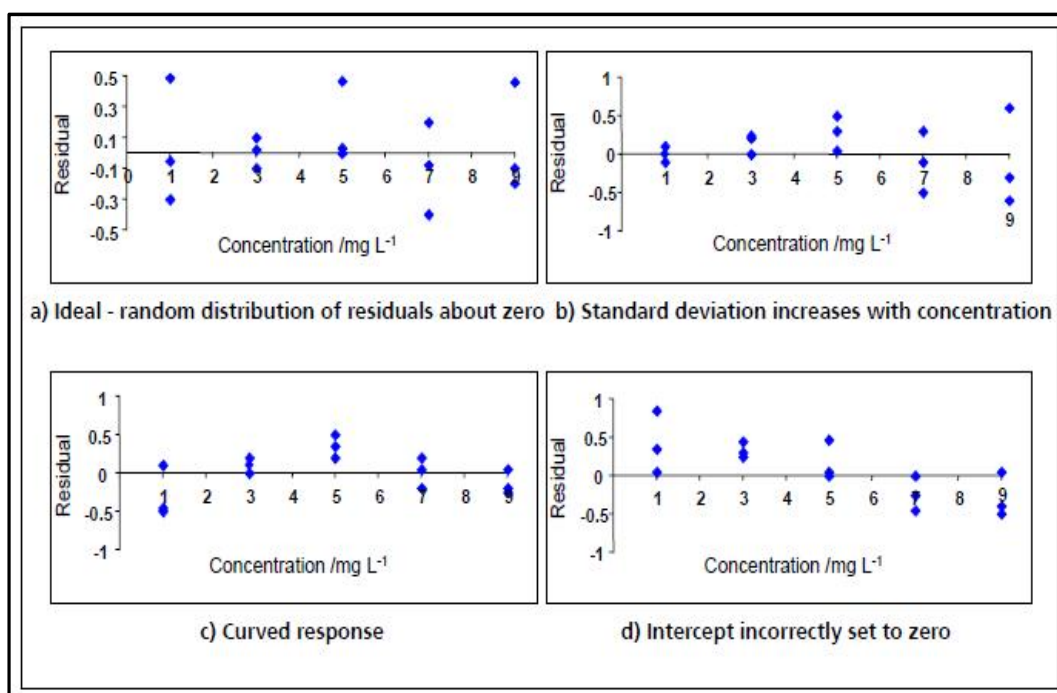


Figure 64: Examples of residual plots⁽⁶³⁾

Figure 64a shows an ideal residual plot. The residuals are scattered randomly around zero and there is no trend in the spread of results with concentration. Figure 64b indicates a residual pattern in which the standard deviation of the instrument response increases with analyte concentration. Figure 64c shows a residual pattern where a straight line has been fitted through non-linear data. Finally, figure 64d shows a residual pattern where the regression line has been incorrectly fitted through zero.⁽⁶³⁾

Regression Statistics

Figure 65 below shows a typical regression output from Excel. The different sections of the outputs are described in detail in the following sections.

SUMMARY OUTPUT								
Regression Statistics								
Multiple R (r)	0.984806789							
R Square (r^2)	0.969844412							
Adjusted R Square	0.969633534							
Standard Error ($s_{y/x}$)	6.78578E-05							
Observations (n)	145							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	2.11773E-05	2.11773E-05	4599.07308	1.2731E-110			
Residual	143	6.5847E-07	4.60469E-09					
Total	144	2.18358E-05						
	Coefficients	Standard Error	t Stat/tcalc	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept (Y)	8.03487E-06	8.01446E-06	1.002546421	0.31777319	-7.80725E-06	2.3877E-05	-7.80725E-06	2.3877E-05
X variable/Slope	0.000189649	2.7965E-06	67.81646615	1.2731E-110	0.000184121	0.000195177	0.000184121	0.000195177
	↑ (b)							
			Tcrit = (TINV(, n-2))					

Figure 65: Typical excel regression data. Red/bold data indicates components used in calculations.

The correlation coefficient (r)

The correlation coefficient (r) and the related, parameters r^2 and adjusted r^2 , are measures of how strong the correlation is between the x and the y values. The closer r is to 1, the stronger the correlation but unfortunately the r value can be easily misinterpreted. It is therefore essential to plot calibration data and not to just rely on the statistics. The parameters r^2 and adjusted r^2 are used to describe the fraction of total variance in the data which can be contributed to by the line that has been fitted. The majority of the variability can be accounted for by the fitted line if there is a good linear relation and r^2 should thus be close to 1. The adjusted r^2 is interpreted in the same manner as r^2 but is always lower. It is a useful parameter for assessing the effect of adding additional terms to the equation of the fitted line if for example a quadratic fit is used instead of a linear fit. Where r^2 always increases on the addition of extra terms to the equation, adjusted r^2 takes into account the reduction in the degrees of freedom which occurs every time an additional term is added and thus

does not automatically increase on addition of extra terms. This prevents over fitting which can occur when the equation fitted has more terms than can be supported by the amount of data available. ⁽⁶³⁾

ANOVA Table

ANOVA is defined as “analysis of variance”. Figure 65 illustrates the origin of some of the terms from an ANOVA table. The sum of squares (SS) indicates different sources of variability in the calibration data. The regression term represents the variability in the data that can be accounted for by the fitted regression line. Ideally the larger this term, the greater the linearity as the fitted line will describe most of the variability in response with concentration. The residual term is the sum of the squared residuals and this value should be small compared to the regression sum of squares as the residuals will be small if the regression line fits the data well. The mean square (MS) for both regression and residual is the sum of squares divided by its degrees of freedom. The F value is the ratio of the regression term MS term to the residual MS and should ideally be very large if there is a good linear relationship. The significance F value represents the probability of obtaining the results in the ANOVA table if there is no correlation between x and y values, more simply put, the results are obtained by chance. A small value would indicate that the results were unlikely to have happened by chance this indicating the likelihood that there is a strong relationship between the x and y values. F Significance should be extremely small for a calibration curve to be of any use. ⁽⁶³⁾

Regression coefficients

The final table in the ANOVA table from figure 65 describes the regression outputs. The first column provides the values of the coefficients followed by the second column which gives the standard errors for each coefficient. These values provide the ranges within which the values for the gradient and intercept could be found. Related to these values are the values in the

last columns, lower and upper 95% confidence limits. These values represent the extremes of the values that gradient and intercept could take at a chosen confidence level, 95% for the work done in this project. The t-stat and p-values relate to the significance of the coefficients and provide an indication of whether the coefficients are statistically significant from zero. The expectation is that the gradient of a line be significantly different from zero and thus the t-value must be large and the p-value must be small, typically less than 0.05 for a regression analyses carried out at the 95% level. Ideally it is preferred that the calibration line pass through the origin. If this is the case then the intercept should not be significantly different from zero. It would thus be expected that the t-value would be small and the p-value would be large, typically greater than 0.05 at the 95% confidence level. A final confirmation of whether the calibration line passes through zero is to assess the upper and lower confidence intervals. If these two values include zero then the intercept is not statistically different from zero. ⁽⁶³⁾

Discussion on results for linear calibration data H₂O

Does r represent significant linearity?

A t-test was performed here as follows:

The hypotheses are as follows:

- $H_0: r = 0$ and there is no linear relation between x and y
- $H_1: r \neq 0$ and there is significant linearity

If $t_{\text{calc}} > t_{\text{crit}}$ then reject H_0 and there is significant linearity. The bigger t_{calc} , the more significant the linearity. All 11 wavenumbers in both ranges had $t_{\text{calc}} > t_{\text{crit}}$, indicating significant linearity for all. In only two cases were the t_{calc} values of the higher ranges better than the lower ranges and that was for 3854 and 1734 cm^{-1} . An Anova analysis was then performed in Excel to determine if the lower ranges indicated greater linearity than the higher

ranges. F_{ANOVA} was compared with F_{crit} and the F_{ANOVA} with the highest value was selected as the more linear range.⁽⁶⁴⁾ In all cases excluding 3854 and 1734 cm^{-1} , the lower ranges displayed higher values for F_{ANOVA} indicating more significant linearity for the lower ranges than for the higher ranges.

Discussion on results for quadratic calibration data H_2O

The t_{calc} and F_{ANOVA} values for all eleven wavenumbers were all higher for the high ranges than for the low ranges indicating that a quadratic fit is the better option on the high range. The r^2 values on the high ranges were also better than the r^2 values obtained for the linear fits indicating that for moisture analyses it is perhaps better to use a quadratic calibration curve rather than the linear option.

Discussion on results for calibration data C_2H_2 for Standard 1

Visual examination of the graphs for Standard 1 indicated that the quadratic fit for wavenumber 3313/3266 cm^{-1} was a more probable fit than the linear fit while 1305 cm^{-1} could be either fit. The t_{calc} and F_{ANOVA} values on the linear low range were both larger than the t_{calc} and F_{ANOVA} values on the linear high range indicating that the lower range has more linearity than the high range on the linear fits. The t_{calc} and F_{ANOVA} values on the quadratic high range for 3313/3266 cm^{-1} was larger than the t_{calc} and F_{ANOVA} values on the quadratic low range indicating that the high range is a better quadratic fit than the low range on the quadratic fits. However for wavenumber 1305 cm^{-1} , the t_{calc} and F_{ANOVA} values on the quadratic low range was larger than the t_{calc} and F_{ANOVA} values on the quadratic high range indicating that the low range is a better quadratic fit than the high range on the quadratic fits.

Discussion on results for calibration data C_2H_2 for Standard 2

Visual examination of the graphs for Standard 2 indicated that the quadratic fit for wavenumber 3313/3266 cm^{-1} was again a more probable

fit than the linear fit while 1305 cm^{-1} and 1305 cm^{-1} could be either fit. The t_{calc} and F_{ANOVA} values on all three linear low ranges were both larger than the t_{calc} and F_{ANOVA} values on the linear high ranges indicating that the lower ranges have more linearity than the high ranges on the linear fits. The t_{calc} and F_{ANOVA} values on the quadratic low ranges for all three wavenumbers were larger than the t_{calc} and F_{ANOVA} values on the quadratic high ranges indicating, strangely enough, that the low ranges are a better quadratic fit than the high ranges on the quadratic fits. Considering the r^2 values for both linear and quadratic fits, the r^2 values for the quadratic fits were better than for the linear fits.

The use of internal standard made a significant difference to the r^2 values obtained on the quadratic ranges but did not seem to have a great effect on the linear fits.

Discussion on results for calibration data C_2H_2 for Standard 3

Visual examination of the graphs for Standard 3 indicated that the quadratic fits for all three wavenumbers was a more probable fit than the linear fit. The t_{calc} and F_{ANOVA} values on all three linear high ranges were both larger than the t_{calc} and F_{ANOVA} values on the linear low ranges indicating that the high ranges have more linearity than the low ranges on the linear fits. This is opposite to what we found on Standard 2. The t_{calc} and F_{ANOVA} values on the quadratic high ranges for all three wavenumbers were larger than the t_{calc} and F_{ANOVA} values on the quadratic low ranges indicating, that the high ranges are a better quadratic fit than the low ranges on the quadratic fits. Considering the r^2 values for both linear and quadratic fits, the r^2 values for the quadratic fits were better than for the linear fits.

The use of internal standard made a small difference to the r^2 values obtained on both the linear and quadratic ranges but did not seem to have as great an effect as it did for standard 2.

4.5. Method 3: analysis on GC/PDHID

Calibration results for C₂H₂

A method was developed for the analysis of acetylene in a difficult matrix. The matrix was removed so as not to have an effect on the PDHID signal allowing for quicker stabilization times of the GC/PDHID system. A calibration curve was drawn up for acetylene using this method. No statistical evaluation was undertaken for the calibration data as was done for the FTIR analyses. The reason for this is that acetylene is a compound commonly run on GC and is known to be linear. In addition it was decided not to spend further time on this method as the conversion of H₂O to C₂H₂ could not be further investigated due to the lack of a proper sealed sampling unit for the conversion process.

4.6. Conversion of moisture to C₂H₂

It was determined that the conversion process from H₂O to C₂H₂ was viable. Unfortunately a number of factors put a stop to any further development of this process. The CaC₂ purchased was found to contain H₂O and also rapidly reacted with H₂O when exposed to air. This resulted in much higher % recoveries for the C₂H₂ than initially anticipated. Purging the vials/sample holder with helium prior to the conversion process appeared to remove the additional moisture/ C₂H₂ present as the recoveries improved but due to air ingress, specifically into the sample holder, no viable results could be obtained.

4.7. In Summary

The purpose of this project was the development of a method (s) by which to analyze the moisture content of gas samples. The Water Gas Shift reaction could not be tested due to the unavailability of the catalysts. Two methods were developed. Initially the FTIR was selected and a method developed whereby moisture could be directly analyzed. Eleven calibration curves, using eleven different wavenumbers, were set up using a moisture permeation standard and an initial working range from 0.514 to 9.890 ppm. Visual inspection of the calibration curves gave the impression that the curves all tended towards quadratic fits. The full range was then split into an additional smaller range of 0.514 to 3.956 ppm. The smaller range proved to have a more linear fit than the full range which tended towards a quadratic fit.

The disadvantages of this method included long stabilization times for each calibration level, at least four hours per level, and when it came to sample analyses, large volumes of sample were required for analyses making it an impractical method for any samples other than cylinders containing large volumes and/or high pressures of gas. The long stabilization times for both standards and samples were largely due to the long path gas cell being constructed of glass and the moisture adsorbing to the glass walls thus indicating that a long path glass gas cell is not suitable for the direct analyses of moisture in gases. Heating the glass cell did not improve desorption of the water on the glass walls but actually appeared to increase the amount of moisture present.

The second method developed for the analyses of the moisture content of gas samples also utilized FTIR. For this method various calibration curves were set up for acetylene with the purpose of quantifying moisture in gas samples, after conversion to acetylene. Standard 1 (Matheson) was used as a preliminary test and data was generated. There were however many interferences from all the additional components in the mixture and only

two of the 3 wavenumbers (3313/3266 and 1305 cm^{-1}) selected could be used for calibration. The concentration range used was from 33.550 to 369.048 ppm. The ranges were split into a smaller range as for the moisture calibrations but no significant difference could be seen between the higher and lower ranges. The quadratic fit gave a better r^2 value for every wavenumber.

Standard 2 provided a calibration range from 147.780 to 2681.19 ppm without internal standard and a range from 194.137 to 596.445 ppm with internal standard. There was a definite improvement in r^2 with the use of internal standard on the linear range as well as the quadratic range.

Standard 3 provided a calibration range from 94.804 to 291.265 ppm without internal standard and a range from 56.691 to 230.238 ppm with internal standard. Again there was a definite improvement in r^2 with the use of internal standard on the linear range as well as the quadratic range.

A calibration curve for acetylene was drawn up using GC/PDHID. This is a standard analyses and it was decided not to spend additional time on the GC method until the conversion process could be confidently implemented.

The principle of the conversion of moisture to acetylene using calcium carbide was tested. The conversion process was proven to be successful but it could not be quantified at the close of this project due to the lack of a sealed sample holder. Calcium carbide proved to be very reactive to moisture and any small ingress of air caused the conversion process to occur resulting in much higher recoveries than anticipated.

No references could be found in literature as to the use of quadratic calibration curves versus linear calibration curves. In most instances from literature, linear regression was used.⁽⁹⁾ Additionally no references could be found regarding the use of an internal standard for the FTIR technique.

In table 59 below, a number of techniques and the detection limits obtained are summarized.

Table 59: Comparison of moisture measurement techniques ⁽¹⁾

Technique	Gases tested	Sensitivity/Detection Limits	Comment
FTIR	Cl ₂ , HCl, HBr, NH ₃ , AsH ₃ and PH ₃	10-50ppbv	Background H ₂ O in bench affects response.
TDLAS	HCl, HBr, NH ₃ , H ₂ , O ₂ , Inerts, N ₂ O, CO and SiH ₄	1-10ppbv	Detection at low P required to keep linewidth narrow.
CRDS	N ₂ , HCl	<500ppt	High mirror reflectivity required.
ILS	N ₂ , HCl	<500ppt	Low resolution may limit applications
MS	Inerts, N ₂ , HCl and WF ₆	500ppbv. Varies with matrix	Detector drifts
APIMS	Inerts, O ₂ , GeH ₄ , SiH ₄ , NH ₃ and HCl	10ppt-10ppv. Varies with matrix	Complex-requires skilled operator and regular maintenance
Oscillating Quartz crystal	O ₂ , H ₂ , NO, CO, Hydrocarbons, inerts, AsH ₃ , PH ₃ , SF ₆ and NH ₃	10-50ppbv	Requires dry reference gas and periodic calibration.
Chilled mirror	HCl, HBr, PH ₃ and AsH ₃	Varies	Long equilibration times at low H ₂ O levels
Capacitance	CO, halocarbons, N ₂ O, inerts, PH ₃ and AsH ₃	>100ppbv	Requires frequent calibration at low H ₂ O levels
Electrolytic	Cl ₂ , inerts, SF ₆ , CO, CO ₂ and freons	2-5ppbv and 1ppmv in Cl ₂	Precise flow control required. Dry cell may not respond to H ₂ O

The detection limits for moisture obtained in this project (on average 0.5ppm) are greater than those obtained from the various techniques illustrated in table 59. The FTIR LOD indicated in table 59 does not give an indication of the type of detector or cell used and can thus not be directly compared to the method set up in this project. It would seem that the long path glass cell used for this project has its limitations and is possibly not suitable if detection limits less than 0.5ppm are required.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

A method was developed for the direct analyses of moisture in gases using FTIR as the analytical technique. Eleven different wavenumbers for moisture were tested, allowing for analyses of moisture in complex matrices where any one of the eleven wavenumbers can be selected for quantitation should there be overlap with the sample matrix components. LOD's for the linear ranges varied from approximately 1 ppm down to 0.5 ppm while LOD's for the quadratic ranges were all approximately around 0.5 ppm. The negative aspects of this method were the huge sample volumes required due to the lengthy stabilization times for moisture and from a commercial viewpoint this method will not be cost or time effective. The use of an internal standard such as methane as well as raising the glass cell temperatures to 200°C with the purchase of a dedicated heating mantle are possibilities that could improve this method. These suggestions might improve the reproducibility of the results and reduce the lengthy stabilization times currently required.

Additionally a method was developed for the analyses of acetylene using FTIR as the analytical technique and methane as an internal standard. The purpose of this method was to utilize the acetylene calibrations once the moisture in the gas samples had been converted to acetylene using CaC_2 . On the whole, the acetylene calibration curves had much better r^2 values than the moisture calibration curves and the reason for this was possibly due to the acetylene not adhering to the glass cell walls as the moisture seemed to do. The use of internal standard provided regression values on the calibration curves that were significantly better than the regressions obtained without the internal standard and it is suggested that the internal standard method for C_2H_2 analysis on FTIR be tested for the FTIR moisture method. Since the stabilization time of acetylene was much less than that for moisture, it makes this method much more cost and time effective than the moisture method.

The principle of the conversion of moisture to acetylene was proved in this study but no quantification could be done due to the lack of a sealed sample holder. A sample holder for both GC and FTIR in which moisture in a gas sample can be converted to acetylene using calcium carbide, without the ingress of atmospheric air/moisture needs to be developed. The design of such a sample holder is crucial to the success of the conversion process. In addition to the air ingress into the sample holder, the sealed CaC_2 container from the supplier, opened for use for the first time for the conversion process contained acetylene indicating some air ingress prior to sealing of the container. This could be removed to an extent by purging with helium. It is recommended that the CaC_2 be stored under an inert gas and when transferring the CaC_2 to the sample holder AND that this be done under an inert gas to prevent air ingress and thus higher acetylene results than expected. 70% purity CaC_2 was utilized for these experiments. It is possible that a higher purity grade CaC_2 might contain less $\text{H}_2\text{O}/\text{C}_2\text{H}_2$ and provide more accurate conversion results.

