

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AIR SAMPLES BY INFRARED
SPECTROSCOPIC ANALYSIS OF SORBENT TUBE SAMPLES

by

Craig A. Lampert

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Thesis Committee:

Dr. Ngee Sing Chong, Chair

Dr. Chengshan Wang

Dr. Keying Ding

Dedication

I dedicate this research to all of my family members, and anyone who had a hand in becoming who I am today.

ACKNOWLEDGMENTS

I would like to thank my wife, Karen, for accepting my time away from her, my children, Breanne and Aaron who inspire me daily, Dr. Chong for all his patience in instilling in me the knowledge and passion of analytical chemistry, both Dr. Chengshan Wang and Dr. Keying Ding for graciously serving as my thesis committee members, Dr. Jane Smoot for her guidance, Mandy Burns for keeping me on track, MTSU and everyone who helped me with completing this thesis in any capacity.

ABSTRACT

Volatile organic compounds (VOCs) have typically been analyzed using gas chromatography/mass spectrometry (GC/MS), which offers low detection limits and high specificity in identifying compound structures. FTIR has the advantage of being high speed, internally calibrated, as well as sensitive for analyte detection down to parts-per-billion levels. FTIR also makes it possible to analyze multiple components simultaneously by spectral deconvolution. Preconcentration with a sorbent tube is prescribed by the EPA method and offers a better option for environmental samples because the concentrations of analytes tend to be significantly lower in the ambient air than industrial emission sources. The research goal of this project is to develop a method for analyzing low molecular weight VOCs with the use of sorbent tube technology in conjunction with a Varian 7000 FTIR. For future work, the technology developed through this research can be combined with remotely controlled sampling modes to facilitate airborne sampling at high altitudes or near industrial emission stacks.

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CHAPTER ONE

Introduction

Volatile organic compounds (VOCs) are a class of compounds that have come under close scrutiny from environmental agencies. There are various working definitions of VOCs given by major environmental agencies. The United Nations Economic Council for Europe (UNECE) defines VOCs as “non-naturally occurring organic compounds with photochemical ozone creation potential (POCP).”¹ Where POCP refers to the likelihood of VOCs, except methane, to create ozone in the environment via secondary reactions. The United States Environmental Protection Agency (EPA) defines VOCs as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate participates in atmospheric photochemical reactions.”² Methane, carbon monoxide and carbonates are not included because these compounds do not react to form ozone under atmospheric conditions. Currently the EPA recognizes VOCs as compounds that react with nitrogen oxides in the presence of sunlight in the atmosphere to form tropospheric ozone. The table below (Table 1) describes how VOCs are defined by The World Health Organization. The World Health Organization (WHO) defines VOCs as organic compounds with boiling points in the range of 50-260 °C.

Table 1. The WHO classification of VOC's and organic compounds based on boiling points³

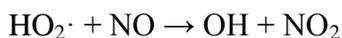
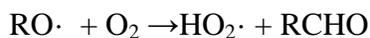
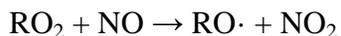
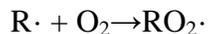
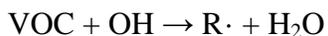
Description	Abbreviation	Boiling point range
Very Volatile organic compounds	VVOC	<50 °C
Volatile organic compounds	VOC	50 °C -260 °C
Semi-Volatile organic compounds	SVOC	240 °C -380 °C
Particle-bound organic matter	POM	> 380 °C

WHO describes VOCs as essentially “composed of aromatic hydrocarbons, aldehydes, ketones, alkanes, cycloalkanes, alkenes, alkynes, and polycyclic aromatic hydrocarbons.”³ Regardless of the definition, VOCs tend to be the class of chemicals that are in the forefront of environmental issues because of their potential toxicity and adverse impact on human health. Furthermore, ozone produced by a series of reactions initiated by the oxidation of VOCs or CO by the hydroxyl radical (OH) may be linked to asthma and respiratory problems.