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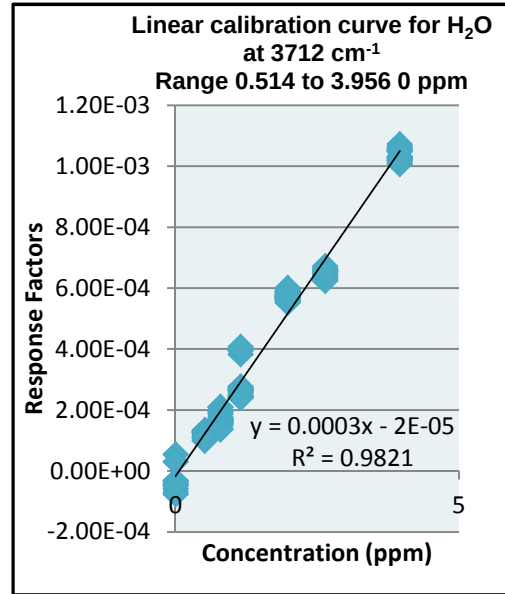
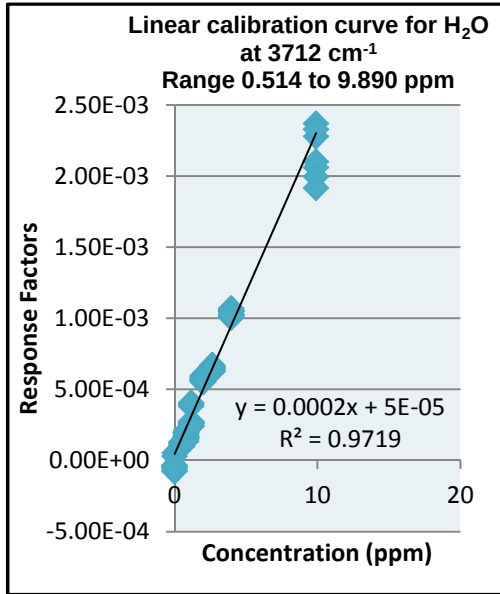
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Trace Source Permeation Tube Certificate of Calibration

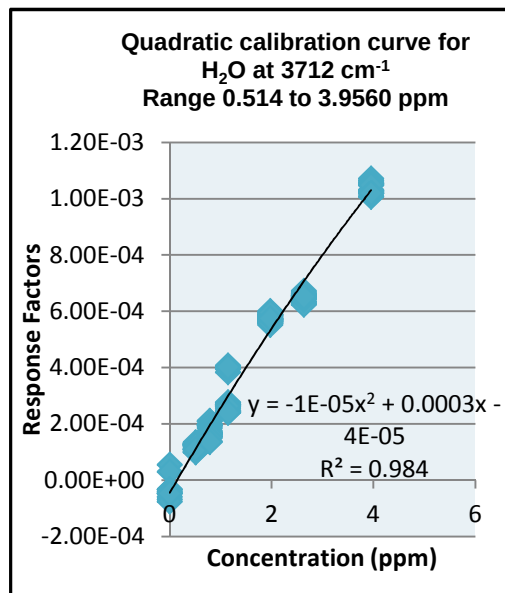
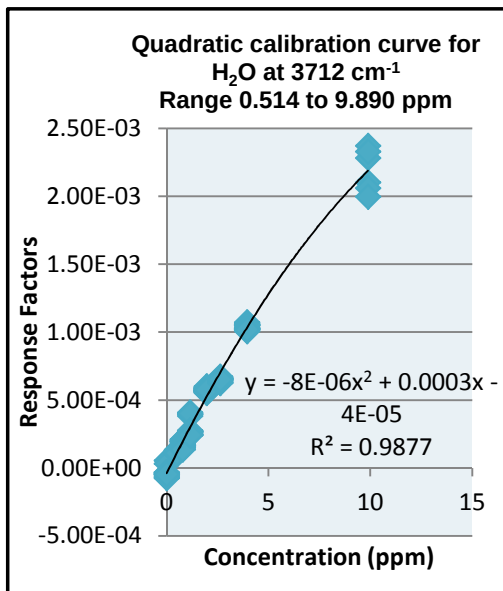
136

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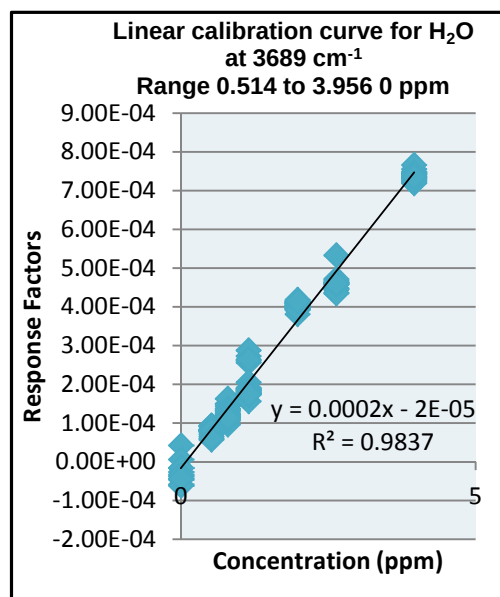
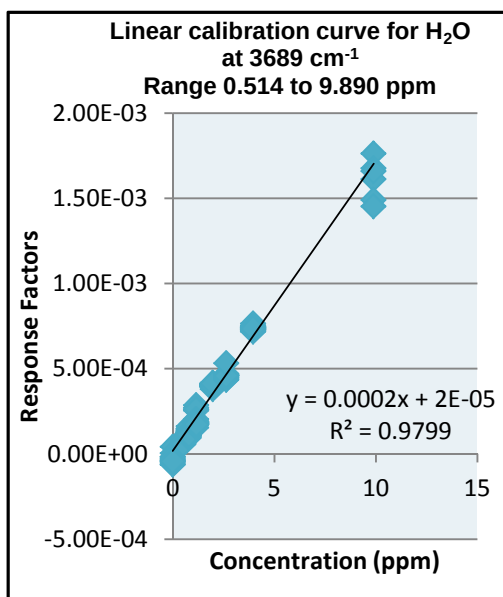
Linear and Quadratic Calibration Data for all H₂O wavenumbers:



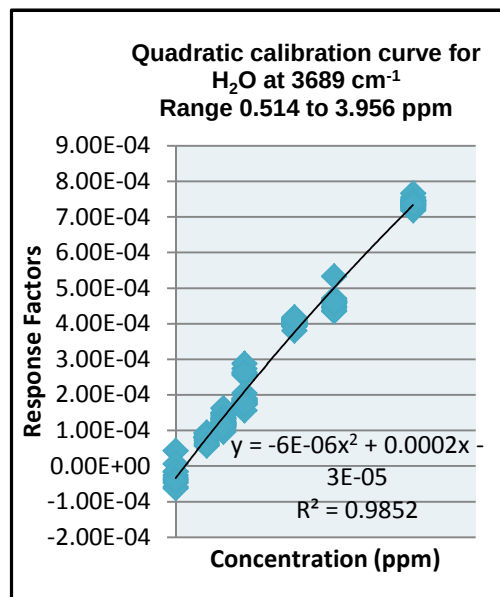
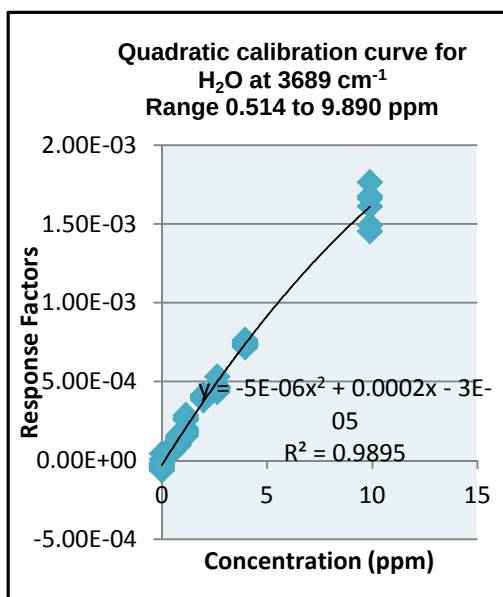
Range:0-9.89								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.985873948							
R Square	0.97194744							
Adjusted R Square	0.971753974							
Standard Error	8.2313E-05							
Observations	147							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	3.40389E-05	3.4E-05	5023.86879	2.0165E-114			
Residual	145	9.82438E-07	6.78E-09					
Total	146	3.50213E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	4.53597E-05	9.52746E-06	4.760943	4.61999E-06	2.65291E-05	6.41903E-05	2.65291E-05	6.41903E-05
X Variable 1	0.000228072	3.21775E-06	70.87926	2.0165E-114	0.000221712	0.000234432	0.000221712	0.000234432
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.990987087							
R Square	0.982055406							
Adjusted R Square	0.981925373							
Standard Error	4.45346E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	1.49788E-05	1.5E-05	7552.338569	2.2725E-122			
Residual	138	2.737E-07	1.98E-09					
Total	139	1.52525E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-1.75661E-05	6.44905E-06	-2.72383	0.007287727	-3.03179E-05	-4.8144E-06	-3.03179E-05	-4.81437E-06
X Variable 1	0.000269812	3.10471E-06	86.90419	2.2725E-122	0.000263673	0.000275951	0.000263673	0.000275951



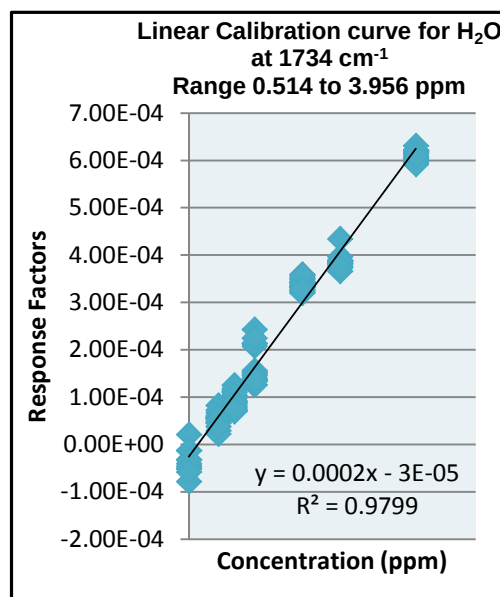
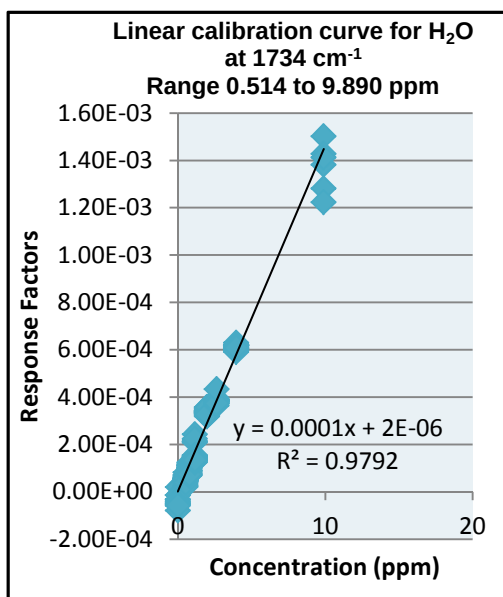
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Regression Statistics								
Multiple R	0.993825719							
R Square	0.987689561							
Adjusted R Square	0.987518582							
Standard Error	5.4717E-05							
Observations	147							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	3.45902E-05	1.73E-05	5776.694571	3.1601E-138			
Residual	144	4.31128E-07	2.99E-09					
Total	146	3.50213E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-4.06424E-05	8.95977E-06	-4.5361	1.19781E-05	-5.8352E-05	-2.2933E-05	-5.8352E-05	-2.29327E-05
X Variable 1	0.000305157	6.06998E-06	50.27317	3.24234E-93	0.00029316	0.000317155	0.00029316	0.000317155
X Variable 2	-8.45574E-06	6.23125E-07	-13.5699	1.55181E-27	-9.68739E-06	-7.2241E-06	-9.68739E-06	-7.22408E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.991953684							
R Square	0.98397211							
Adjusted R Square	0.983738126							
Standard Error	4.22424E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	1.5008E-05	7.5E-06	4205.300298	1.0815E-123			
Residual	137	2.44466E-07	1.78E-09					
Total	139	1.52525E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-4.45975E-05	9.05646E-06	-4.92439	2.39731E-06	-6.25061E-05	-2.6689E-05	-6.25061E-05	-2.6689E-05
X Variable 1	0.000311713	1.07626E-05	28.96258	2.87288E-60	0.00029043	0.000332995	0.00029043	0.000332995
X Variable 2	-1.01149E-05	2.49897E-06	-4.04762	8.60962E-05	-1.50564E-05	-5.1733E-06	-1.50564E-05	-5.17333E-06



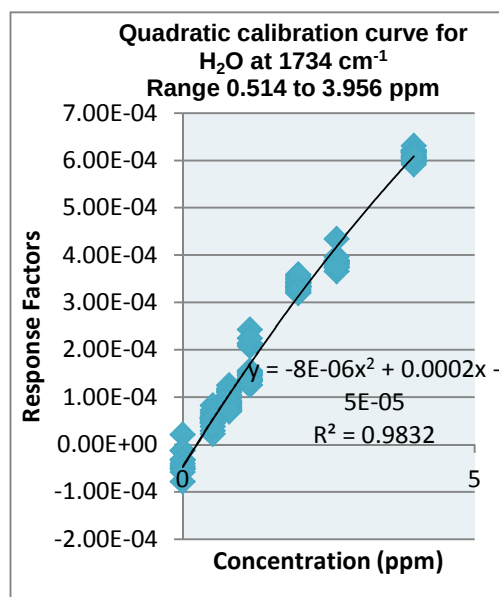
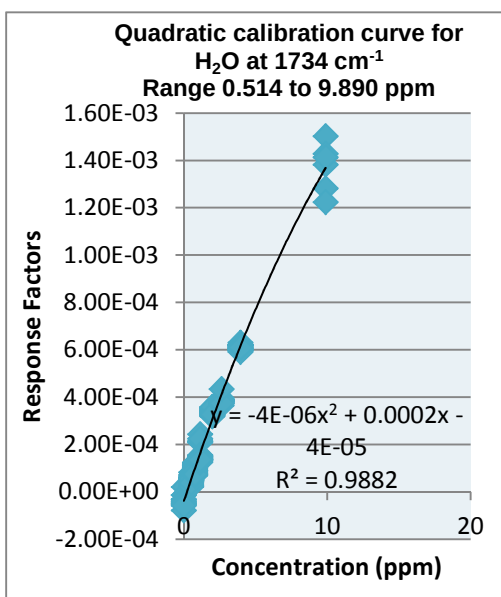
Range: 0-9.89								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.989926577							
R Square	0.979954629							
Adjusted R Square	0.979815425							
Standard Error	4.94799E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	1.7235E-05	1.7235E-05	7039.703299	3.727E-124			
Residual	144	3.52549E-07	2.44826E-09					
Total	145	1.75876E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	1.73039E-05	5.80356E-06	2.98160015	0.003367965	5.83273E-06	2.87751E-05	5.83273E-06	2.87751E-05
X Variable 1	0.000170492	2.03202E-06	83.90293975	3.727E-124	0.000166476	0.000174509	0.000166476	0.000174509
Range: 0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.991802738							
R Square	0.983672672							
Adjusted R Square	0.983554358							
Standard Error	3.03261E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	7.64622E-06	7.64622E-06	8314.087177	3.3564E-125			
Residual	138	1.26915E-07	9.19671E-10					
Total	139	7.77314E-06						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-1.62853E-05	4.39151E-06	-3.70836802	0.000301328	-2.49687E-05	-7.602E-06	-2.49687E-05	-7.60199E-06
X Variable 1	0.000192773	2.11417E-06	91.18161644	3.3564E-125	0.000188593	0.000196953	0.000188593	0.000196953



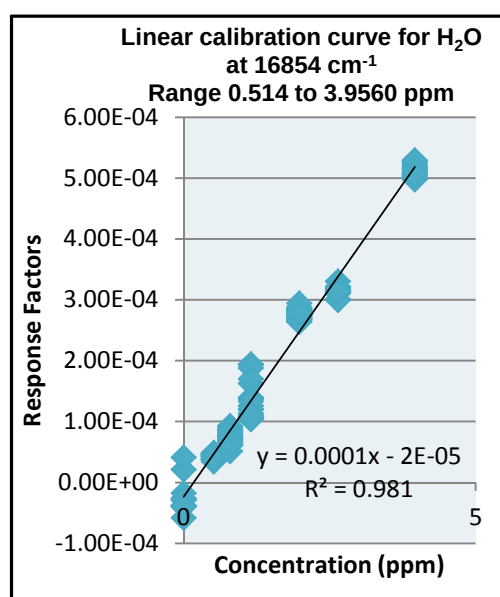
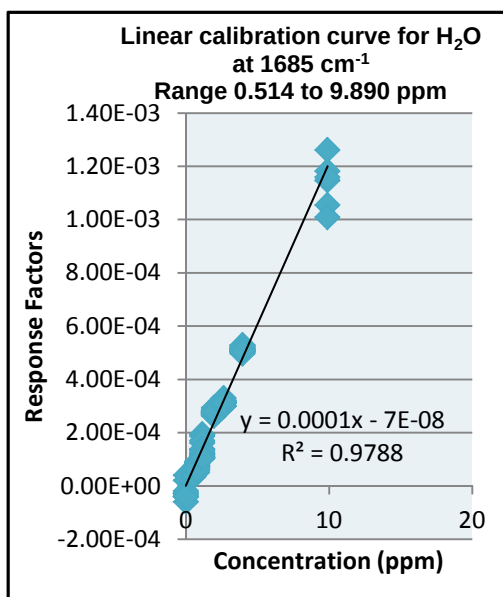
Range:0-9.89								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.9947273							
R Square	0.989482402							
Adjusted R Square	0.989335302							
Standard Error	3.59661E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	1.74026E-05	8.7E-06	6726.629824	3.6901E-142			
Residual	143	1.84979E-07	1.29E-09					
Total	145	1.75876E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-2.95333E-05	5.89324E-06	-5.01138	1.57241E-06	-4.11824E-05	-1.7884E-05	-4.11824E-05	-1.78841E-05
X Variable 1	0.00021287	4.00558E-06	53.14331	4.65265E-96	0.000204952	0.000220788	0.000204952	0.000220788
X Variable 2	-4.77229E-06	4.19296E-07	-11.3817	9.01167E-22	-5.60111E-06	-3.9435E-06	-5.60111E-06	-3.94347E-06
Range: 0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.9925818							
R Square	0.98521863							
Adjusted R Square	0.985002844							
Standard Error	2.89598E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	7.65824E-06	3.83E-06	4565.711878	4.2214E-126			
Residual	137	1.14898E-07	8.39E-10					
Total	139	7.77314E-06						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-3.36161E-05	6.20876E-06	-5.4143	2.67778E-07	-4.58935E-05	-2.1339E-05	-4.58935E-05	-2.13387E-05
X Variable 1	0.000219637	7.37843E-06	29.76744	1.12067E-61	0.000205047	0.000234227	0.000205047	0.000234227
X Variable 2	-6.48498E-06	1.7132E-06	-3.78531	0.000228788	-9.87271E-06	-3.0973E-06	-9.87271E-06	-3.09726E-06



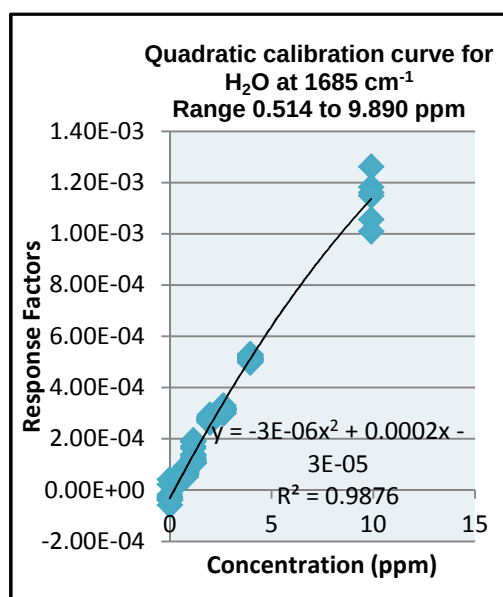
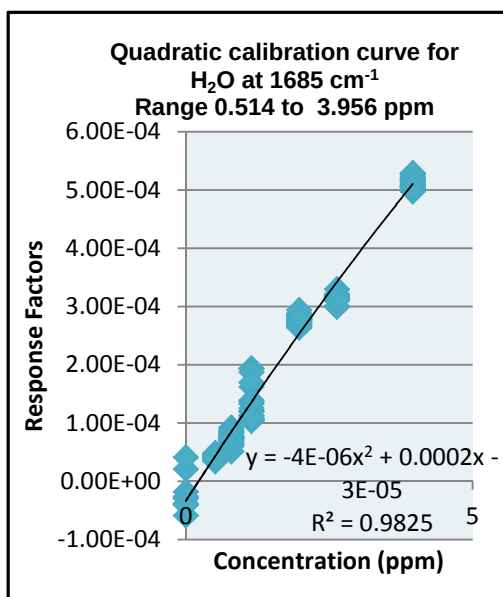
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Regression Statistics									
Multiple R	0.989557332								
R Square	0.979223713								
Adjusted R Square	0.979079433								
Standard Error	4.322E-05								
Observations	146								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	1.26778E-05	1.26778E-05	6786.978461	4.9135E-123				
Residual	144	2.68987E-07	1.86797E-09						
Total	145	1.29468E-05							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	1.58388E-06	5.06933E-06	0.312443613	0.755155405	-8.43603E-06	1.16038E-05	-8.43603E-06	1.16038E-05	
X Variable 1	0.000146225	1.77494E-06	82.38312	4.9135E-123	0.000142717	0.000149733	0.000142717	0.000149733	
Range:0-3.956									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.989910124								
R Square	0.979922054								
Adjusted R Square	0.979776561								
Standard Error	2.8718E-05								
Observations	140								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	5.55469E-06	5.55469E-06	6735.212971	5.2867E-119				
Residual	138	1.13812E-07	8.24724E-10						
Total	139	5.6685E-06							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	-2.56737E-05	4.15865E-06	-6.173565	7.00E-09	-3.38966E-05	-1.7451E-05	-3.38966E-05	-1.74508E-05	
X Variable 1	0.000164306	2.00206E-06	82.06834329	5.2867E-119	0.000160347	0.000168264	0.000160347	0.000168264	