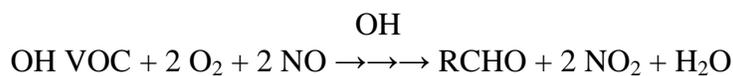
VOCs are involved in the formation of ozone. In general, the oxidation of VOCs, which ultimately forms photochemical ozone, can be shown by the following series of mechanisms (Figure 1), where *RH* represents generic hydrocarbons or VOCs, *R* is a

hydrocarbon radical, $h\nu$ represents photons from sunlight, and M is a nonreactive, energy-absorbing third body.⁴

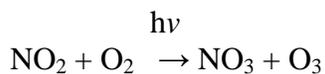
SIMPLIFIED EXAMPLE



OVERALL



COMBINED WITH



YIELDS

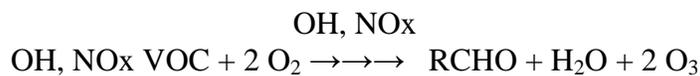


Figure 1. A Mechanism of generation of O₃ by VOCs

With the passage of the Clean Air Act in 1990, many more hazardous air pollutants (HAPs) have been routinely monitored and their emission rates measured. Traditional methods of analysis are described by the EPA and include many methods (see Table 2 below).⁵ The use of Gas Chromatography (GC) coupled to Mass Spectrophotometry (MS), which is commonly referred to as GC-MS, has been

established for years and GC-MS methods are well known for the analysis of both polar and non-polar compounds. Most of the methods recommend the use of GC-MS or GC in the analysis. An example is EPA Method 18 in which the “VOCs of a gas mixture are separated by gas chromatography (GC) and quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles”.⁶ This method, while effective for analyzing VOCs, is cumbersome and requires standards for quantitative calibration by GC columns with appropriate phases. The method is complicated for most users and, according to the description in the method, “should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.”⁷ Many of the EPA methods are complex and expensive to implement because they require a multitude of chemical standards for quantitative calibration.

Implementation of methodologies associated with the analysis of VOCs in the United States has fallen under the regulation of two government agencies. Industrial hygiene monitoring of workers’ exposure to chemical vapors is required and regulated by Occupational Safety and Health Administration (OSHA). OSHA’s responsibility is “to assure safe and healthful conditions for working men and women by setting and enforcing standards and providing training, outreach, education and compliance assistance”⁸. OSHA is responsible for monitoring how workers are protected and setting limits for how much exposure is tolerated. The two sampling periods for which OSHA define exposures are related to the short term exposure limits (STELs), which is normally

5-15 minutes of human exposures to air toxicants, and threshold weighted averages (TWA), which is based on an 8-hour period of exposure. The EPA assumes responsibility for developing and approving the methods used in environmental analysis. The EPA test methods are different from OSHA because the VOCs being investigated in the ambient environment are at significantly lower concentrations than those of the VOCs inside buildings. This accounts for the considerable differences in methods of analysis for VOCs. A common method of sampling chemical exposures at workplace entails having a worker carry around a sampling pump to draw workplace air samples across sorbent-based collection media for the desired sampling period. The media used are typically materials that adsorb the target compounds and can be used with solvent extraction or thermal desorption procedures for analyzing VOCs with GC-MS at the end of the sampling period.

A detailed analytical method for air samples includes the description of procedures as well as the accessories or materials, flow rates, analyte extraction methods, and limits of detection associated with the sampling or analysis. OSHA has procedures with details on how the worker should be monitored for exposure to chemicals. An example for this type of monitoring is the sampling of methanol. OSHA's Method No. 91 is designed to analyze methanol samples at the 200-250 parts per million (ppm) level depending on contact. "A sample is collected by drawing air through two Anasorb 747 sampling tubes connected in series. The samples are desorbed with a carbon disulfide/dimethyl formamide solution and analyzed by gas chromatography with flame ionization detection (FID)."⁹ This method is applicable to the sampling and analysis of a wide range of compounds.

The EPA has many methods to evaluate VOCs but for analysis of VOCs in ambient air there are two primary methods, namely TO14A (formally TO14) and TO-15. TO-14A targets non-polar compounds through the use of a Nafion dryer, and allows the use of either GC/FID or GC/MSD. TO-14 method was revised in 1997 as the TO-14A method; to target another 40 VOCs.¹⁰ TO-15 is currently applicable to a subset of the 97 VOCs which are from the list of 189 hazardous air pollutants (HAPs) included in Title III of the Clean Air Amendments. “Method TO-15 is based on GC-MS and does not provide the option for a different detector such as FID, electron capture detector (ECD), photoionization detector (PID), or a multi-detector arrangement as specified in TO-14A.”¹¹ It should be noted that TO-14 and TO-15 are designed to be complementary to each other (see Table 2). The TO-15 method analyzes more compounds, both polar and non-polar VOCs. When an expanded analyte list is needed (especially for polar compounds), the TO-15 method is chosen and requires the collection of samples using special canisters. Quality control parameters and method performance criteria for acceptance of data are specified in TO-15 method. “The TO-14 method could be used in situations when the screening of analytes can be achieved with non-specific GC detectors that are less expensive than GC-MS and when only a sub-set of non-polar analytes are to be measured.”¹² The differences between TO-14A and TO-15 are given in Table 2.

Table 2. Comparison of TO-14A and TO-15

Method Specifications	TO-14a	TO-15
Non-Polar VOC's (e.g., toluene, benzene, Freons)	√	√
Polar VOC's (eg.,methanol, alcohol's, ketone)		√
GC/MS Instrumentation	√	√
Sample collection by prepared canister (holding time=30d)	√	√
Sample collection by sorbent tube	√	√
Waste management techniques (avoid loss of polar compounds)		√
Enhanced provision for quality control		√
Method performance provisions		√
Selected Ion Monitoring (SIM)		√
Specific Cleaning procedures		√
Air sample concentrated onto solid sorbent trap	√	√
Use of other detectors for GC	√	
Detection Limit 0.2 – 25 ppbv	√	√

Choice of the sampling methods should be based upon the target analyte in question. Two general sampling approaches are available. The silica-lined canister and the multi-bed sorbent tubes are the methods discussed in the EPA TO-14A and TO-15 methods for collection and transporting ambient air samples. Canisters are silica-lined to keep the VOCs in sample from reacting at the walls of the canister. “Canisters with a 6-liter capacity are preferred when the samples are to be analyzed by different methods or in replicates by taking multiple samples of different volumes from the same canister.

Canister sampling is performed in two modes: grab sampling or time integrated sampling. Samples can be collected either on sub-atmospheric (passive) pressure or pressurized (active) with pump.”¹²

In contrast, sorbent tubes are used when the concentrations of the target VOCs are very low and analyte preconcentration by collecting air samples over extended period is necessary. Both the EPA and OSHA have approved methods based on collection of VOCs on sorbent media. There are many types of sorbent tubes having unique properties suited for the sampling of particular types of the analytes. The extraction of VOCs from the sorbent tubes can be achieved by using a solvent extraction or thermal desorption. One of the attractive features of sorbent tube sampling is the sample after collection can be readily transported back to the laboratory and the analytes extracted for GC analysis or thermally desorbed for FTIR analysis. An example of a traditional multiple bed sorbent tube is shown in Figure 2.

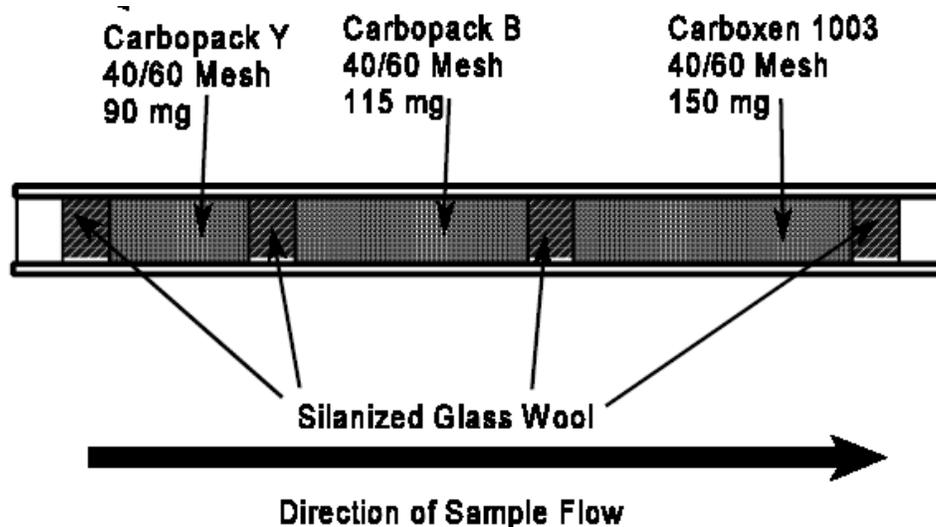


Figure 2. An example of a multi bed sorbent tube using Carbopack Y, B and Carboxen 1003¹³