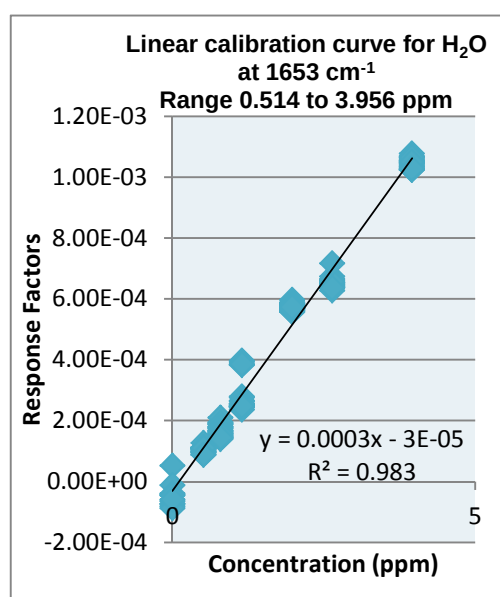
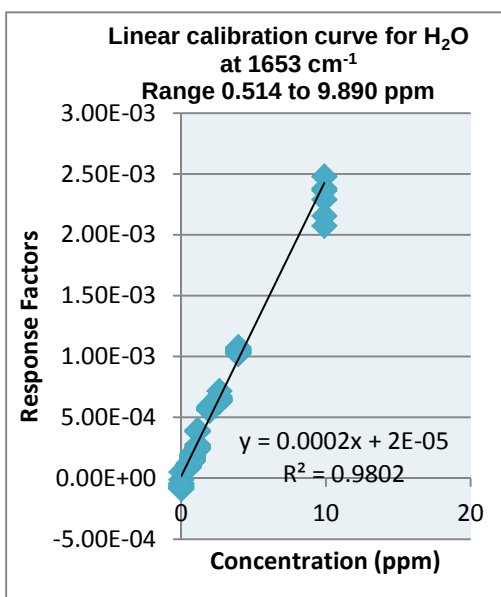
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Regression Statistics								
Multiple R	0.994101458							
R Square	0.988237708							
Adjusted R Square	0.988073201							
Standard Error	3.26332E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	1.27945E-05	6.4E-06	6007.247482	1.0969E-138			
Residual	143	1.52284E-07	1.06E-09					
Total	145	1.29468E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-3.75031E-05	5.34713E-06	-7.0137	8.52281E-11	-4.80727E-05	-2.6934E-05	-4.80727E-05	-2.69335E-05
X Variable 1	0.00018159	3.6344E-06	49.96439	2.01311E-92	0.000174406	0.000174406	0.000174406	0.000188774
X Variable 2	-3.98262E-06	3.80441E-07	-10.4684	2.16311E-19	-4.73463E-06	-3.2306E-06	-4.73463E-06	-3.2306E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.991576327							
R Square	0.983223612							
Adjusted R Square	0.982978701							
Standard Error	2.63465E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	5.5734E-06	2.79E-06	4014.619591	2.4652E-122			
Residual	137	9.5097E-08	6.94E-10					
Total	139	5.6685E-06						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-4.73016E-05	5.6485E-06	-8.37419	5.82366E-14	-5.84711E-05	-3.6132E-05	-5.84711E-05	-3.61321E-05
X Variable 1	0.00019783	6.71261E-06	29.47144	3.66723E-61	0.000184557	0.000211104	0.000184557	0.000211104
X Variable 2	-8.09292E-06	1.5586E-06	-5.19243	7.34024E-07	-1.1175E-05	-5.0109E-06	-1.1175E-05	-5.0109E-06



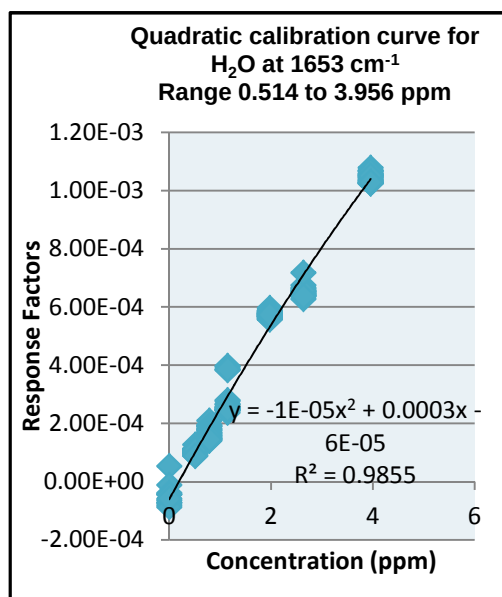
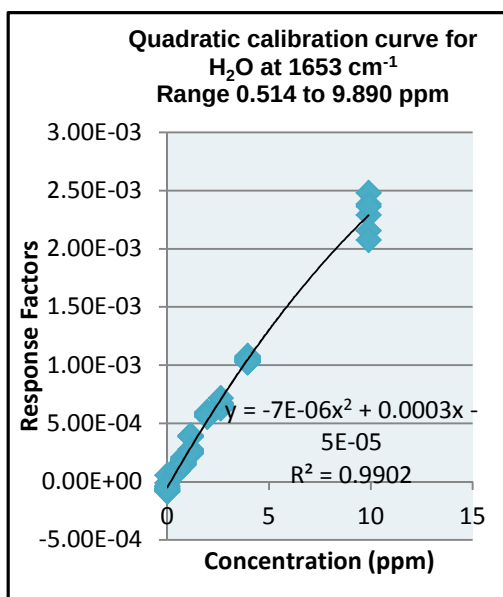
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SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.989342275								
R Square	0.978798138								
Adjusted R Square	0.978650903								
Standard Error	3.62502E-05								
Observations	146								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	8.73579E-06	8.73579E-06	6647.856312	2.116E-122				
Residual	144	1.89227E-07	1.31408E-09						
Total	145	8.92502E-06							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	-7.35897E-08	4.25183E-06	-0.017307748	0.986215062	-8.47766E-06	8.33048E-06	-8.47766E-06	8.33048E-06	
X Variable 1	0.000121381	1.48871E-06	81.5343873	2.116E-122	0.000118438	0.000124323	0.000118438	0.000124323	
Range:0-3.956									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.990640969								
R Square	0.98136953								
Adjusted R Square	0.981234527								
Standard Error	2.30125E-05								
Observations	140								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	3.84959E-06	3.84959E-06	7269.220602	3.0247E-121				
Residual	138	7.30812E-08	5.29574E-10						
Total	139	3.92267E-06							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	-2.32921E-05	3.33243E-06	-6.989519429	1.07707E-10	-2.98813E-05	-1.6703E-05	-2.98813E-05	-1.67029E-05	
X Variable 1	0.000136782	1.6043E-06	85.25972439	3.0247E-121	0.00013361	0.000139955	0.00013361	0.000139955	



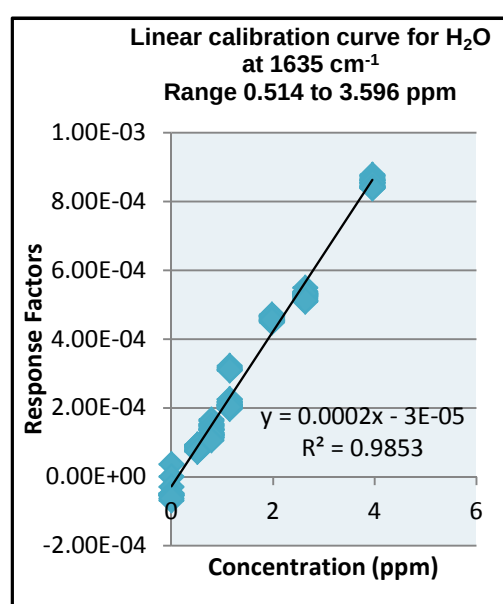
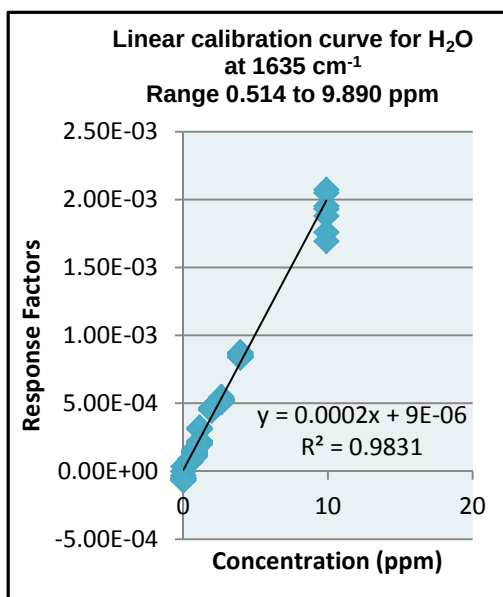
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SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.993805731							
R Square	0.987649831							
Adjusted R Square	0.987477101							
Standard Error	2.77634E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	8.81479E-06	4.41E-06	5717.894341	3.586E-137			
Residual	143	1.10225E-07	7.71E-10					
Total	145	8.92502E-06						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-3.22331E-05	4.54919E-06	-7.08547	5.81295E-11	-4.12255E-05	-2.3241E-05	-4.12255E-05	-2.32408E-05
X Variable 1	0.000150478	3.09204E-06	48.6663	7.05489E-91	0.000144366	0.00015659	0.000144366	0.00015659
X Variable 2	-3.27677E-06	3.23669E-07	-10.1238	1.69034E-18	-3.91656E-06	-2.637E-06	-3.91656E-06	-2.63697E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.991204199							
R Square	0.982485765							
Adjusted R Square	0.982230082							
Standard Error	2.23937E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	3.85397E-06	1.93E-06	3842.604249	4.7021E-121			
Residual	137	6.87025E-08	5.01E-10					
Total	139	3.92267E-06						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-3.37535E-05	4.80105E-06	-7.03044	8.88E-11	-4.32472E-05	-2.426E-05	-4.32472E-05	-2.42597E-05
X Variable 1	0.000152998	5.70551E-06	26.81585	2.27955E-56	0.000141716	0.00016428	0.000141716	0.00016428
X Variable 2	-3.91454E-06	1.32476E-06	-2.9549	0.003683124	-6.53416E-06	-1.2949E-06	-6.53416E-06	-1.29491E-06



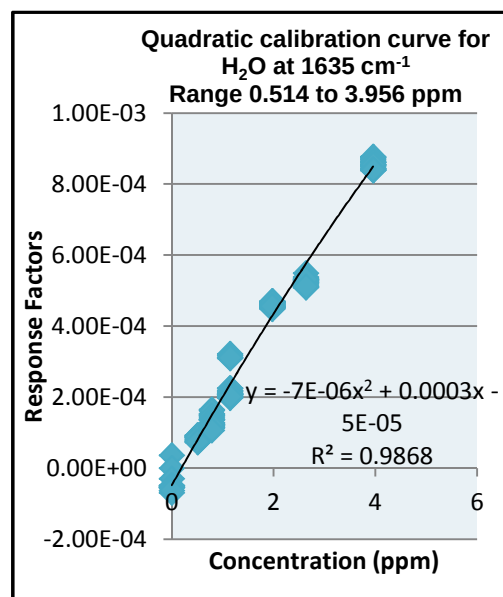
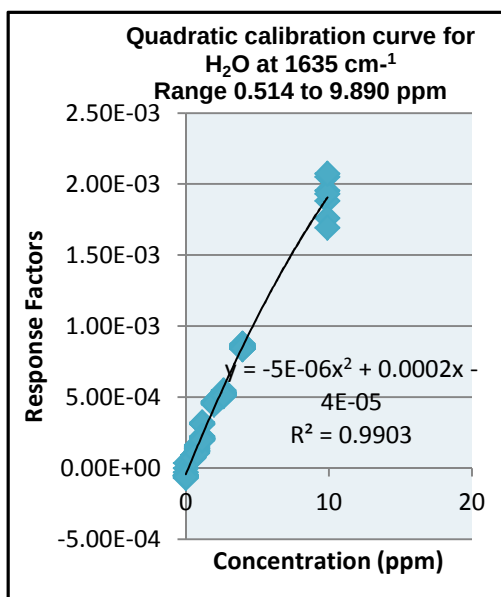
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SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.990056956							
R Square	0.980212776							
Adjusted R Square	0.980075364							
Standard Error	7.01924E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	3.51461E-05	3.51461E-05	7133.42288	1.4655E-124			
Residual	144	7.09483E-07	4.92697E-09					
Total	145	3.58556E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	1.81611E-05	8.23296E-06	2.205901228	0.028975813	1.88803E-06	3.44341E-05	1.88803E-06	3.44341E-05
X Variable 1	0.000243466	2.88263E-06	84.45959318	1.4655E-124	0.000237768	0.000249164	0.000237768	0.000249164
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.991643441							
R Square	0.983356714							
Adjusted R Square	0.983236111							
Standard Error	4.38137E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	1.5652E-05	1.5652E-05	8153.631907	1.2598E-124			
Residual	138	2.6491E-07	1.91964E-09					
Total	139	1.59169E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-3.05976E-05	6.34465E-06	-4.822588271	3.70E-06	-4.31429E-05	-1.8052E-05	-4.31429E-05	-1.80523E-05
X Variable 1	0.000275809	3.05445E-06	90.29746346	1.2598E-124	0.000269769	0.000281848	0.000269769	0.000281848



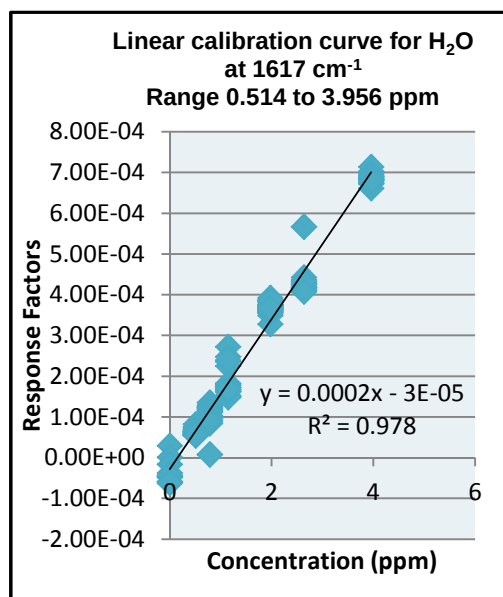
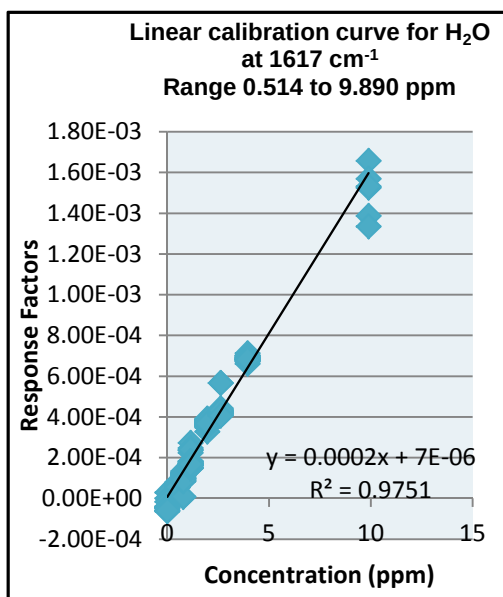
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SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.995107997							
R Square	0.990239927							
Adjusted R Square	0.990103422							
Standard Error	4.94695E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	3.55057E-05	1.78E-05	7254.264588	1.7616E-144			
Residual	143	3.49953E-07	2.45E-09					
Total	145	3.58556E-05						
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-5.04445E-05	8.10584E-06	-6.22323	5.0879E-09	-6.64672E-05	-3.4422E-05	-6.64672E-05	-3.44217E-05
X Variable 1	0.000305539	5.50947E-06	55.45708	1.38888E-98	0.000294648	0.00031643	0.000294648	0.00031643
X Variable 2	-6.99029E-06	5.7672E-07	-12.1208	1.05348E-23	-8.13029E-06	-5.8503E-06	-8.13029E-06	-5.85029E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.992744024							
R Square	0.985540697							
Adjusted R Square	0.985329613							
Standard Error	4.09867E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	1.56868E-05	7.84E-06	4668.934586	9.3345E-127			
Residual	137	2.30148E-07	1.68E-09					
Total	139	1.59169E-05						
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-6.00741E-05	8.78725E-06	-6.83651	2.44955E-10	-7.74502E-05	-4.2698E-05	-7.74502E-05	-4.26979E-05
X Variable 1	0.000321499	1.04427E-05	30.78706	2.01545E-63	0.000300849	0.000342149	0.000300849	0.000342149
X Variable 2	-1.10298E-05	2.42468E-06	-4.54895	1.17574E-05	-1.58244E-05	-6.2351E-06	-1.58244E-05	-6.23512E-06



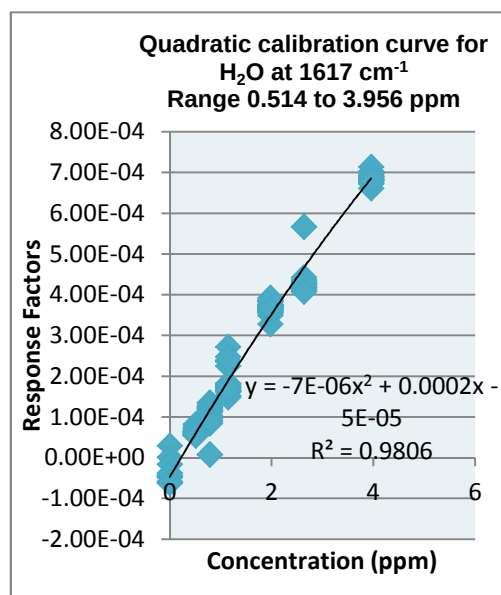
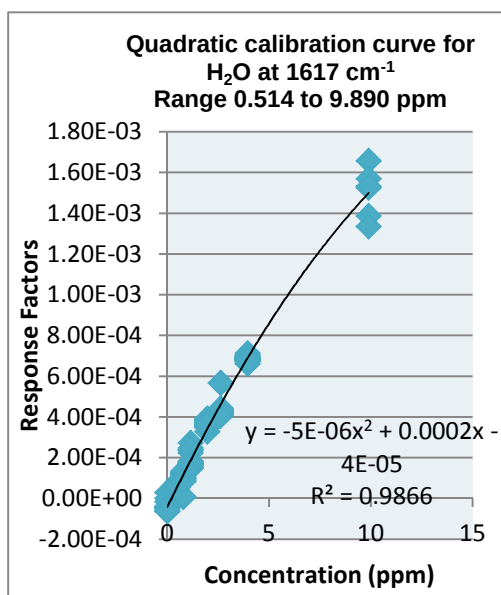
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SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.991519086								
R Square	0.983110097								
Adjusted R Square	0.982992806								
Standard Error	5.60848E-05								
Observations	146								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	2.6365E-05	2.6365E-05	8381.803815	1.6399E-129				
Residual	144	4.52953E-07	3.1455E-09						
Total	145	2.6818E-05							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	8.68267E-06	6.49779E-06	1.336249081	0.183575588	-4.1607E-06	2.1526E-05	-4.1607E-06	2.1526E-05	
X Variable 1	0.000200772	2.19298E-06	91.55219175	1.6399E-129	0.000196437	0.000205106	0.000196437	0.000205106	
Range:0-3.95									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.992605419								
R Square	0.985265518								
Adjusted R Square	0.985157967								
Standard Error	3.36797E-05								
Observations	139								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	1.03915E-05	1.03915E-05	9160.91791	2.3276E-127				
Residual	137	1.55403E-07	1.13433E-09						
Total	138	1.05469E-05							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	-2.80116E-05	4.87721E-06	-5.743362816	5.74E-08	-3.76559E-05	-1.8367E-05	-3.76559E-05	-1.83672E-05	
X Variable 1	0.000225228	2.35317E-06	95.71268417	2.3276E-127	0.000220575	0.000229882	0.000220575	0.000229882	



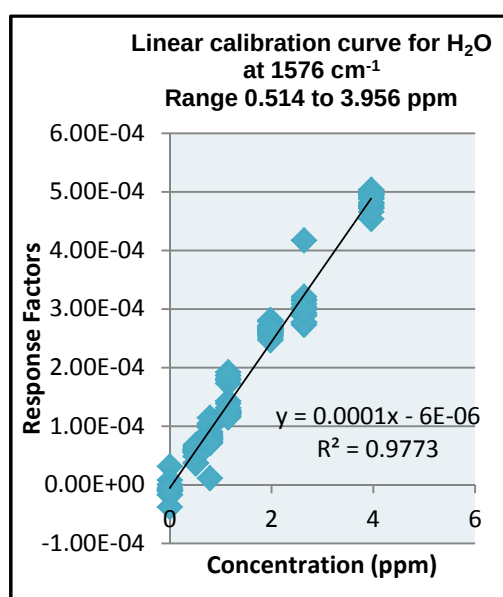
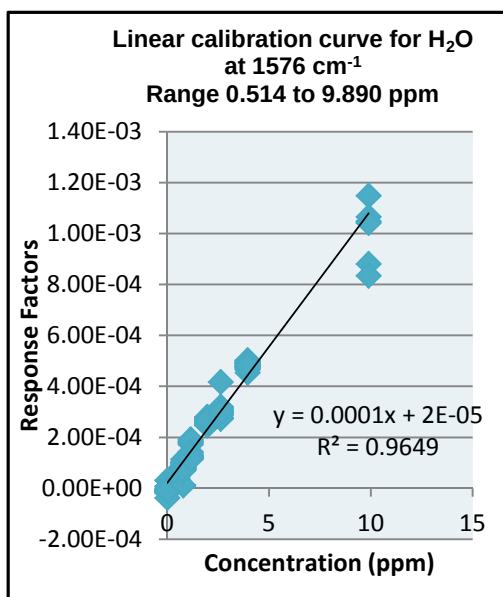
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SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.995130579							
R Square	0.990284868							
Adjusted R Square	0.990148992							
Standard Error	4.26844E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	2.65574E-05	1.33E-05	7288.153236	1.2664E-144			
Residual	143	2.6054E-07	1.82E-09					
Total	145	2.6818E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-4.21088E-05	6.99168E-06	-6.02271	1.38E-08	-5.59292E-05	-2.8288E-05	-5.59292E-05	-2.82884E-05
X Variable 1	0.000246484	4.75104E-06	51.88008	1.22627E-94	0.000237093	0.000255876	0.000237093	0.000255876
X Variable 2	-5.01108E-06	4.87622E-07	-10.2766	6.80292E-19	-5.97496E-06	-4.0472E-06	-5.97496E-06	-4.0472E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.993358448							
R Square	0.986761007							
Adjusted R Square	0.986566316							
Standard Error	3.2042E-05							
Observations	139							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	1.04072E-05	5.2E-06	5068.342213	1.9326E-128			
Residual	136	1.3963E-07	1.03E-09					
Total	138	1.05469E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-4.79325E-05	6.88198E-06	-6.96493	1.28028E-10	-6.1542E-05	-3.4323E-05	-6.1542E-05	-3.4323E-05
X Variable 1	0.000256143	8.19877E-06	31.24158	6.4095E-64	0.000239929	0.000272356	0.000239929	0.000272356
X Variable 2	-7.45183E-06	1.90121E-06	-3.91953	0.000139987	-1.12116E-05	-3.6921E-06	-1.12116E-05	-3.69208E-06



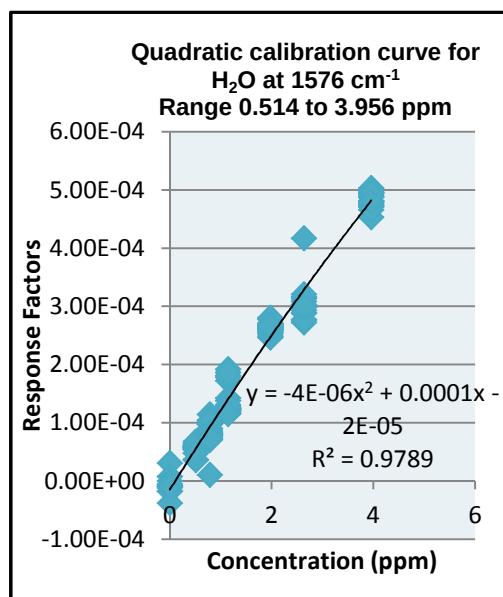
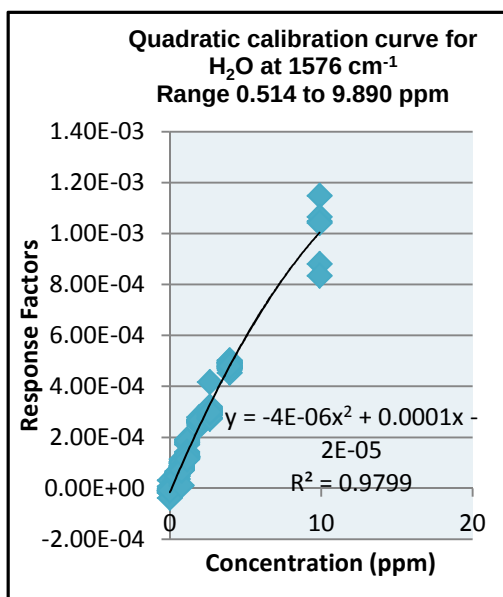
Range:0-9.89									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.987490462								
R Square	0.975137413								
Adjusted R Square	0.974964756								
Standard Error	5.21098E-05								
Observations	146								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	1.53363E-05	1.53363E-05	5647.834912	2.0264E-117				
Residual	144	3.91022E-07	2.71543E-09						
Total	145	1.57273E-05							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	6.79796E-06	6.11203E-06	1.11222654	0.26789414	-5.28292E-06	1.88789E-05	-5.28292E-06	1.88789E-05	
X Variable 1	0.000160827	2.14002E-06	75.15207856	2.0264E-117	0.000156597	0.000165057	0.000156597	0.000165057	
Range:0-3.956									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.989172395								
R Square	0.978462027								
Adjusted R Square	0.978305955								
Standard Error	3.33054E-05								
Observations	140								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	6.95421E-06	6.95421E-06	6269.288229	6.7144E-117				
Residual	138	1.53076E-07	1.10925E-09						
Total	139	7.10728E-06							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	-2.78992E-05	4.82295E-06	-5.784680608	4.65611E-08	-3.74357E-05	-1.8363E-05	-3.74357E-05	-1.83628E-05	
X Variable 1	0.000183843	2.32187E-06	79.178837	6.7144E-117	0.000179252	0.000188434	0.000179252	0.000188434	



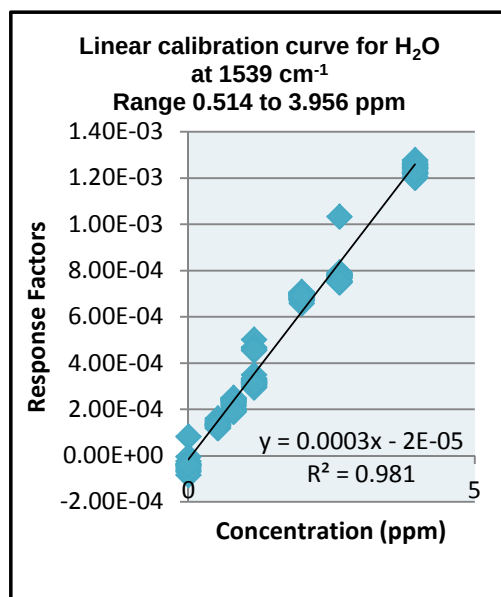
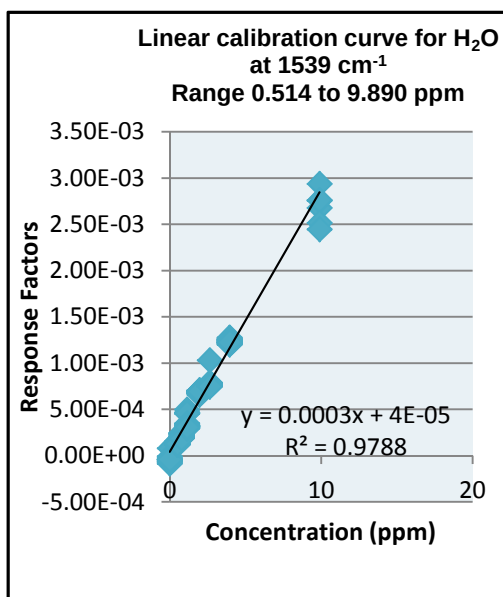
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SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.993283941							
R Square	0.986612987							
Adjusted R Square	0.986425756							
Standard Error	3.83708E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	1.55168E-05	7.76E-06	5269.497337	1.1426E-134			
Residual	143	2.10542E-07	1.47E-09					
Total	145	1.57273E-05						
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-4.18099E-05	6.28727E-06	-6.64993	5.76431E-10	-5.42379E-05	-2.9382E-05	-5.42379E-05	-2.93819E-05
X Variable 1	0.000204807	4.2734E-06	47.92594	5.57092E-90	0.00019636	0.000213254	0.00019636	0.000213254
X Variable 2	-4.95271E-06	4.47331E-07	-11.0717	5.81156E-21	-5.83695E-06	-4.0685E-06	-5.83695E-06	-4.06847E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.990252211							
R Square	0.980599441							
Adjusted R Square	0.980316222							
Standard Error	3.17248E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	6.9694E-06	3.48E-06	3462.326158	5.1913E-118			
Residual	137	1.37885E-07	1.01E-09					
Total	139	7.10728E-06						
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-4.7385E-05	6.80156E-06	-6.96678	1.24045E-10	-6.08346E-05	-3.3935E-05	-6.08346E-05	-3.39353E-05
X Variable 1	0.000214047	8.0829E-06	26.48146	9.65095E-56	0.000198064	0.00023003	0.000198064	0.00023003
X Variable 2	-7.29135E-06	1.87677E-06	-3.88506	0.000158626	-1.10025E-05	-3.5802E-06	-1.10025E-05	-3.58017E-06



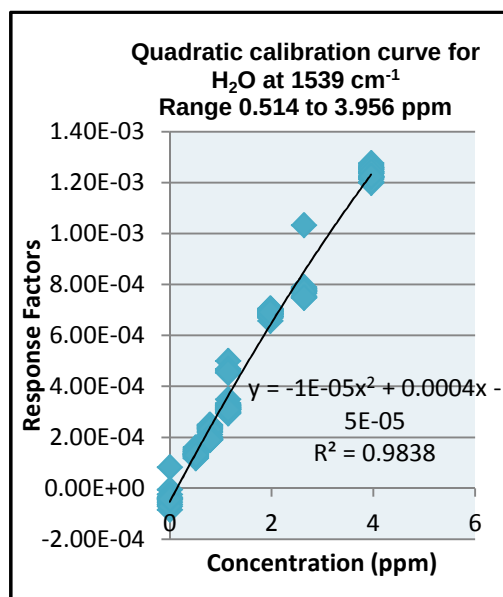
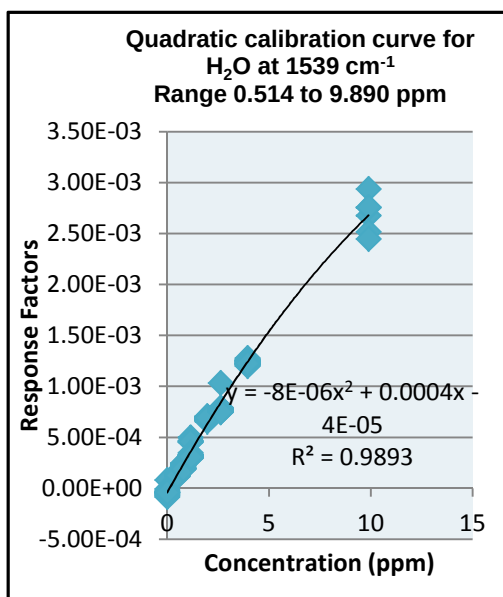
Range:0-9.89									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.982307617								
R Square	0.964928255								
Adjusted R Square	0.964684701								
Standard Error	4.13578E-05								
Observations	146								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	6.77665E-06	6.77665E-06	3961.869212	1.1657E-106				
Residual	144	2.46307E-07	1.71047E-09						
Total	145	7.02296E-06							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	2.14844E-05	4.85091E-06	4.428944603	1.86088E-05	1.18962E-05	3.10726E-05	1.18962E-05	3.10726E-05	
X Variable 1	0.000106907	1.69847E-06	62.943381	1.1657E-106	0.00010355	0.000110264	0.00010355	0.000110264	
Range:0-3.956									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.988822898								
R Square	0.977770723								
Adjusted R Square	0.977609641								
Standard Error	2.29873E-05								
Observations	140								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	3.20751E-06	3.20751E-06	6070.029146	5.9412E-116				
Residual	138	7.29216E-08	5.28417E-10						
Total	139	3.28043E-06							
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	-5.57329E-06	3.32879E-06	-1.674268078	0.096342857	-1.21553E-05	1.00874E-06	-1.21553E-05	1.00874E-06	
X Variable 1	0.000124855	1.60255E-06	77.91039177	5.9412E-116	0.000121687	0.000128024	0.000121687	0.000128024	



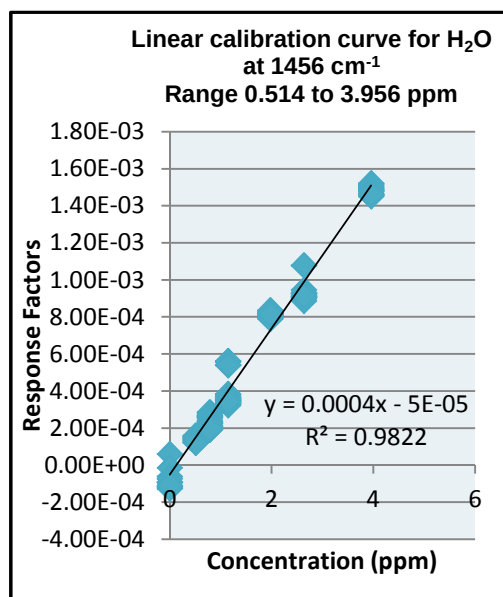
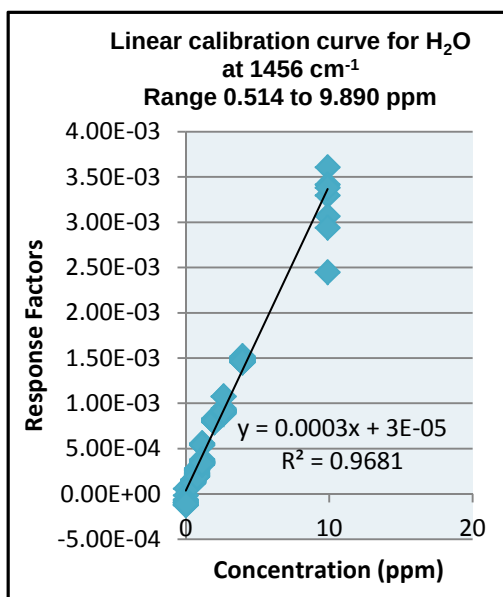
Range:0-9.89								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.989896906							
R Square	0.979895885							
Adjusted R Square	0.979614709							
Standard Error	3.1422E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	6.88177E-06	3.44E-06	3484.985908	4.8403E-122			
Residual	143	1.4119E-07	9.87E-10					
Total	145	7.02296E-06						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-1.56117E-05	5.14867E-06	-3.03218	0.002883602	-2.5789E-05	-5.4344E-06	-2.5789E-05	-5.43436E-06
X Variable 1	0.000140471	3.49951E-06	40.14024	9.90592E-80	0.000133554	0.000147389	0.000133554	0.000147389
X Variable 2	-3.77976E-06	3.66322E-07	-10.3182	5.30763E-19	-4.50387E-06	-3.0557E-06	-4.50387E-06	-3.05566E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.989381622							
R Square	0.978875995							
Adjusted R Square	0.978567615							
Standard Error	2.24902E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	3.21113E-06	1.61E-06	3174.25623	1.7667E-115			
Residual	137	6.92958E-08	5.06E-10					
Total	139	3.28043E-06						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-1.50929E-05	4.82173E-06	-3.13019	0.002135475	-2.46276E-05	-5.5583E-06	-2.46276E-05	-5.55828E-06
X Variable 1	0.000139611	5.73009E-06	24.36457	1.19988E-51	0.00012828	0.000150942	0.00012828	0.000150942
X Variable 2	-3.56215E-06	1.33047E-06	-2.67736	0.008327421	-6.19306E-06	-9.3123E-07	-6.19306E-06	-9.31233E-07



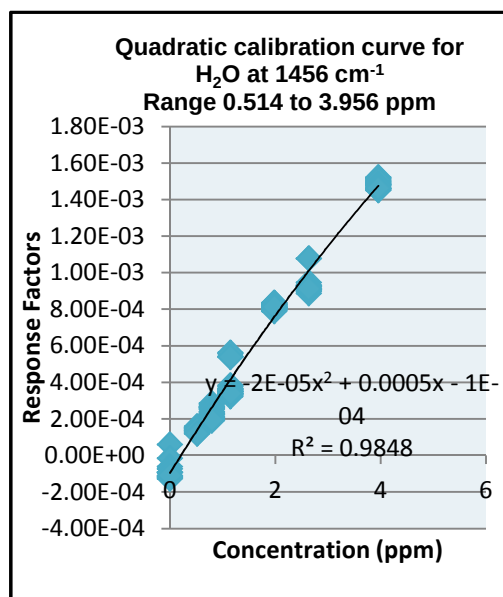
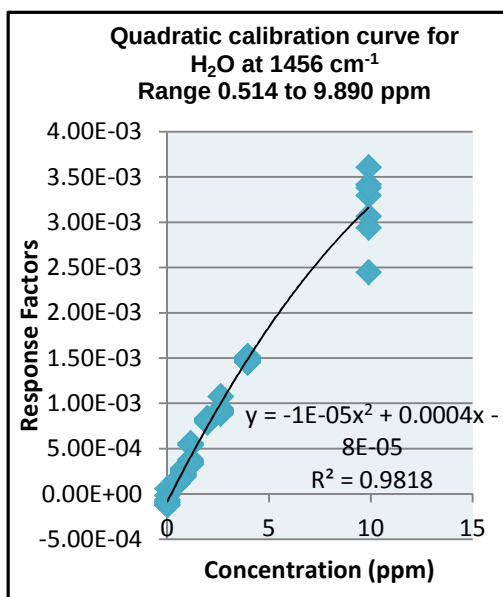
Range:0-9.89									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.989326798								
R Square	0.978767513								
Adjusted R Square	0.978620065								
Standard Error	8.47255E-05								
Observations	146								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	4.76507E-05	4.76507E-05	6638.059869	2.3478E-122				
Residual	144	1.03369E-06	7.1784E-09						
Total	145	4.86844E-05							
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	4.13489E-05	9.93756E-06	4.160871361	5.42776E-05	2.17066E-05	6.09913E-05	2.17066E-05	6.09913E-05	
X Variable 1	0.000283487	3.47947E-06	81.47428962	2.3478E-122	0.00027661	0.000290365	0.00027661	0.000290365	
Range:0-3.956									
SUMMARY OUTPUT									
Regression Statistics									
Multiple R	0.990666753								
R Square	0.981420615								
Adjusted R Square	0.981285982								
Standard Error	5.41132E-05								
Observations	140								
ANOVA									
	df	SS	MS	F	Significance F				
Regression	1	2.13456E-05	2.13456E-05	7289.587259	2.5026E-121				
Residual	138	4.04096E-07	2.92823E-09						
Total	139	2.17497E-05							
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%	
Intercept	-1.68466E-05	7.83612E-06	-2.149866062	0.033309235	-3.2341E-05	-1.3522E-06	-3.2341E-05	-1.3522E-06	
X Variable 1	0.00032209	3.77247E-06	85.37907975	2.5026E-121	0.000314631	0.000329549	0.000314631	0.000329549	