Sorbent tube analysis is approved by both OSHA and National Institute of Health and Safety. Sorbent tubes can be made of glass or metal but the glass types are smaller in size. Sorbent tubes should be chosen based upon the characteristics of the target analytes. Numerous sorbents are available for the preconcentration of compounds of different molecular weights, boiling points, and polarity. Numerous types of sorbent tubes are available from companies such as SKC, and Supelco. The most common types are molecular sieves and activated charcoal. Activated charcoal offers a vast surface area to enhance the probability of capturing the VOCs. Multi-bed sorbent tubes are typically loaded with several sorbents with the weakest sorbent contacting the analyte molecules first followed by the strongest sorbent downstream. As in the above example, Carbopak Y, B, and Carboxen are all products of Sigma Aldrich. SKC offers Anasorb GCB1/2 and Anasorb 347. Other sorbent manufacturers include Markes and Camsco. Below is a list of types of sorbent and the analytes that would be targeted (Table 3).

Table 3. Comparison of sorbent types, particle mesh size, analyte size, and adsorbent materials

Description	Mesh Size	Analyte Size	ADSORBENT TYPE
Carbopack B	60-80	C ₅ -C ₁₂	Graphitized carbon black
Carbopack Y	20-40	C ₁₂ -C ₂₀	Carbon molecular sieve
Carbopack C	80-100	C ₈ -C ₂₀	Graphitized carbon black
Carbosieve S-III	60-80	C ₁ -C ₂	Carbon molecular sieve
Anasorb GCB1	20-40	C ₅ -C ₁₂	Graphitized carbon black
Anasorb GCB2	20-40	C ₁₂ -C ₂₀	Graphitized carbon black
Anasorb 347	20-45	C ₂ -C ₅	Carbon molecular sieve

Sorbent tubes have been shown to be capable of achieving detection limits in the ppb range (Method 17 EPA) or even in the parts-per-trillion (ppt) levels for extended sampling periods.

An issue of concern for sorbent-based analysis is the quantity of water vapor in the sample. Since both the analytical techniques of GC and FTIR are adversely affected by the presence of even small amounts of water, it is necessary to reduce the water and the CO₂ levels prior to the analysis of VOCs. This can be done with water traps specifically designed to reduce the amount of water vapor that gets into the testing instrument. TO-14 mandates the use of a Nafion dryer specifically to reduce the amount of water collected. Nafion is a sulfonated tetrafluoroethylene copolymer that allows the preferential removal of water molecules from the sample stream. Nafion's unique ionic properties stems from incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone.

Although GC is the main method for analysis of VOCs, Fourier Transform Infrared (FTIR) spectrometry is also useful for both qualitative and quantitative analysis of gaseous samples. The FTIR technique measures the absorption of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample and quantify the concentrations of specific analytes. Different functional groups absorb characteristic frequencies of IR radiation. Samples of FTIR spectrometry can be gaseous, liquid, and solid samples when implemented with the appropriate sampling accessories.¹⁴

FTIR can also be used in the following analytical applications:

1. Identification of all types of organic and many types of inorganic compound
Determination of functional groups in organic materials
2. Determination of the molecular composition of surfaces
3. Identification of chromatographic effluents
4. Quantitative determination of compounds in mixtures
5. Determination of molecular conformation (structural isomers) and stereochemistry (geometric isomers)
6. Determination of molecular orientation (polymers and solutions)¹⁴

The infrared radiation is emitted from a radiation emitting source (see Figure 3). The light energy proceeds to the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer. The IR beam generated passes through an aperture, which regulates the amount of energy. When the beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample. This is where photons with specific wavelengths or frequencies of energy, which are uniquely characteristic of the sample, are absorbed by the analytes. The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the interferogram signals. The measured signal is digitized and sent to the computer where the Fourier transformation takes place.

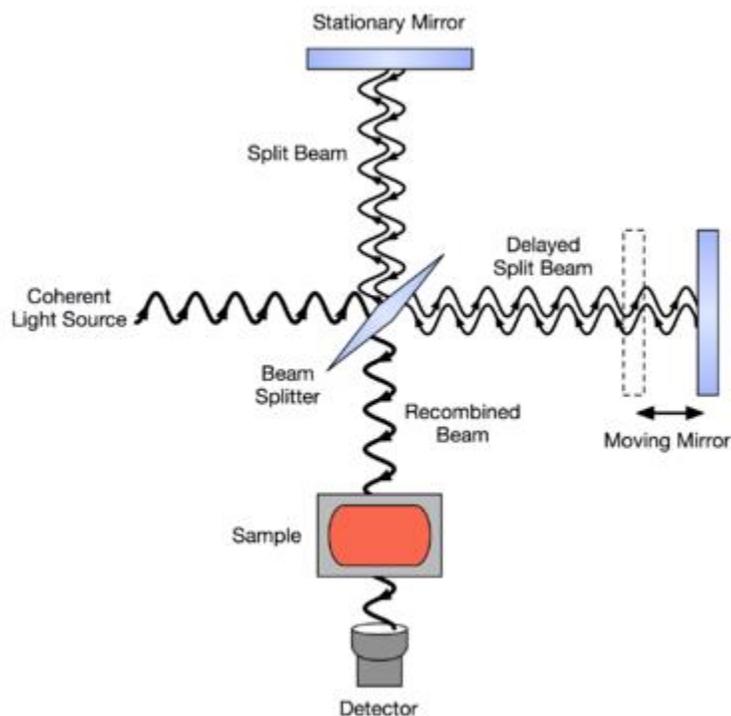
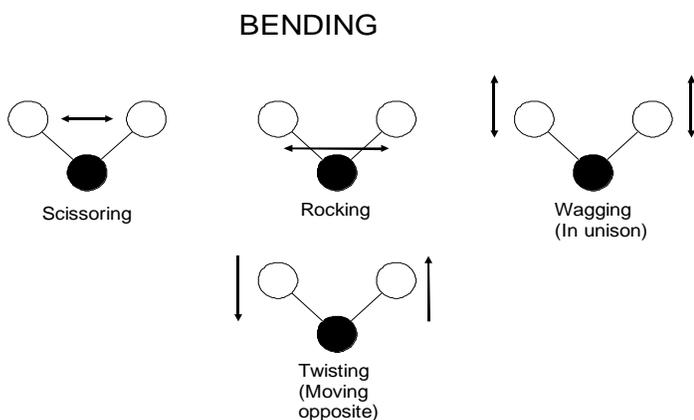


Figure 3. Schematic of an FTIR spectrometer showing the major instrumental components¹⁵

FTIR spectrometry coupled with sorbent tube technology is a powerful analytical technique. It can be used to analyze many VOCs in gas samples. The EPA has validated methods that give good results for VOCs present at the sub-ppm levels when used according to their guidelines. The infrared spectral libraries that are constantly being updated greatly facilitate the use of the FTIR method for the analysis of VOCs. The benefits of FTIR are now becoming increasingly known. The EPA has developed two methods that use the FTIR spectroscopy. When an FTIR spectrometer is in conjunction with a long pathlength gas cell, samples with VOCs can be analyzed in the gas cell of 1-100 meter pathlength via the so-called extractive FTIR method. In addition, special FTIR spectrometers can be used to analyze samples at the site of the emission source based on

the open-path FTIR method where the IR beam traverses a large distance (i.e. 100 meter to 1 km) to probe the composition of air in real time analysis.

IR Spectroscopy probes the characteristic vibrational frequencies of covalent bonds of IR-active compounds. Two regions of interest are the “C-H” stretching at mode 2970 cm^{-1} where all organic compounds absorb infrared energy, and the fingerprint region from 1800 cm^{-1} to 650 cm^{-1} where differences in molecular structures can be distinguished. Each infrared absorbance signal or spectral peak corresponds to a specific vibrational motion or modes in FTIR spectroscopy. The two major types of vibrational motions are stretching and bending.