Range:0-9.89								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.994643048							
R Square	0.989314794							
Adjusted R Square	0.98916535							
Standard Error	6.0314E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	4.81642E-05	2.41E-05	6619.994603	1.1428E-141			
Residual	143	5.20202E-07	3.64E-09					
Total	145	4.86844E-05						
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-4.06403E-05	9.88278E-06	-4.11224	6.58052E-05	-6.01755E-05	-2.1105E-05	-6.01755E-05	-2.11051E-05
X Variable 1	0.00035767	6.71724E-06	53.24657	3.57188E-96	0.000344392	0.000370948	0.000344392	0.000370948
X Variable 2	-8.35397E-06	7.03147E-07	-11.8808	4.46555E-23	-9.74388E-06	-6.9641E-06	-9.74388E-06	-6.96407E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.991864097							
R Square	0.983794387							
Adjusted R Square	0.983557809							
Standard Error	5.07223E-05							
Observations	140							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	2.13972E-05	1.07E-05	4158.430516	2.3019E-123			
Residual	137	3.52467E-07	2.57E-09					
Total	139	2.17497E-05						
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-5.27691E-05	1.08745E-05	-4.85256	3.27011E-06	-7.42727E-05	-3.1266E-05	-7.42727E-05	-3.12656E-05
X Variable 1	0.000377772	1.29231E-05	29.23225	9.61935E-61	0.000352218	0.000403327	0.000352218	0.000403327
X Variable 2	-1.34418E-05	3.00062E-06	-4.47968	1.56245E-05	-1.93753E-05	-7.5083E-06	-1.93753E-05	-7.5083E-06



Range:0-9.89		LOQ		0.446466473				
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.983936522							
R Square	0.96813108							
Adjusted R Square	0.967909768							
Standard Error	0.000129989							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	7.39164E-05	7.39164E-05	4374.508926	1.1787E-109			
Residual	144	2.43318E-06	1.68971E-08					
Total	145	7.63495E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	3.48653E-05	1.50462E-05	2.317222063	0.021901266	5.12543E-06	6.46051E-05	5.12543E-06	6.46051E-05
X Variable 1	0.000337005	5.09533E-06	66.1400705	1.1787E-109	0.000326934	0.000347077	0.000326934	0.000347077
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.991059485							
R Square	0.982198903							
Adjusted R Square	0.982068968							
Standard Error	6.43003E-05							
Observations	139							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	3.12536E-05	3.12536E-05	7559.154936	9.8228E-122			
Residual	137	5.66431E-07	4.13453E-09					
Total	138	3.182E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-5.14466E-05	9.3414E-06	-5.50737156	1.74121E-07	-6.99185E-05		-6.99185E-05	-3.29746E-05
X Variable 1	0.000394745	4.54025E-06	86.94340076	9.8228E-122	0.000385767	0.000403723	0.000385767	0.000403723

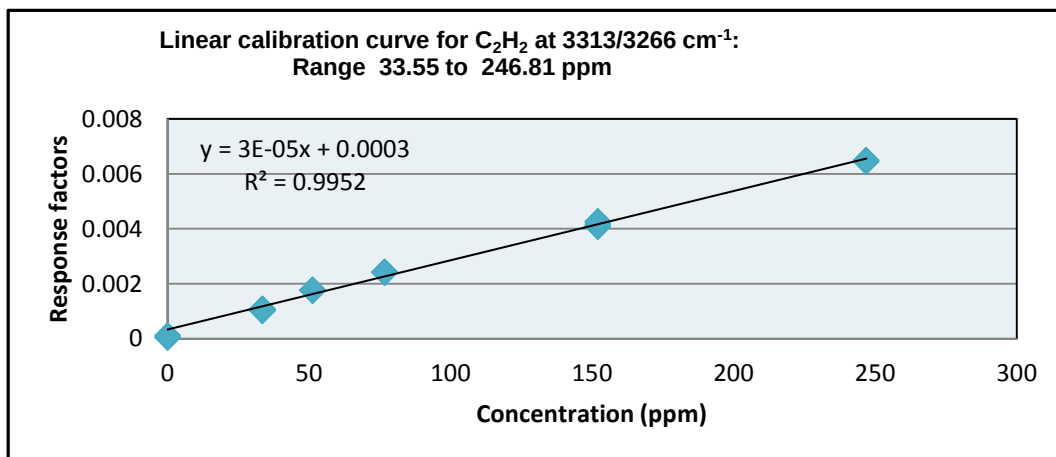


Range:0-9.89								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.990837316							
R Square	0.981758587							
Adjusted R Square	0.981503462							
Standard Error	9.8688E-05							
Observations	146							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	7.49568E-05	3.75E-05	3848.152467	4.6311E-125			
Residual	143	1.39272E-06	9.74E-09					
Total	145	7.63495E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-8.40021E-05	1.62095E-05	-5.18227	7.32946E-07	-0.000116043	-5.1961E-05	-0.000116043	-5.19609E-05
X Variable 1	0.000443988	1.10499E-05	40.18033	8.68789E-80	0.000422146	0.00046583	0.000422146	0.00046583
X Variable 2	-1.16971E-05	1.1317E-06	-10.3359	4.7751E-19	-1.39341E-05	-9.4601E-06	-1.39341E-05	-9.46005E-06
Range:0-3.956								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.992366151							
R Square	0.984790578							
Adjusted R Square	0.984566911							
Standard Error	5.96537E-05							
Observations	139							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	3.1336E-05	1.57E-05	4402.912972	2.4192E-124			
Residual	136	4.83964E-07	3.56E-09					
Total	138	3.182E-05						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-9.67657E-05	1.27957E-05	-7.56235	5.31E-12	-0.00012207	-7.1461E-05	-0.00012207	-7.14614E-05
X Variable 1	0.000465223	1.52342E-05	30.53816	9.66624E-63	0.000435097	0.000495349	0.000435097	0.000495349
X Variable 2	-1.71046E-05	3.55311E-06	-4.81397	3.88367E-06	-2.4131E-05	-1.0078E-05	-2.4131E-05	-1.00781E-05

APPENDIX 3:

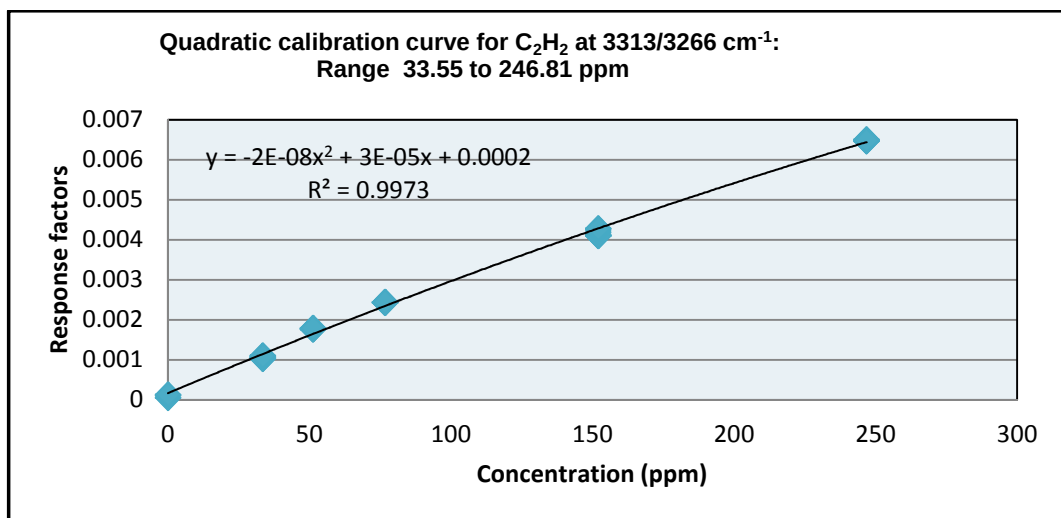
Linear and Quadratic Calibration Data for all C₂H₂ wavenumbers:

Standard 1: Low range linear data for C₂H₂ at 3313/3266 cm⁻¹



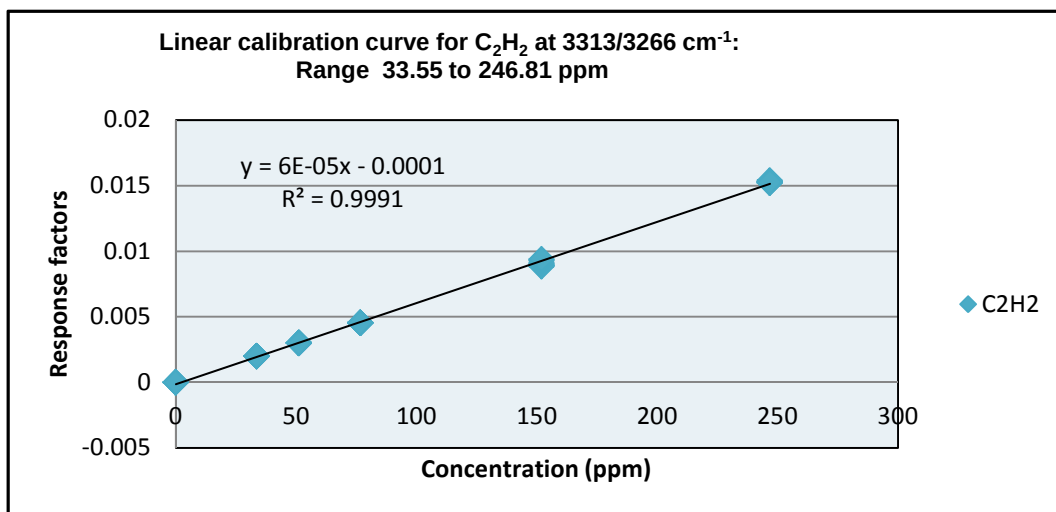
Range: 0-369.048								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.993773918							
R Square	0.9875866							
Adjusted R Square	0.98737971							
Standard Error	0.000300009							
Observations	62							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.000429639	0.000429639	4773.486496	6.76708E-59			
Residual	60	5.40031E-06	9.00052E-08					
Total	61	0.000435039						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000541173	5.7874E-05	9.350877632	2.55E-13	0.000425408	0.000656938	0.000425408	0.000657
X Variable 1	2.24595E-05	3.25075E-07	69.09042261	6.76708E-59	2.18093E-05	2.31098E-05	2.18093E-05	2.31E-05
Range: 0-246.815								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.997585075							
R Square	0.995175981							
Adjusted R Square	0.995083212							
Standard Error	0.000142647							
Observations	54							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.000218282	0.000218282		6.47881E-62			
Residual	52	1.0581E-06	2.03481E-08					
Total	53	0.00021934						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000335694	3.09555E-05	10.84441669	5.8721E-15	0.000273578	0.000397811	0.000273578	0.000398
X Variable 1	2.51789E-05	2.43103E-07	103.5731347	6.47881E-62	2.46911E-05	2.56668E-05	2.46911E-05	2.57E-05

Standard 1: Low range quadratic data for C₂H₂ at 3313/3266 cm⁻¹



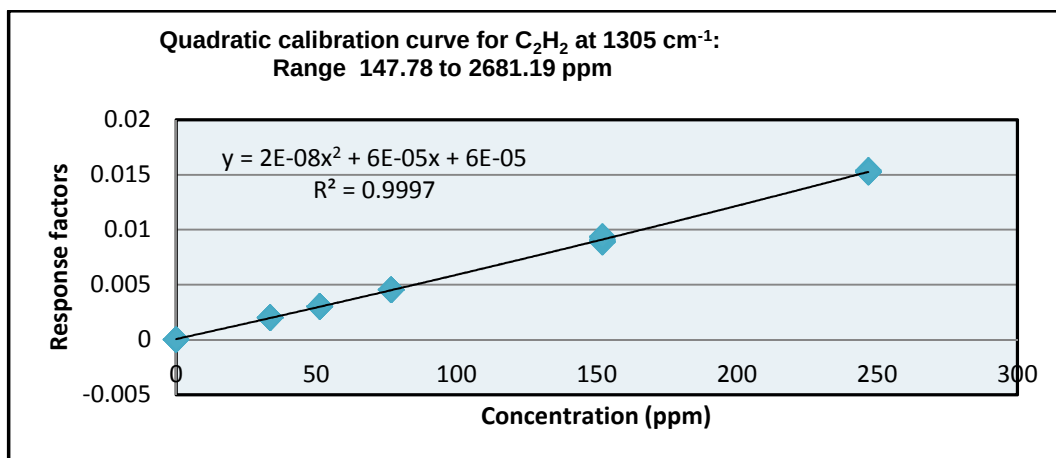
Range: 0-369.048								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.999176807							
R Square	0.998354292							
Adjusted R Square	0.998298505							
Standard Error	0.000110158							
Observations	62							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	0.000434323	0.000217161	17895.91529	7.62794E-83			
Residual	59	7.15947E-07	1.21347E-08					
Total	61	0.000435039						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000119442	3.02044E-05	3.954469892	0.000208073	5.90035E-05	0.000179881	5.90035E-05	0.00018
X Variable 1	3.11699E-05	4.59114E-07	67.89139454	1.04101E-57	3.02512E-05	3.20886E-05	3.02512E-05	3.21E-05
X Variable 2	-2.35213E-08	1.19715E-09	-19.64766375	1.43584E-27	-2.59168E-08	-2.11258E-08	-2.59168E-08	-2.1E-08
Range: 0-246.815								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.998673412							
R Square	0.997348584							
Adjusted R Square	0.997244607							
Standard Error	0.000106786							
Observations	54							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	0.000218759	0.000109379	9592.002902	1.98923E-66			
Residual	51	5.81563E-07	1.14032E-08					
Total	53	0.00021934						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000165768	3.50422E-05	4.730525481	1.81124E-05	9.54179E-05	0.000236118	9.54179E-05	0.000236
X Variable 1	2.97686E-05	7.32934E-07	40.61569695	1.63999E-40	2.82972E-05	3.12401E-05	2.82972E-05	3.12E-05
X Variable 2	-1.75965E-08	2.72201E-09	-6.464520777	3.81502E-08	-2.30612E-08	-1.21318E-08	-2.30612E-08	-1.2E-08

Standard 1: Low range linear data for C₂H₂ at 1305 cm⁻¹



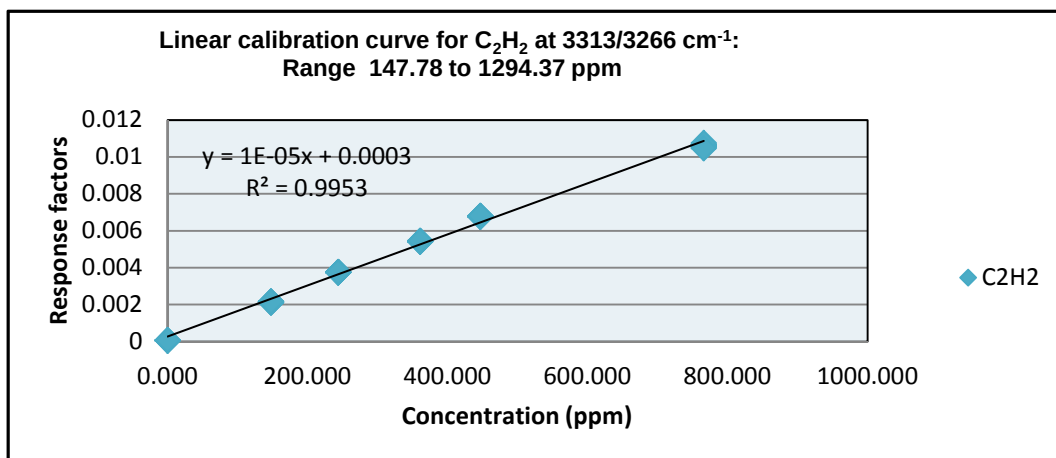
Range: 0-369.048								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.998258828							
R Square	0.996520687							
Adjusted	0.996462699							
Standard	0.000409161							
Observati	62							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.002876952	0.002876952	17184.78473	1.80548E-75			
Residual	60	1.00448E-05	1.67413E-07					
Total	61	0.002886997						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000137034	7.89304E-05	1.736136429	0.087672483	-2.08504E-05	0.000294918	-2.08504E-05	0.000295
X Variable	5.81187E-05	4.43347E-07	131.09075	1.80548E-75	5.72318E-05	5.90055E-05	5.72318E-05	5.9E-05
Range: 0-246.815								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.999559015							
R Square	0.999118225							
Adjusted	0.999101267							
Standard	0.000149635							
Observati	54							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.001319257	0.001319257	58919.93956	4.18159E-81			
Residual	52	1.16432E-06	2.23907E-08					
Total	53	0.001320422						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-0.000148709	3.2472E-05	-4.579608482	2.94031E-05	-0.000213869	-8.35493E-05	-0.000213869	-8.4E-05
X Variable	6.19003E-05	2.55013E-07	242.7342983	4.18159E-81	6.13886E-05	6.2412E-05	6.13886E-05	6.24E-05

Standard 1: Low range quadratic data for C₂H₂ at 1305 cm⁻¹



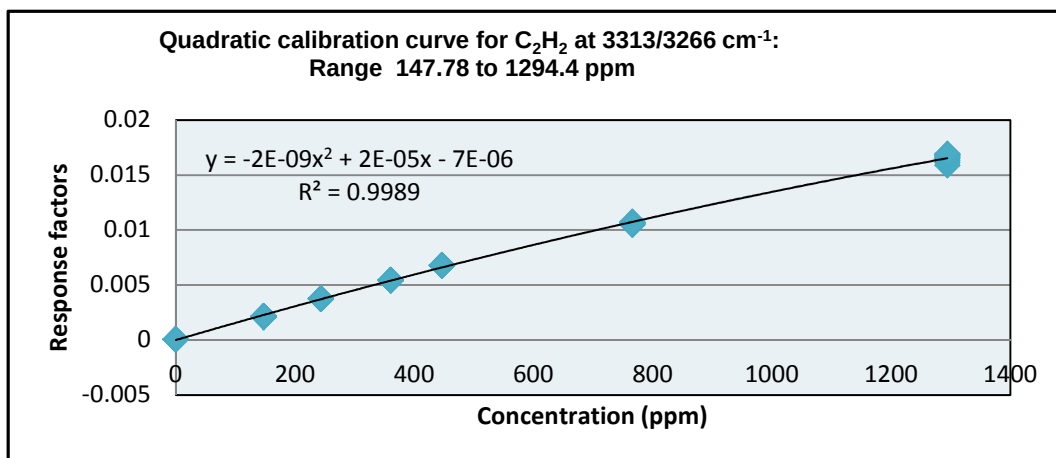
Range: 0-369.048								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.999128871							
R Square	0.998258501							
Adjusted	0.998199467							
Standard	0.000291917							
Observati	62							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	0.002881969	0.001440985	16909.92704	4.04797E-82			
Residual	59	5.0277E-06	8.52153E-08					
Total	61	0.002886997						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	-0.000299416	8.00414E-05	-3.740765936	0.000417336	-0.000459578	-0.000139254	-0.000459578	-0.00014
X Variable	6.7133E-05	1.21665E-06	55.17869324	1.77188E-52	6.46985E-05	6.95675E-05	6.46985E-05	6.96E-05
X Variable	-2.43422E-08	3.17245E-09	-7.673013107	1.95761E-10	-3.06903E-08	-1.79942E-08	-3.06903E-08	-1.8E-08
Range: 0-246.815								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.99983002							
R Square	0.999660068							
Adjusted	0.999646738							
Standard	9.38139E-05							
Observati	54							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	0.001319973	0.000659986	74989.56556	3.55212E-89			
Residual	51	4.48853E-07	8.80104E-09					
Total	53	0.001320422						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	5.95021E-05	3.07854E-05	1.932801297	0.058822628	-2.30221E-06	0.000121307	-2.30221E-06	0.000121
X Variable	5.62766E-05	6.439E-07	87.3994687	3.16092E-57	5.49839E-05	5.75692E-05	5.49839E-05	5.76E-05
X Variable	2.15611E-08	2.39136E-09	9.016255578	3.89607E-12	1.67602E-08	2.63619E-08	1.67602E-08	2.64E-08