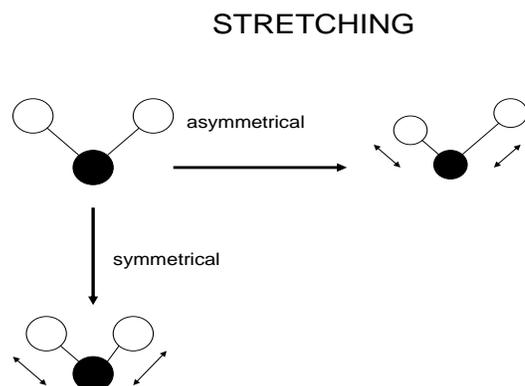


Figure 4. Vibrational modes of organic compounds

A molecule of N atoms has $3N-6$ vibrational modes for a non-linear molecule, or $3N-5$ modes for a linear molecule. For example, a non-linear molecule with a total of 4 atoms can have a total of 6 vibrational modes. Homonuclear diatomics like N_2 and O_2 are not IR-active because they do not have a dipole moment. Other heteronuclear diatomics like HCl and CO can generate an IR spectral peak because these compounds can generate a dipole moment in their vibrational modes. In practice, spectra do not normally show a peak for each $3N-6$ vibrational mode. This is due to reasons such as spectrometer limitations, molecular symmetry, additive or subtractive modes of the fundamental vibrations and spectroscopic selection rules. In IR spectroscopy, the number of vibrational modes can be calculated using the formulas given above and these vibrational modes have unique names such as stretching (both symmetrical and asymmetrical), scissoring, rocking, wagging, and twisting. These types of motion are bond-specific and characteristic of all compounds as long as their bonded atoms show a dipole moment. Therefore, FTIR spectra are unique for each compound and help identify compounds via

the fingerprint region of $650\text{-}1800\text{ cm}^{-1}$ of the IR spectra. Below is a chart (Table 4) that shows vibrational frequencies associated with specific bonds of compounds.

Traditionally GC and variable detectors have been used for air analysis. It is the goal of this research project to develop a TD-FTIR method that offers high sensitivity, longer storage time, lower analysis and operating cost, mobile collection and in some cases analysis, and more rapid analysis times. FTIR quantitative analysis relies on widely available spectral reference libraries so that reagent standardization is not necessary.

Table 4. Characteristic IR band frequencies¹⁶

Functional Groups	Compound Types	Frequency Range (cm ⁻¹)
C-H	Alkanes	2960-2850(s) stretch 1470-1350(v) scissoring and bending
	CH ₃ Umbrella Deformation	1380(m-w) - Doublet - isopropyl, <i>t</i> -butyl
C-H	Alkenes	3080-3020(m) stretch 1000-675(s) bend
C-H	Aromatic rings	3100-3000 (m) stretch
	Phenyl Ring Substitution Bands	870-675 (s) bend
	Phenyl Ring Substitution Overtones	2000-1600(w) - fingerprint region
C=C	Alkenes	1680-1640(m,w) stretch
C≡C	Alkynes	2260-2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch
C-O	Alcohols, Ethers, Carboxylic acids, Esters	1260-1000(s) stretch
C=O	Aldehydes, Ketones, Carboxylic acids, Esters	1760-1670(s) stretch
O-H	Monomeric -- Alcohols, Phenols Hydrogen-bonded -- Alcohols, Phenols Carboxylic Acids	3640-3160(s,br) stretch 3600-3200 (b) stretch 3000-2500 (b) stretch
N-H	Amines	3500-3300 (m) stretch 1650-1580 (m) bend
C-N	Amines	1340-1020 (m) bend
C≡N	Nitriles	2260-2220 (v) stretch
NO ₂	Nitro Compounds	1660-1500(s) asymmetrical stretch 1390-1260(s) symmetrical stretch

CHAPTER TWO

Materials and Methods

Preparation of a Multi-component Gas Standards

I. A six-liter SilcoCan[™] canister (Restek, Bellefonte, PA) was evacuated with a RV-5 Edwards vacuum pump to a minimum of $-28''$ Hg and then filled with ultra-high purity (UHP) nitrogen to 15 pounds per square inch gauge pressure (psig). This cleaning process was repeated 2 more times. On the third time, the canister was pressurized with UHP nitrogen to 15 psig and placed in a Restek 110 V canister heating jacket (Restek, Bellefonte, PA) and heated to 150°C for 10 minutes. The canister was then evacuated then filled and with N_2 at least two more times. The canister was removed from the heating jacket and when being cooled, 2 more cycles of purging and evacuating is done. The last step was evacuating the canister to at least $-28''$ Hg on the differential pressure gauge.

II. The standard mixture was made by injecting into the canister a $1\text{-}\mu\text{l}$ sample of each component with a Hamilton $10\ \mu\text{l}$ fixed needle syringe (Hamilton, Reno NE). Each component was injected through a septum at the top of the 6-liter canister that had been previously evacuated to at least $-28''$ Hg. The canister was then pressurized to 25 psig with UHP N_2 gas. The standard concentrations of the target compounds were calculated according to the ideal gas law. Usually, $1\ \mu\text{l}$ of any organic compound in liquid state will give a concentration of 5 to 15 parts per million depending on its molar mass and density.