Standard 2: Low range linear data for C₂H₂ at 3313/3266 cm⁻¹



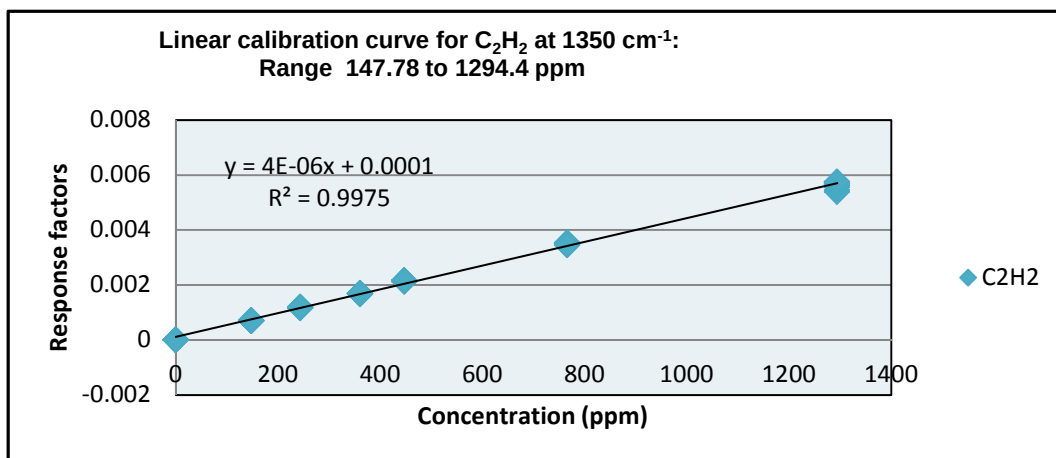
Range:0-2681.19								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.996657419							
R Square	0.993326011							
Adjusted R Square	0.993230668							
Standard Error	0.000684011							
Observations	72							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.004874508	0.004874508	10418.47935	6.80372E-78			
Residual	70	3.2751E-05	4.67871E-07					
Total	71	0.004907259						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.001105505	0.000110851	9.972908057	4.47E-15	0.00088442	0.001326591	0.00088442	0.001327
X Variable 1	1.14859E-05	1.12529E-07	102.0709525	6.80372E-78	1.12615E-05	1.17104E-05	1.12615E-05	1.17E-05
Range:0-1294.37								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.99697278							
R Square	0.993954725							
Adjusted R Square	0.993860267							
Standard Error	0.000400784							
Observations	66							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.001690251	0.001690251	10522.77993	1.00866E-72			
Residual	64	1.02802E-05	1.60628E-07					
Total	65	0.001700531						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000634403	7.82194E-05	8.11056398	2.05824E-11	0.000478142	0.000790665	0.000478142	0.000791
X Variable 1	1.26071E-05	1.229E-07	102.5806021	1.00866E-72	1.23616E-05	1.28527E-05	1.23616E-05	1.29E-05

Standard 2: Low range quadratic data for C₂H₂ at 3313/3266 cm⁻¹



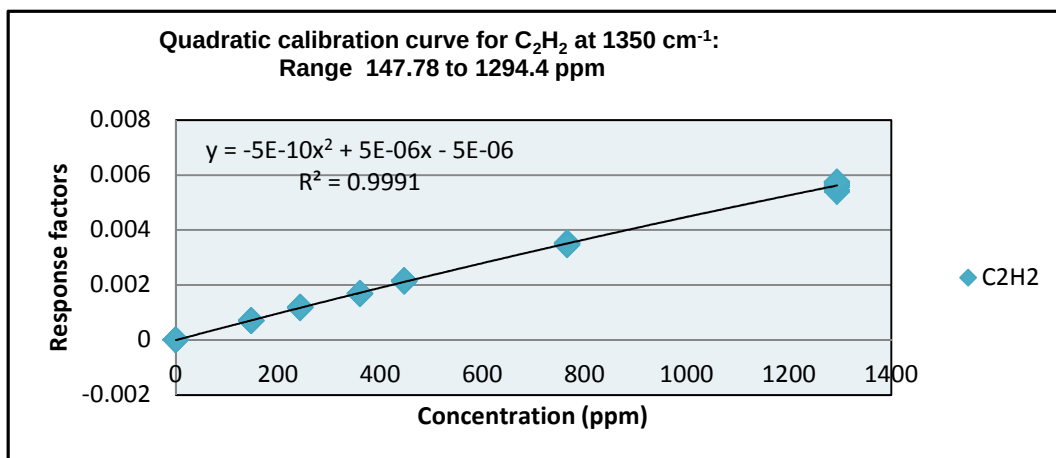
Range:0-2681.19								
SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple F	0.99911964							
R Square	0.998240054							
Adjusted	0.998189041							
Standard	0.000353789							
Observati	72							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regressio	2	0.004898623	0.002449311	19568.3788	9.32661E-96			
Residual	69	8.63651E-06	1.25167E-07					
Total	71	0.004907259						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.000319925	8.05641E-05	3.971055945	0.000173226	0.000159204	0.000480646	0.000159204	0.000481
X Variable	1.4077E-05	1.95537E-07	71.99126204	1.18457E-66	1.36869E-05	1.44671E-05	1.36869E-05	1.45E-05
X Variable	-9.95937E-10	7.17525E-11	-13.88015888	1.18488E-21	-1.13908E-09	-8.52794E-10	-1.13908E-09	-8.5E-10
Range:0-1294.37								
SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple F	0.999440714							
R Square	0.998881742							
Adjusted	0.998846241							
Standard	0.000173737							
Observati	66							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regressio	2	0.001698629	0.000849315	28137.30517	1.06924E-93			
Residual	63	1.90163E-06	3.01846E-08					
Total	65	0.001700531						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-6.58446E-06	5.12899E-05	-0.128377245	0.898259377	-0.000109079	9.59103E-05	-0.000109079	9.59E-05
X Variable	1.58585E-05	2.02329E-07	78.37962879	1.61266E-64	1.54541E-05	1.62628E-05	1.54541E-05	1.63E-05
X Variable	-2.38214E-09	1.42987E-10	-16.65984766	9.09852E-25	-2.66788E-09	-2.09641E-09	-2.66788E-09	-2.1E-09

Standard 2: Low range linear data for C₂H₂ at 1350 cm⁻¹



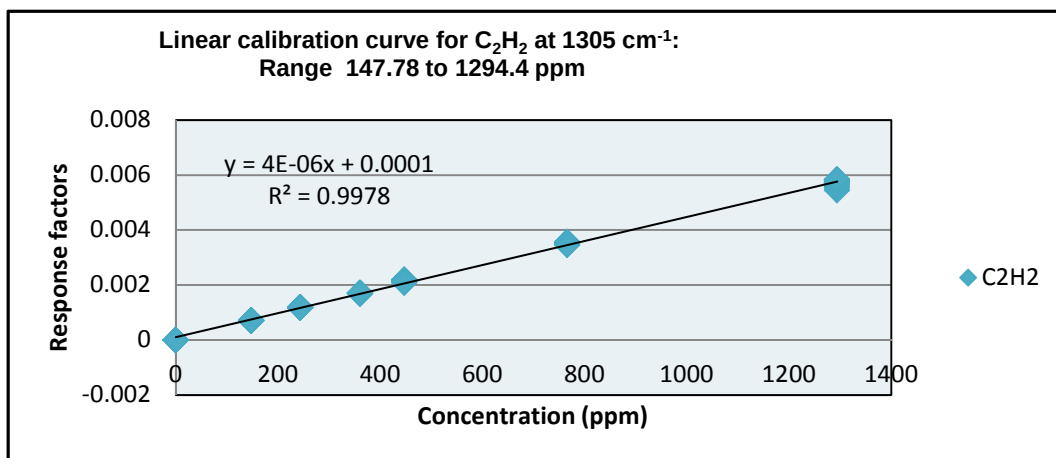
Range:0-2681.19								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.998230541							
R Square	0.996464214							
Adjusted R	0.99641297							
Standard Error	0.000175299							
Observations	71							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.000597565	0.000597565	19445.75386	2.5378E-86			
Residual	69	2.12036E-06	3.07298E-08					
Total	70	0.000599685						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000238549	2.86696E-05	8.320600617	5.18137E-12	0.000181354	0.000295743	0.000181354	0.000296
X Variable	4.03192E-06	2.89134E-08	139.4480328	2.5378E-86	3.97423E-06	4.0896E-06	3.97423E-06	4.09E-06
Range:0-1294.37								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.998745248							
R Square	0.99749207							
Adjusted R	0.997452261							
Standard Error	8.85994E-05							
Observations	65							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.000196696	0.000196696	25057.31497	1.20091E-83			
Residual	63	4.94541E-07	7.84986E-09					
Total	64	0.000197191						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000119346	1.74567E-05	6.836717215	3.84532E-09	8.4462E-05	0.000154231	8.4462E-05	0.000154
X Variable	4.31355E-06	2.725E-08	158.2950251	1.20E-83	4.25909E-06	4.368E-06	4.25909E-06	4.37E-06

Standard 2: Low range quadratic data for C₂H₂ at 1350 cm⁻¹



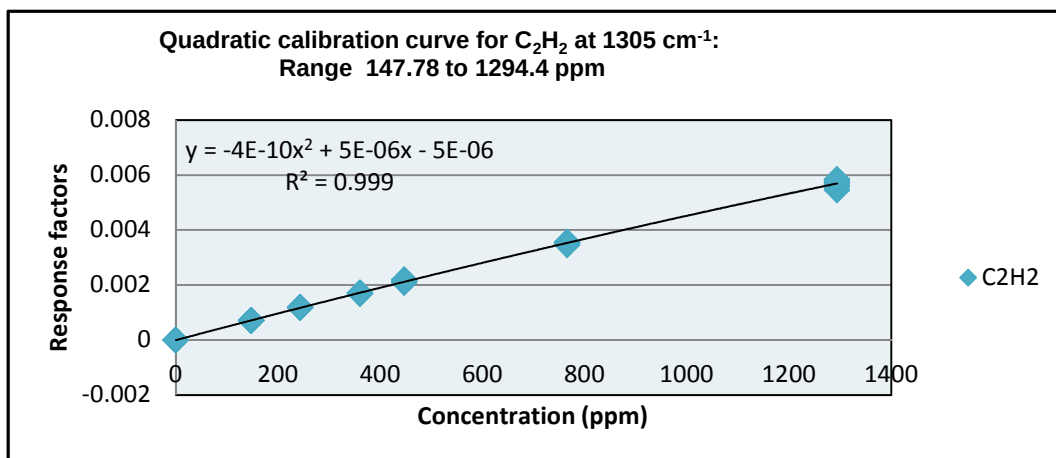
Range:0-2681.19								
SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.999412471							
R Square	0.998825288							
Adjusted R Square	0.998790738							
Standard Error	0.000101782							
Observations	71							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	0.000598981	0.00029949	28909.26302	2.386E-100			
Residual	68	7.04457E-07	1.03597E-08					
Total	70	0.000599685						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	4.68541E-05	2.33658E-05	2.005244339	0.048919132	2.2841E-07	9.34798E-05	2.2841E-07	9.34798E-05
X Variable 1	4.66101E-06	5.6369E-08	82.68742775	5.7473E-70	4.54853E-06	4.77349E-06	4.54853E-06	4.77349E-06
X Variable 2	-2.41568E-10	2.06631E-11	-11.69078217	6.27893E-18	-2.828E-10	-2.00335E-10	-2.828E-10	-2.00335E-10
Range:0-1294.37								
SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.999546136							
R Square	0.999092478							
Adjusted R Square	0.999063204							
Standard Error	5.3725E-05							
Observations	65							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	0.000197012	9.8506E-05	34127.96725	4.93817E-95			
Residual	62	1.78955E-07	2.88637E-09					
Total	64	0.000197191						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-5.03718E-06	1.59233E-05	-0.316340058	0.752807008	-3.68674E-05	2.67931E-05	-3.68674E-05	2.67931E-05
X Variable 1	4.94463E-06	6.25749E-08	79.01936911	5.99392E-64	4.81954E-06	5.06972E-06	4.81954E-06	5.06972E-06
X Variable 2	-4.62334E-10	4.42154E-11	-10.45641528	2.58555E-15	-5.50719E-10	-3.73949E-10	-5.50719E-10	-3.73949E-10

Standard 2: Low range linear data for C₂H₂ at 1305 cm⁻¹



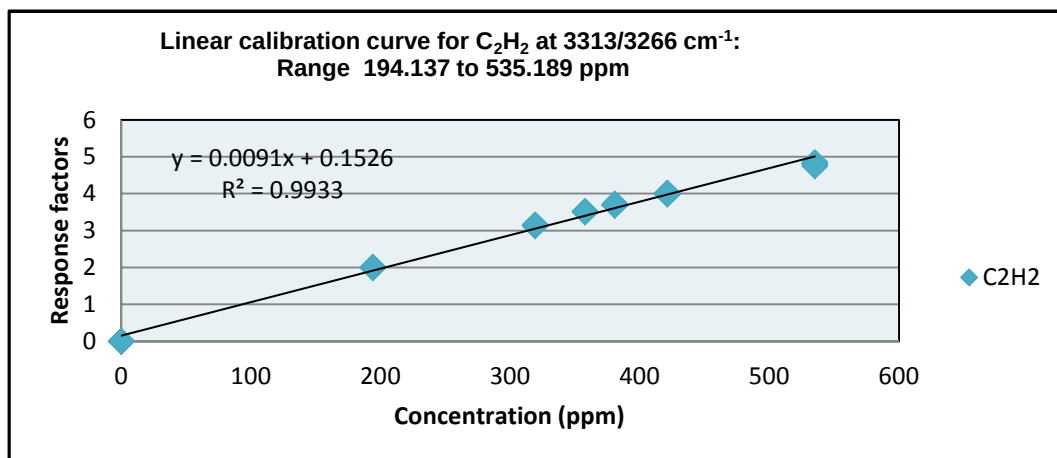
Range:0-2681.19								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.998416462							
R Square	0.996835432							
Adjusted R	0.996789568							
Standard Error	0.000170072							
Observations	71							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.000628674	0.000628674	21734.92206	5.52663E-88			
Residual	69	1.9958E-06	2.89246E-08					
Total	70	0.000630669						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000205868	2.7815E-05	7.401334886	2.47993E-10	0.000150379	0.000261357	0.000150379	0.000261357
X Variable 1	4.13557E-06	2.80515E-08	147.4276842	5.52663E-88	4.08E-06	4.19153E-06	4.07961E-06	4.19153E-06
Range:0-1294.37								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.998913998							
R Square	0.997829175							
Adjusted R	0.997794718							
Standard Error	8.3611E-05							
Observations	65							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.000202441	0.000202441	28958.22594	1.27258E-85			
Residual	63	4.4042E-07	6.9908E-09					
Total	64	0.000202882						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000104041	1.64741E-05	6.315445483	3.06535E-08	7.11203E-05	0.000136962	7.11203E-05	0.000136962
X Variable 1	4.37615E-06	2.57161E-08	170.1711666	1.27258E-85	4.32476E-06	4.42754E-06	4.32476E-06	4.42754E-06

Standard 2: Low range quadratic data for C₂H₂ at 1305 cm⁻¹



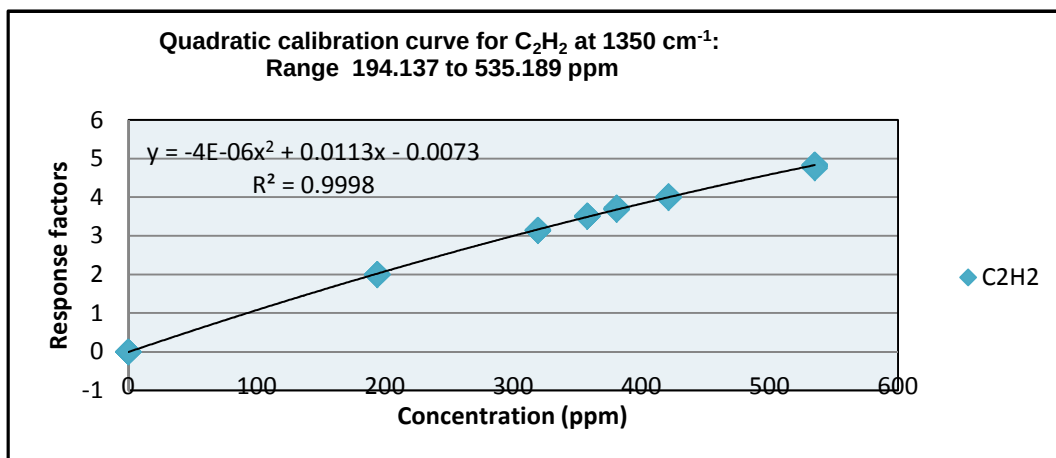
Range:0-2681.19								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.999241231							
R Square	0.998483037							
Adjusted	0.99843842							
Standard	0.000118613							
Observati	71							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	0.000629713	0.000314856	22379.20361	1.42282E-96			
Residual	68	9.56702E-07	1.40691E-08					
Total	70	0.000630669						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	4.16488E-05	2.72298E-05	1.529532093	0.130771472	-1.26874E-05	9.59851E-05	-1.26874E-05	9.6E-05
X Variable	4.67449E-06	6.56899E-08	71.15991139	1.39068E-65	4.54341E-06	4.80557E-06	4.54341E-06	4.81E-06
X Variable	-2.06942E-10	2.40799E-11	-8.593964518	1.8312E-12	-2.54992E-10	-1.58891E-10	-2.54992E-10	-1.6E-10
Range:0-1294.37								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.99951038							
R Square	0.999020999							
Adjusted	0.998989418							
Standard	5.66001E-05							
Observati	65							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	0.000202683	0.000101341	31633.92567	5.1794E-94			
Residual	62	1.98621E-07	3.20357E-09					
Total	64	0.000202882						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	-4.83448E-06	1.67756E-05	-0.28818597	0.774165614	-3.83683E-05	2.86994E-05	-3.83683E-05	2.87E-05
X Variable	4.92856E-06	6.59246E-08	74.76050061	1.79579E-62	4.79678E-06	5.06034E-06	4.79678E-06	5.06E-06
X Variable	-4.04709E-10	4.65835E-11	-8.68780861	2.55682E-12	-4.97828E-10	-3.1159E-10	-4.97828E-10	-3.1E-10

Standard 2: Low range linear data for C₂H₂ at 3313/3266 cm⁻¹ with internal standard



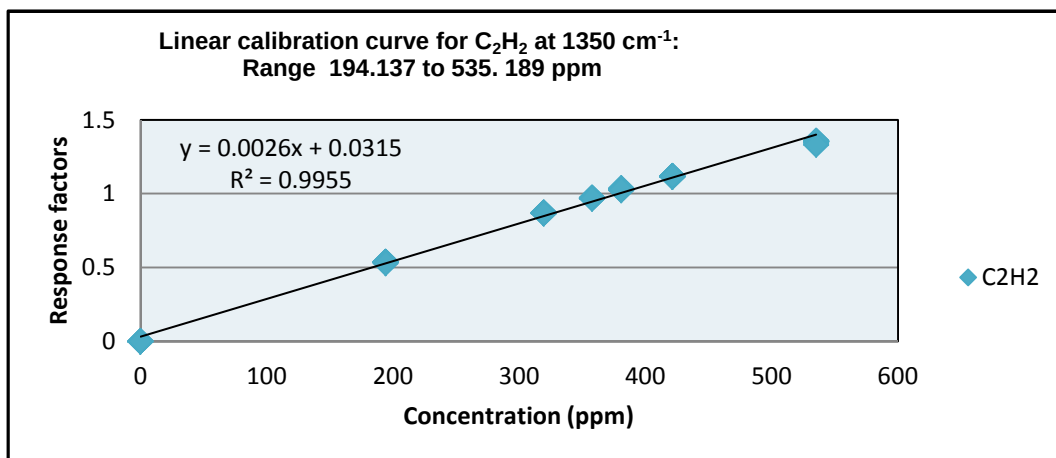
Range:0-596.445								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.996831142							
R Square	0.993672327							
Adjusted R Square	0.993585646							
Standard Error	0.127090073							
Observations	75							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	185.1591831	185.1591831	11463.62576	5.19447E-82			
Residual	73	1.179087721	0.016151887					
Total	74	186.3382709						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.196101358	0.033390231	5.873015879	1.17521E-07	0.129554723	0.262647993	0.129554723	0.262648
X Variable	0.00889412	8.30696E-05	107.0683229	5.19447E-82	0.008728562	0.009059677	0.008728562	0.00906
Range:0-535.189								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.996627339							
R Square	0.993266053							
Adjusted R Square	0.993159164							
Standard Error	0.122918605							
Observations	65							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	140.4014729	140.4014729	9292.582353	3.91259E-70			
Residual	63	0.951865957	0.015108983					
Total	64	141.3533388						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.152646699	0.034198527	4.463545944	3.40448E-05	0.084306395	0.220987003	0.084306395	0.220987
X Variable	0.009084318	9.42376E-05	96.39804123	3.91259E-70	0.008895999	0.009272637	0.008895999	0.009273

Standard 2: Low range quadratic data for C₂H₂ at 3313/3266 cm⁻¹ with internal standard