FTIR Analysis of Gas Standards

For analysis, 50 ml aliquot samples are transferred into the 10-meter gas cell using a 50-ml Hamilton gas-tight syringe. To obtain a linear response data set, five 50-ml samples were added successively to the gas cell followed by infrared absorbance measurements of the 50 ml, 100 ml, 150 ml, 200 ml, and 250 ml samples. Since the canister was pressurized, the valve needed only to be opened to allow the gas sample to pass into the syringe, which was then used to inject the sample into the gas cell via the inlet septum. Care was taken to keep the gas syringe clear of pieces of the septum that may be cut out from the needle and slow or completely block the migration of the sample.

Sorbent Tube and Sorbent Tube Preparation

The preconcentration of the samples was accomplished with the use of sorbent tubes. The Carbotrap™ 300 sorbent tubes were purchased from Supelco (currently Sigma Aldrich) contained a three-layer adsorbent bed consisting of Carbosieve S-III and Carbotrap B&C (Table 3). Carbosieve S-III is a carbon molecular sieve with a 60-80 mesh size. It has a moderate affinity for water and an average pore size of 15-40 Angstroms and a large surface area of 975m²/g for adsorbing low molecular weight VOCs. The other two components of the sorbent tube are called Carbotrap™ B&C, which are graphitized carbon black that is generally non-porous and suited for sorptive interactions depending solely on London dispersion forces. Carbotrap™ B has a surface area of 100m²/and the C form has a 10m²/g surface area. One particular characteristic of Carbotrap is the 20/40-mesh size. Ultimately, a 3-bed sorbent tube provides the analyst a

platform to collect many different types of organics. Carbosieve S-III is specific for C2-C5, Carbotrap B is specific for C5-C12 and Carbotrap C is best suited for C12-C20 sizes so each section of the sorbent tube is an adsorbent material that is specific for collection of a particular class of hydrocarbons or organic compounds according to molecular weight. Before preconcentration or adsorption of the analyte, the sorbent tube must be conditioned and cleaned. This is accomplished by heating it to 230°C by the Watlow heating unit while it is purged with N₂. This is necessary because the affinity of the sorbent for moisture together with CO₂ is high, and the infrared spectra of these compounds overlap the region of all organic analytes. When the sorbent tube is sufficiently cooled (i.e. 15-25°C), a sample of N₂ is run through the instrument and collected into the cell. If the CO₂, H₂O, and any trace organics are significantly low then the sorbent tube is ready to be used.

FTIR Analysis of Thermally Desorbed Samples

Analysis of low carbon number VOCs was accomplished using a Varian 7000 FTIR spectrometer. The sample is injected into the 6-liter canister evacuated to approximately -30" Hg via a septum and then pressurized to 15 psig being transferred into an evacuated 1-liter stainless steel canister (Restek, Bellefonte, PA). The mixed sample was allowed to flow through a sorbent tube at a rate of 40 mL/min. The tank was then again pressurized to 10 psig and allowed to move across the sorbent tube again for about 20 more minutes. The sample was then thermally desorbed at 204 °C with a Watlow Model WU-89002-06 heat controller in which the sorbent tube was inserted into the metal heating block. Once the desired temperature was reached, N₂ was used to

desorb the pre-concentrated analytes into the Cyclone C-10 (Specac London, UK) gas cell and pressurized to 15 psig. In order to check for percent recovery of analytes, the sample was also injected directly into the Specac Cyclone C-10 gas cell through a septum at the cell inlet and then analyzed by the FTIR spectrometer and the spectra obtained.