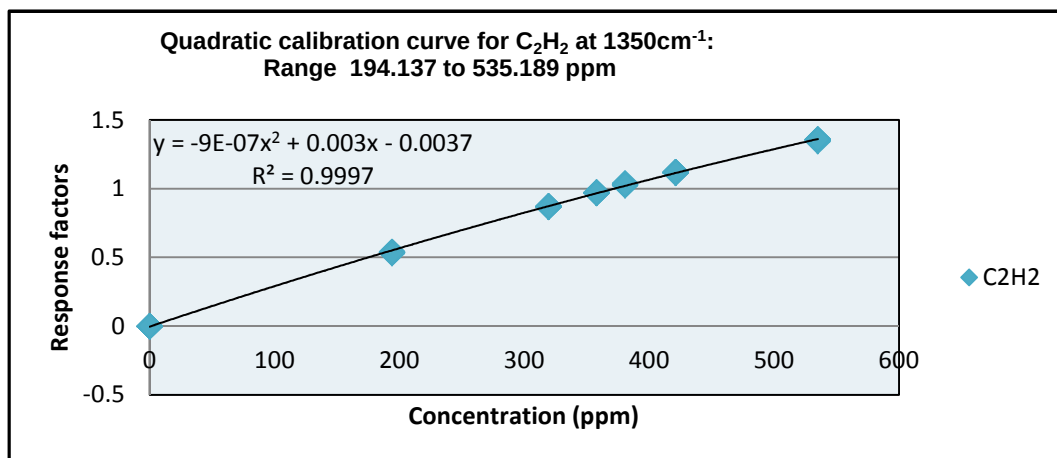
Range:0-596.445								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.999704024							
R Square	0.999408136							
Adjusted R Square	0.999391696							
Standard Error	0.039137724							
Observations	75							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	186.227984	93.11399202	60788.83511	6.3092E-117			
Residual	72	0.110286822	0.001531761					
Total	74	186.3382709						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.004388551	0.012585948	0.348686525	0.728342244	-0.020701079	0.02947818	-0.020701079	0.029478
X Variable 1	0.010920093	8.08512E-05	135.064149	2.37736E-88	0.010758919	0.011081267	0.010758919	0.011081
X Variable 2	-3.34083E-06	1.26474E-07	-26.41513549	8.86497E-39	-3.59295E-06	-3.0887E-06	-3.59295E-06	-3.1E-06
Range:0-535.189								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.999894114							
R Square	0.999788238							
Adjusted R Square	0.999781407							
Standard Error	0.021972571							
Observations	65							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	141.3234056	70.6617028	146359.9764	1.2626E-114			
Residual	62	0.029933221	0.000482794					
Total	64	141.3533388						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-0.007291936	0.007125124	-1.023411827	0.310089809	-0.021534856	0.006950984	-0.021534856	0.006951
X Variable 1	0.011255369	5.24605E-05	214.549467	9.89911E-91	0.011150502	0.011360236	0.011150502	0.01136
X Variable 2	-4.14067E-06	9.47549E-08	-43.6987218	2.72658E-48	-4.33008E-06	-3.95126E-06	-4.33008E-06	-4E-06

Standard 2: Low range linear data for C₂H₂ at 1350 cm⁻¹ with internal standard



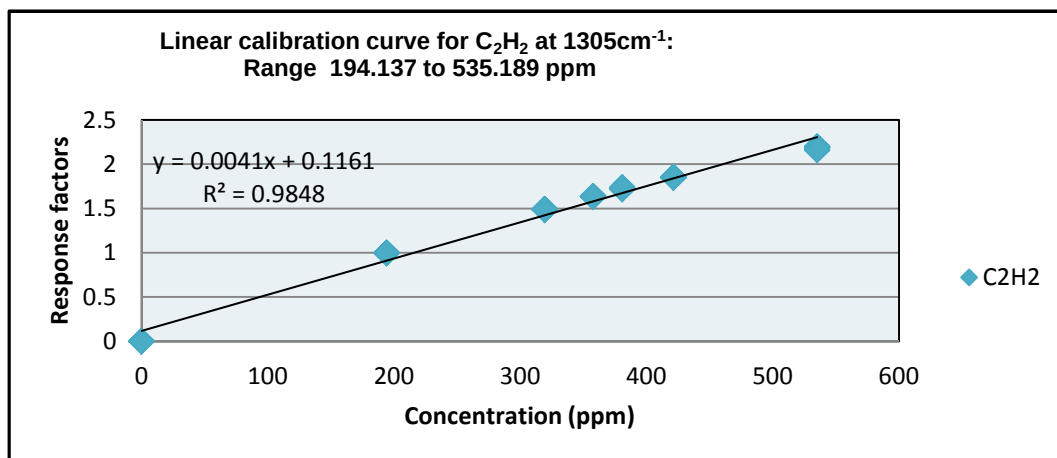
Range:0-596.445								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.998055443							
R Square	0.996114667							
Adjusted R Square	0.996062162							
Standard Error	0.028800514							
Observations	76							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	15.73668441	15.73668441	18971.98451	5.96385E-91			
Residual	74	0.06138075	0.00082947					
Total	75	15.79806516						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.037624884	0.007318361	5.14116285	2.15446E-06	0.023042732	0.052207036	0.023042732	0.052207
X Variable	0.002524462	1.83279E-05	137.7388272	5.96385E-91	0.002487943	0.002560981	0.002487943	0.002561
Range:0-535.189								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.997831336							
R Square	0.995667376							
Adjusted R Square	0.995599679							
Standard Error	0.028388203							
Observations	66							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	11.85274788	11.85274788	14707.64901	2.36646E-77			
Residual	64	0.051576963	0.00080589					
Total	65	11.90432484						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.029247675	0.007609179	3.843735871	0.000281237	0.014046592	0.044448757	0.014046592	0.044449
X Variable	0.002562368	2.11286E-05	121.2750964	2.36646E-77	0.002520158	0.002604577	0.002520158	0.002605

Standard 2: Low range quadratic data for C₂H₂ at 1350 cm⁻¹ with internal standard



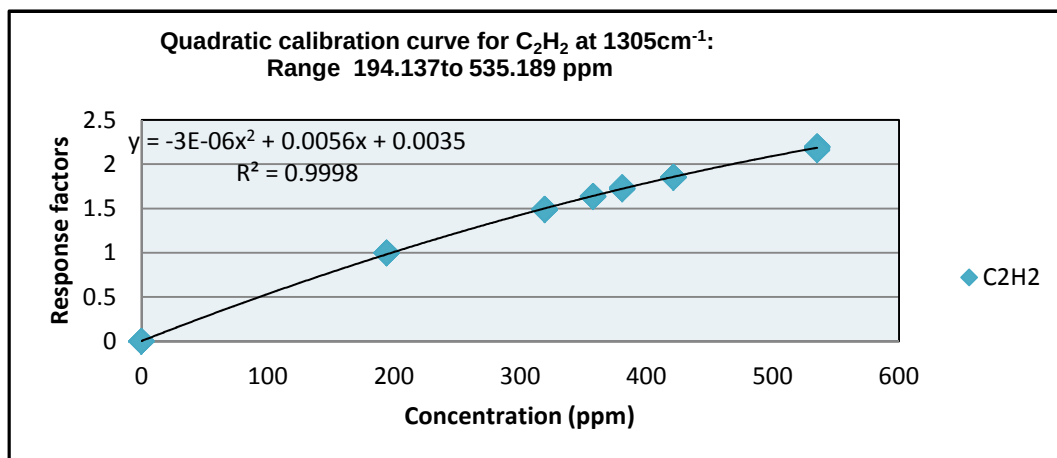
Range:0-596.445								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.99969374							
R Square	0.999387574							
Adjusted R	0.999370795							
Standard Error	0.011512438							
Observations	76							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	15.78839001	7.894195007	59562.54224	5.3389E-118			
Residual	73	0.009675145	0.000132536					
Total	75	15.79806516						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-0.001199806	0.003524426	-0.340425946	0.734513489	-0.008223977	0.005824365	-0.008223977	0.005824365
X Variable 1	0.002957084	2.30959E-05	128.0348657	1.1902E-87	0.002911054	0.003003114	0.002911054	0.003003114
X Variable 2	-7.23268E-07	3.66183E-08	-19.7515645	5.22739E-31	-7.96248E-07	-6.50288E-07	-7.96248E-07	-6.50288E-07
Range:0-535.189								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.999811388							
R Square	0.999622812							
Adjusted R	0.999610838							
Standard Error	0.0084423							
Observations	66							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	11.89983468	5.949917339	83481.32631	1.4506E-108			
Residual	63	0.004490163	7.12724E-05					
Total	65	11.90432484						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-0.003877045	0.00260412	-1.488811678	0.141526035	-0.009080964	0.001326875	-0.009080964	0.001326875
X Variable 1	0.003040493	1.96343E-05	154.856497	4.77396E-83	0.003001257	0.003079729	0.003001257	0.003079729
X Variable 2	-9.23952E-07	3.59468E-08	-25.70329433	4.2033E-35	-9.95786E-07	-8.52118E-07	-9.95786E-07	-8.52118E-07

Standard 2: Low range linear data for C₂H₂ at 1305 cm⁻¹ with internal standard



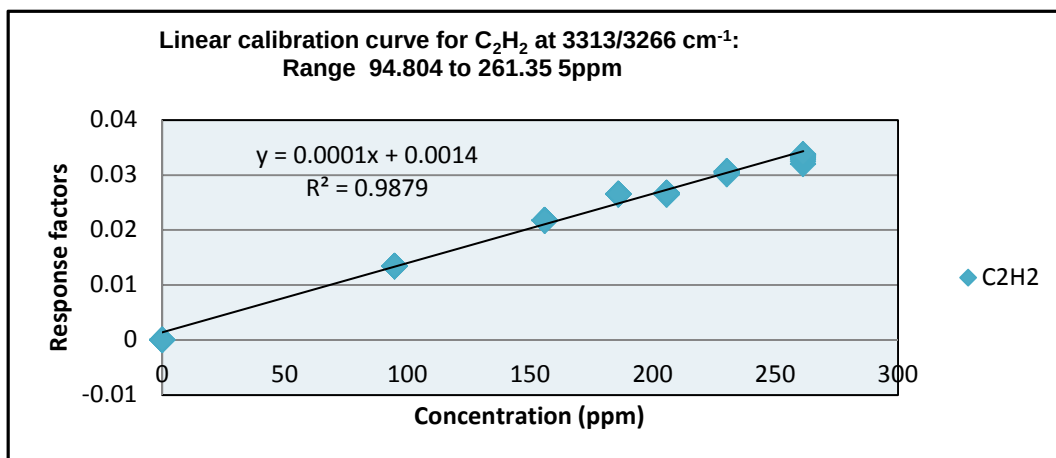
Range:0-596.445								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.992858711							
R Square	0.98576842							
Adjusted R Square	0.985578665							
Standard Error	0.087499707							
Observations	77							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	39.77372289	39.77372289	5194.969985	5.16399E-71			
Residual	75	0.574214909	0.007656199					
Total	76	40.3479378						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.135365629	0.022207248	6.095560816	4.35106E-08	0.091126523	0.179604735	0.091126523	0.179605
X Variable	0.003987957	5.53298E-05	72.07614019	5.16399E-71	0.003877734	0.00409818	0.003877734	0.004098
Range:0-535.189								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.992664807							
R Square	0.985383419							
Adjusted R Square	0.985158548							
Standard Error	0.084510748							
Observations	67							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	31.29656577	31.29656577	4382.004283	2.26153E-61			
Residual	65	0.464234319	0.007142066					
Total	66	31.76080009						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.107812332	0.022572025	4.776369594	1.05569E-05	0.062732886	0.152891778	0.062732886	0.152892
X Variable	0.00411204	6.21185E-05	66.196709	2.26153E-61	0.003987981	0.0042361	0.003987981	0.004236

Standard 2: Low range quadratic data for C₂H₂ at 1305 cm⁻¹ with internal standard



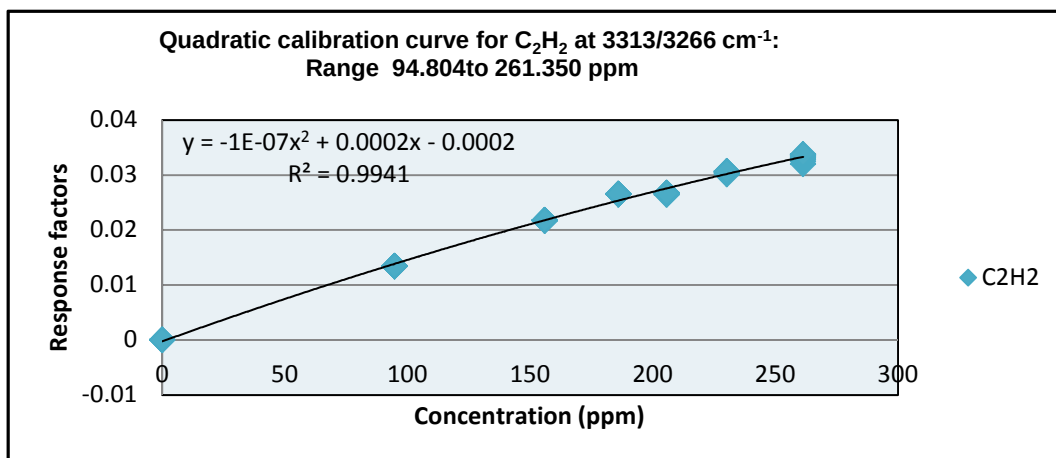
Range:0-596.445								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.999466111							
R Square	0.998932507							
Adjusted R Square	0.998903656							
Standard Error	0.024125552							
Observations	77							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	40.30486667	20.15243334	34623.6601	1.1207E-110			
Residual	74	0.043071127	0.000582042					
Total	76	40.3479378						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.010603962	0.007385689	1.435744346	0.155288864	-0.004112346	0.025320269	-0.004112346	0.02532
X Variable 1	0.005375081	4.83863E-05	111.0869054	4.50372E-84	0.00527867	0.005471493	0.00527867	0.005471
X Variable 2	-2.31357E-06	7.65869E-08	-30.20847433	2.29859E-43	-2.46617E-06	-2.16097E-06	-2.46617E-06	-2.2E-06
Range:0-535.189								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.999890855							
R Square	0.999781721							
Adjusted R Square	0.9997749							
Standard Error	0.010407865							
Observations	67							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	31.75386737	15.87693369	146569.3965	7.0531E-118			
Residual	64	0.006932714	0.000108324					
Total	66	31.76080009						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.003548294	0.003209766	1.10546804	0.273095266	-0.002863951	0.009960539	-0.002863951	0.009961
X Variable 1	0.005590788	2.40104E-05	232.848527	1.93225E-95	0.005542821	0.005638754	0.005542821	0.005639
X Variable 2	-2.82921E-06	4.35437E-08	-64.97401393	3.74658E-60	-2.9162E-06	-2.74222E-06	-2.9162E-06	-2.7E-06

Standard 3: Low range linear data for C₂H₂ at 3313/3266/ cm⁻¹



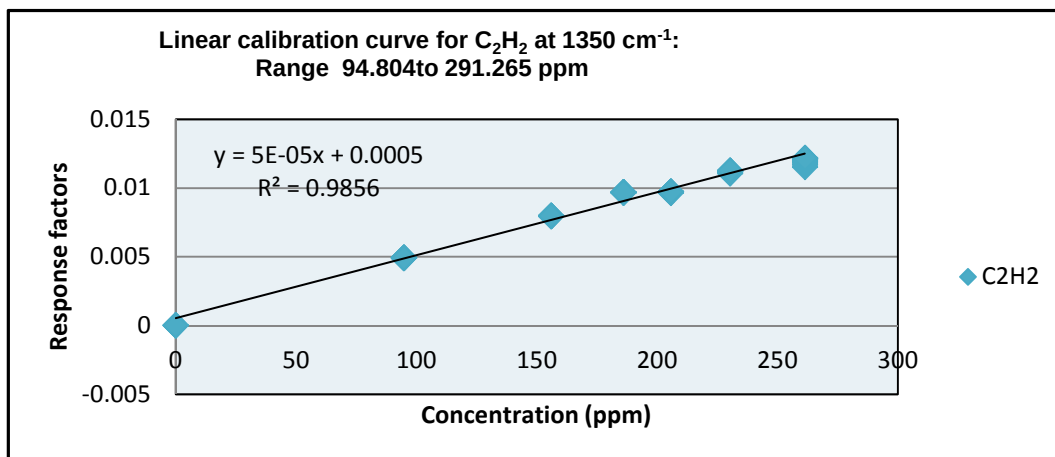
Range:0-291.265								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.993790698							
R Square	0.987619951							
Adjusted	0.987445584							
Standard	0.001084318							
Observati	73							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.006659456	0.006659456	5664.033717	1.85805E-69			
Residual	71	8.34779E-05	1.17574E-06					
Total	72	0.006742934						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	0.001837665	0.000331735	5.539557167	4.82942E-07	0.001176204	0.002499126	0.001176204	0.002499
X Variable	0.000122627	1.62939E-06	75.2597749	1.85805E-69	0.000119379	0.000125876	0.000119379	0.000126
Range:0-261.35								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.993925402							
R Square	0.987887706							
Adjusted	0.987692346							
Standard	0.001024631							
Observati	64							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.005308945	0.005308945	5056.765973	3.85989E-61			
Residual	62	6.50919E-05	1.04987E-06					
Total	63	0.005374037						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	0.001382415	0.000333533	4.144760488	0.000105007	0.000715692	0.002049139	0.000715692	0.002049
X Variable	0.000126148	1.77397E-06	71.1109413	3.85989E-61	0.000122602	0.000129695	0.000122602	0.00013

Standard 3: Low range quadratic data for C₂H₂ at 3313/3266 cm⁻¹



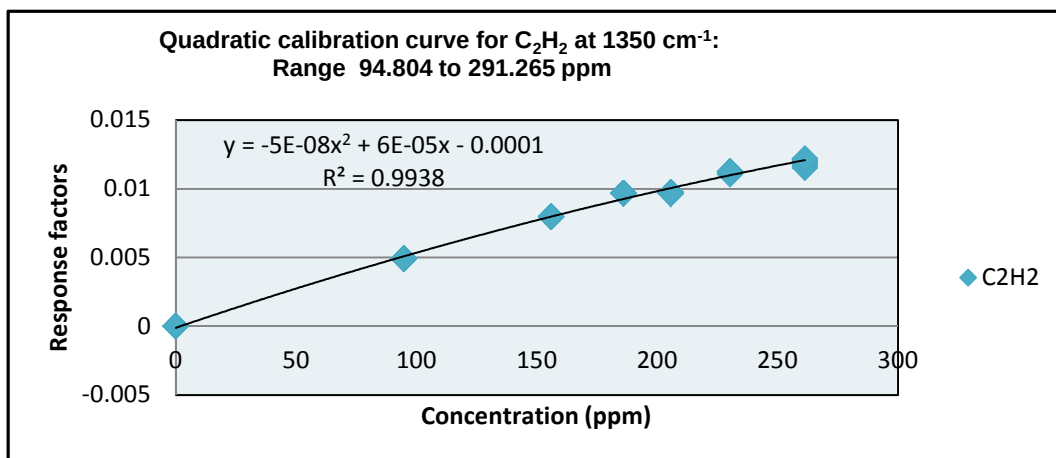
Range:0-291.265								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.997526345							
R Square	0.99505881							
Adjusted R	0.994917633							
Standard Error	0.000689908							
Observations	73							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	0.006709616	0.003354808	7048.313603	1.92356E-81			
Residual	70	3.33181E-05	4.75973E-07					
Total	72	0.006742934						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-0.000170128	0.000287756	-0.591221796	0.556276214	-0.000744038	0.000403783	-0.000744038	0.000404
X Variable 1	0.000157479	3.54975E-06	44.36350934	5.50298E-53	0.000150399	0.000164559	0.000150399	0.000165
X Variable 2	-1.10049E-07	1.07201E-08	-10.26564868	1.32846E-15	-1.31429E-07	-8.86682E-08	-1.31429E-07	-8.9E-08
Range:0-261.35								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.99706091							
R Square	0.994130458							
Adjusted R	0.993938013							
Standard Error	0.000719097							
Observations	64							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	0.005342494	0.002671247	5165.816414	8.7585E-69			
Residual	61	3.15431E-05	5.17101E-07					
Total	63	0.005374037						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-0.000202824	0.00030582	-0.663215089	0.509691418	-0.000814349	0.0004087	-0.000814349	0.000409
X Variable 1	0.000158585	4.21503E-06	37.62358589	6.41199E-44	0.000150156	0.000167013	0.000150156	0.000167
X Variable 2	-1.14904E-07	1.42654E-08	-8.05472703	3.54145E-11	-1.43429E-07	-8.63783E-08	-1.43429E-07	-8.6E-08

Standard 3: Low range linear data for C₂H₂ at 1350 cm⁻¹



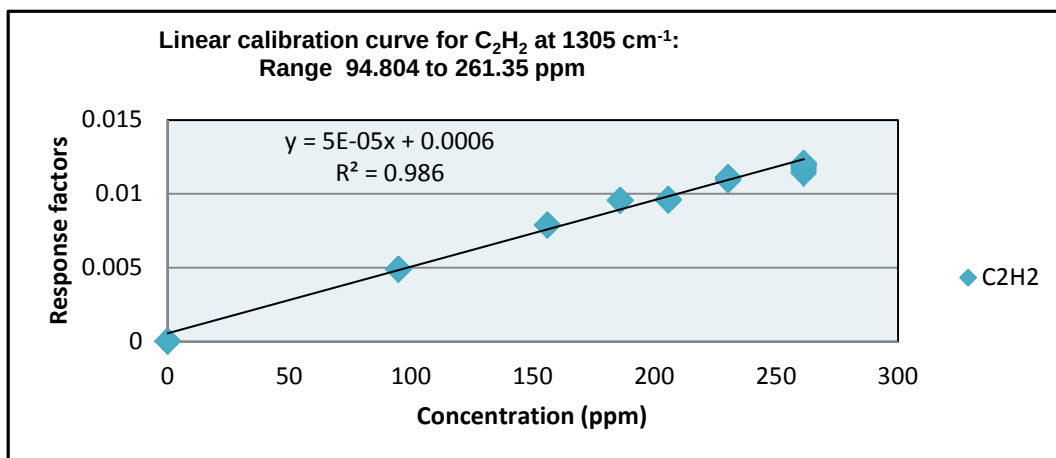
Range:0-230.238								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.99617305							
R Square	0.992360746							
Adjusted	0.992241382							
Standard	0.014039891							
Observati	66							
ANOVA								
		df	SS	MS	F	Significance F		
Regressio	1	1.638800346	1.638800346	8313.781135	1.80468E-69			
Residual	64	0.012615586	0.000197119					
Total	65	1.651415932						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	0.013855922	0.003398537	4.07702548	0.000128463	0.007066564	0.02064528	0.007066564	0.020645
X Variable	0.002013821	2.20862E-05	91.17993822	1.80468E-69	0.001969699	0.002057944	0.001969699	0.002058
Range:0-205.745								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.995618453							
R Square	0.991256104							
Adjusted	0.991097124							
Standard	0.014165128							
Observati	57							
ANOVA								
		df	SS	MS	F	Significance F		
Regressio	1	1.25107854	1.25107854	6235.102241	2.68233E-58			
Residual	55	0.011035797	0.000200651					
Total	56	1.262114337						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	0.012945711	0.003542476	3.654424032	0.000576734	0.005846429	0.020044992	0.005846429	0.020045
X Variable	0.002026851	2.56685E-05	78.96266359	2.68233E-58	0.001975411	0.002078292	0.001975411	0.002078

Standard 3: Low range quadratic data for C₂H₂ at 1350 cm⁻¹



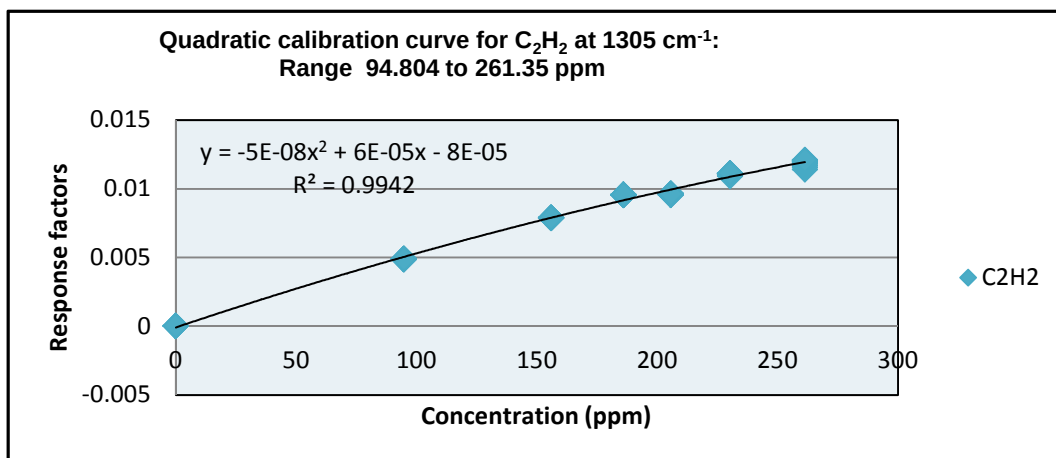
Range:0-291.265								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.997315792							
R Square	0.994638788							
Adjusted	0.994485611							
Standard	0.000260516							
Observati	73							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	0.000881389	0.000440695	6493.375032	3.34351E-80			
Residual	70	4.75078E-06	6.78684E-08					
Total	72	0.00088614						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	-7.82532E-05	0.00010815	-0.723561266	0.471746201	-0.000293952	0.000137445	-0.000293952	0.000137
X Variable	5.85184E-05	1.35324E-06	43.24304126	3.09938E-52	5.58194E-05	6.12174E-05	5.58194E-05	6.12E-05
X Variable	-4.48241E-08	4.11495E-09	-10.8929974	1.01132E-16	-5.30311E-08	-3.66171E-08	-5.30311E-08	-3.7E-08
Range:0-261.35								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.996896468							
R Square	0.993802569							
Adjusted	0.993599374							
Standard	0.000268179							
Observati	64							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	0.000703507	0.000351754	4890.893863	4.59682E-68			
Residual	61	4.38713E-06	7.19201E-08					
Total	63	0.000707894						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	-0.000108363	0.000113765	-0.952513824	0.344595642	-0.00033585	0.000119124	-0.00033585	0.000119
X Variable	5.95484E-05	1.60674E-06	37.06170789	1.54586E-43	5.63356E-05	6.27613E-05	5.63356E-05	6.28E-05
X Variable	-4.93176E-08	5.49026E-09	-8.982742916	9.15023E-13	-6.0296E-08	-3.83391E-08	-6.0296E-08	-3.8E-08

Standard 3: Low range linear data for C₂H₂ at 1305 cm⁻¹



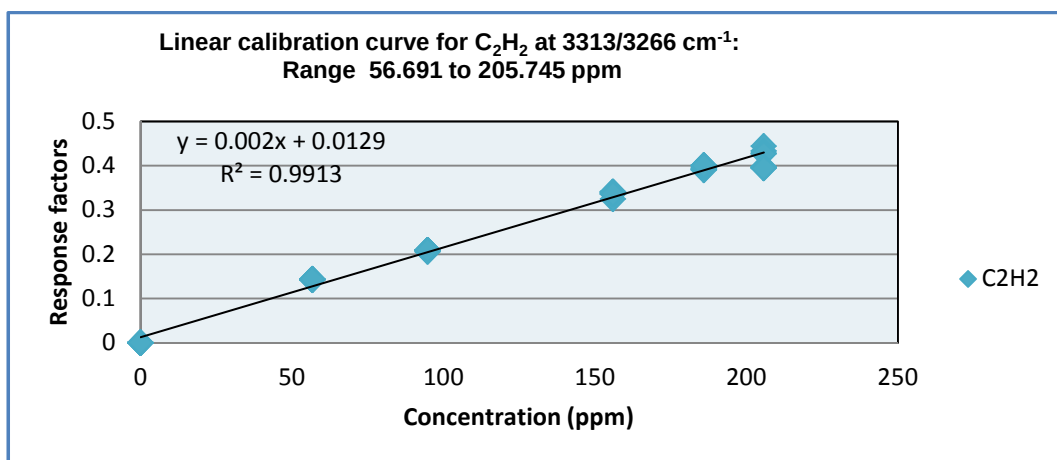
Range:0-291.265								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.993115197							
R Square	0.986277795							
Adjusted R	0.986084525							
Standard Error	0.000409223							
Observations	73							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.00085458	0.00085458	5103.095644	7.18204E-68			
Residual	71	1.18899E-05	1.67463E-07					
Total	72	0.00086647						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000720059	0.000125197	5.751395741	2.06572E-07	0.000470422	0.000969695	0.000470422	0.00097
X Variable	4.39284E-05	6.14933E-07	71.43595484	7.18204E-68	4.27022E-05	4.51545E-05	4.27022E-05	4.52E-05
Range:0-261.35								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.992976783							
R Square	0.986002892							
Adjusted R	0.985777132							
Standard Error	0.000394545							
Observations	64							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.000679867	0.000679867	4367.486425	3.42094E-59			
Residual	62	9.65126E-06	1.55666E-07					
Total	63	0.000689518						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.000563017	0.00012843	4.383830355	4.59395E-05	0.000306288	0.000819745	0.000306288	0.00082
X Variable	4.51429E-05	6.83084E-07	66.08696108	3.42094E-59	4.37775E-05	4.65084E-05	4.37775E-05	4.65E-05

Standard 3: Low range quadratic data for C₂H₂ at 1305 cm⁻¹



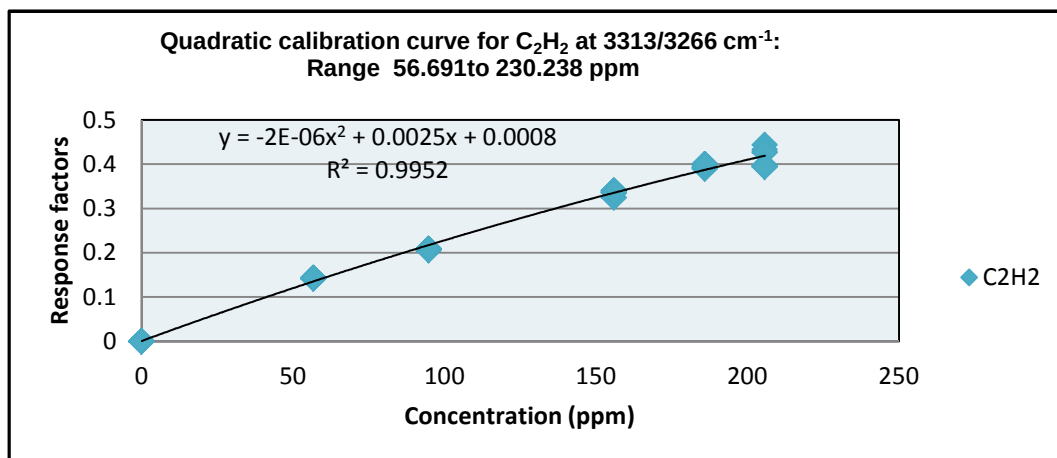
Range:0-291.265								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.99742926							
R Square	0.994865128							
Adjusted	0.994718417							
Standard	0.000252111							
Observati	73							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	0.000862021	0.000431011	6781.138366	7.38818E-81			
Residual	70	4.44921E-06	6.35602E-08					
Total	72	0.00086647						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	-4.53756E-05	0.000104661	-0.433547099	0.665950528	-0.000254116	0.000163365	-0.000254116	0.000163
X Variable	5.74918E-05	1.30959E-06	43.90063748	1.11826E-52	5.48799E-05	6.01037E-05	5.48799E-05	6.01E-05
X Variable	-4.3086E-08	3.9822E-09	-10.81965309	1.36391E-16	-5.10283E-08	-3.51438E-08	-5.10283E-08	-3.5E-08
Range:0-261.35								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.997072979							
R Square	0.994154526							
Adjusted	0.993962871							
Standard	0.00025705							
Observati	64							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	0.000685488	0.000342744	5187.21234	7.72682E-69			
Residual	61	4.03056E-06	6.60748E-08					
Total	63	0.000689518						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	-8.18934E-05	0.000109044	-0.751013406	0.455532128	-0.00029994	0.000136153	-0.00029994	0.000136
X Variable	5.87411E-05	1.54006E-06	38.14207441	2.87708E-44	5.56615E-05	6.18206E-05	5.56615E-05	6.18E-05
X Variable	-4.85358E-08	5.26242E-09	-9.223110461	3.58022E-13	-5.90587E-08	-3.8013E-08	-5.90587E-08	-3.8E-08

Standard 3: Low range linear data for C₂H₂ at 3313/3266 cm⁻¹ with internal standard



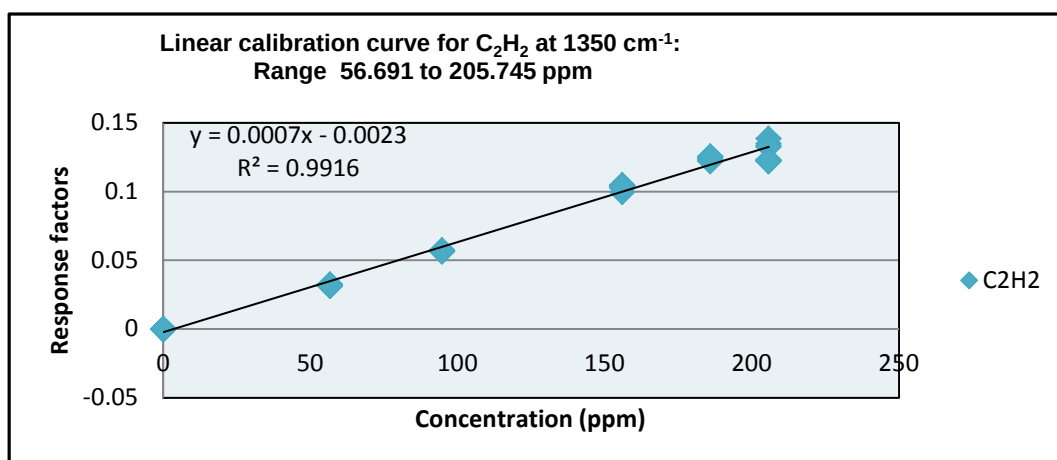
Range:0-230.238								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.99617305							
R Square	0.992360746							
Adjusted R Square	0.992241382							
Standard Error	0.014039891							
Observations	66							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	1.638800346	1.638800346	8313.781135	1.80468E-69			
Residual	64	0.012615586	0.000197119					
Total	65	1.651415932						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.013855922	0.003398537	4.07702548	0.000128463	0.007066564	0.02064528	0.007066564	0.020645
X Variable	0.002013821	2.20862E-05	91.17993822	1.80468E-69	0.001969699	0.002057944	0.001969699	0.002058
Range:0-205.745								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.995618453							
R Square	0.991256104							
Adjusted R Square	0.991097124							
Standard Error	0.014165128							
Observations	57							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	1.25107854	1.25107854	6235.102241	2.68233E-58			
Residual	55	0.011035797	0.000200651					
Total	56	1.262114337						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.012945711	0.003542476	3.654424032	0.000576734	0.005846429	0.020044992	0.005846429	0.020045
X Variable	0.002026851	2.56685E-05	78.96266359	2.68233E-58	0.001975411	0.002078292	0.001975411	0.002078

Standard 3: Low range quadratic data for C₂H₂ at 3313/3266 cm⁻¹ with internal standard



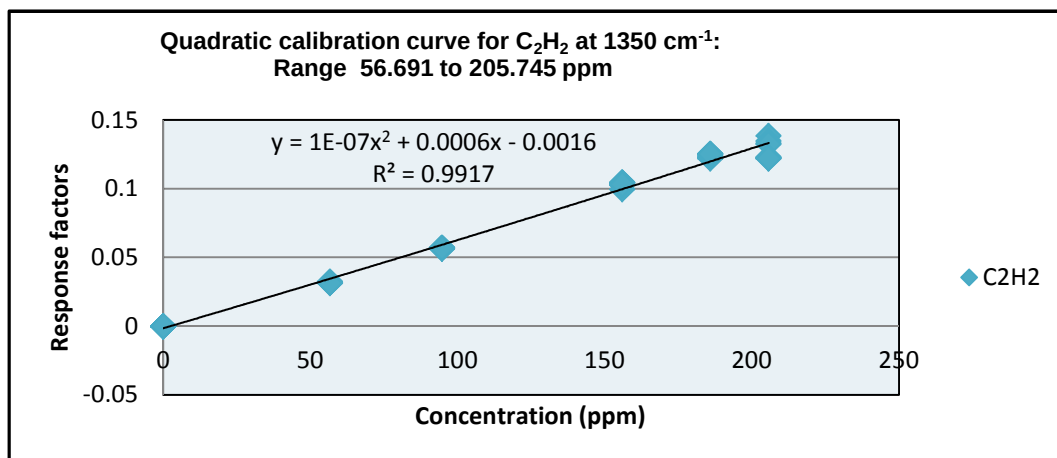
Range:0-230.238								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.99741317							
R Square	0.994833032							
Adjusted	0.994669002							
Standard E	0.011637932							
Observati	66							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	1.642883119	0.82144156	6064.919021	9.26672E-73			
Residual	63	0.008532813	0.000135441					
Total	65	1.651415932						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	0.002738763	0.003469311	0.789425523	0.432824423	-0.004194103	0.009671629	-0.004194103	0.009672
X Variable	0.002383721	6.98155E-05	34.14313573	2.35885E-42	0.002244205	0.002523236	0.002244205	0.002523
X Variable	-1.60036E-06	2.91484E-07	-5.490372449	7.64412E-07	-2.18284E-06	-1.01787E-06	-2.18284E-06	-1E-06
Range:0-205.745								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.997588708							
R Square	0.99518323							
Adjusted	0.995004831							
Standard E	0.010610367							
Observati	57							
ANOVA								
	df	SS	MS	F	Significance F			
Regressio	2	1.256035023	0.628017511	5578.416173	2.719E-63			
Residual	54	0.006079314	0.00011258					
Total	56	1.262114337						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	0.000777122	0.003225571	0.240925289	0.810525443	-0.005689759	0.007244002	-0.005689759	0.007244
X Variable	0.002499359	7.37619E-05	33.88416076	4.56278E-38	0.002351476	0.002647243	0.002351476	0.002647
X Variable	-2.26523E-06	3.41393E-07	-6.635235672	1.61015E-08	-2.94968E-06	-1.58077E-06	-2.94968E-06	-1.6E-06

Standard 3: Low range linear data for C₂H₂ at 1350 cm⁻¹ with internal standard



Range:0-230.238								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.996420453							
R Square	0.992853719							
Adjusted	0.992742059							
Standard	0.004450818							
Observati	66							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.17614278	0.17614278	8891.707591	2.13415E-70			
Residual	64	0.001267826	1.98098E-05					
Total	65	0.177410606						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	-0.002611383	0.001077378	-2.423831865	0.018194373	-0.004763693	-0.000459073	-0.004763693	-0.00046
X Variable	0.000660223	7.00161E-06	94.2958514	2.13415E-70	0.000646235	0.00067421	0.000646235	0.000674
Range:0-205.745								
SUMMARY OUTPUT								
Regression Statistics								
Multiple F	0.995801132							
R Square	0.991619895							
Adjusted	0.99146753							
Standard	0.004484473							
Observati	57							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0.13088243	0.13088243	6508.163771	8.33504E-59			
Residual	55	0.001106078	2.01105E-05					
Total	56	0.131988507						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	pper 95.0%
Intercept	-0.002286511	0.001121496	-2.038803182	0.046287699	-0.00453404	-3.89814E-05	-0.00453404	-3.9E-05
X Variable	0.000655572	8.12627E-06	80.67319116	8.34E-59	0.000639286	0.000671857	0.000639286	0.000672

Standard 3: Low range quadratic data for C₂H₂ at 1350 cm⁻¹ with internal standard



Range:0-230.238								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.996392807							
R Square	0.992798625							
Adjusted R Square	0.992566323							
Standard Error	0.004444891							
Observations	65							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	0.168872757	0.084436378	4273.733503	3.80083E-67			
Residual	62	0.001224937	1.97571E-05					
Total	64	0.170097694						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-0.001652326	0.001388153	-1.190305055	0.238464267	-0.004427204	0.001122553	-0.004427204	0.001122553
X Variable 1	0.000625632	2.73799E-05	22.85005442	6.76113E-32	0.000570901	0.000680364	0.000570901	0.000680364
X Variable 2	1.51997E-07	1.13161E-07	1.343191383	0.184106234	-7.42089E-08	3.78203E-07	-7.42089E-08	3.78203E-07
Range:0-205.745								
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.995861869							
R Square	0.991740861							
Adjusted R Square	0.991434967							
Standard Error	0.004493022							
Observations	57							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	2	0.130898396	0.065449198	3242.106026	5.71793E-57			
Residual	54	0.001090111	2.01872E-05					
Total	56	0.131988507						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-0.001595868	0.001365887	-1.168374937	0.247787979	-0.004334306	0.00114257	-0.004334306	0.00114257
X Variable 1	0.000628754	3.12349E-05	20.12985852	9.12358E-27	0.000566132	0.000691376	0.000566132	0.000691376
X Variable 2	1.28566E-07	1.44565E-07	0.889326696	0.377772294	-1.6127E-07	4.18401E-07	-1.6127E-07	4.18401E-07