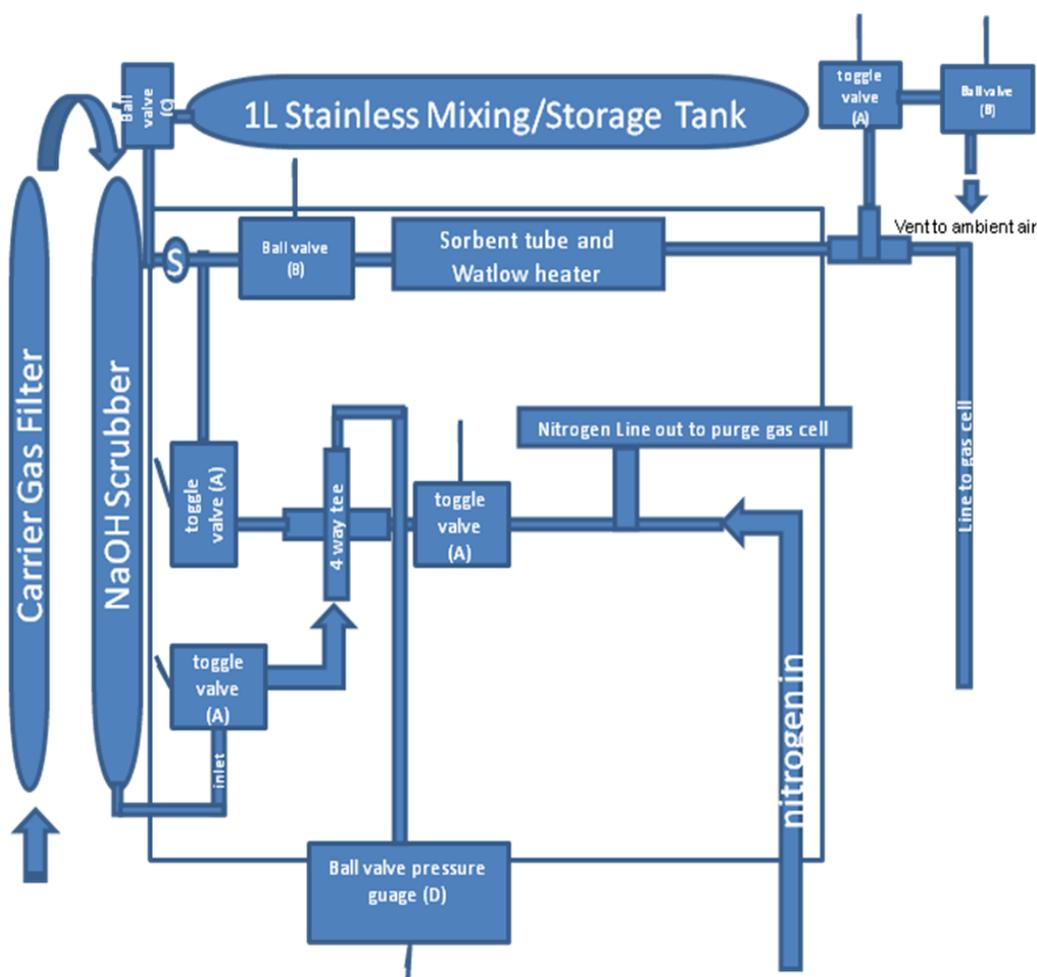


Figure 5. Schematic of the setup for analyte sorption followed by thermal desorption into an FTIR gas cell



Figure 6. Photo of the setup for the sorption and thermal desorption of analytes

CHAPTER THREE

Results

The analysis of VOCs is accomplished primarily with the thermal desorption of VOCs preconcentrated on sorbent tubes into a 10-meter gas cell for FTIR analysis. The set-up is intended to reduce the loss of analyte gases in order to provide a method that maximizes the percent recovery of analytes without the need to deconvolve the spectra from other spectral bands from water vapor and carbon dioxide. Good results were finally obtained with changes mentioned above. The final instrument (Figure 6) with respect to this paper is shown above. Yields of 50%-60% were obtained against standards and these can be increased as well with small changes. Numerous types of analytes can be investigated by TD-FTIR but the types of compounds are dependent on their vapor pressure, molecular size, and vibrational motion.

Five components were used in the research of this paper. Methanol, acetone, carbon tetrachloride, methylene chloride, and chloroform were chosen because of the low molecular size and vapor pressure. This made them ideal for the sorbent tube chosen and the temperatures and pressures utilized. For assessing the analytical parameters of the sorbent-based FTIR method, methanol, acetone, and methylene chloride were the primary analytes.

The EPA database has available spectra that show target compound peaks in low humidity environments. Since methanol, methylene chloride, and acetone all have identifying peaks associated with their vibrational modes, we looked at the fingerprint regions somewhere between 600 to 1800 cm^{-1} .

Infrared Absorption Spectra of VOCs

In Figure 7 below, the EPA has IR spectra readily available. This figure has acetone/methylene chloride, and methanol overlaid onto one spectra. Methanol has 2 IR peaks associated with its molecular structure in the range we were investigating. The peaks we are using for identification is a strong peak at around 1030 cm^{-1} for the CH_3 rock. There is also a peak at 1380 cm^{-1} for the CH_3 umbrella deformation. (Figure 7)

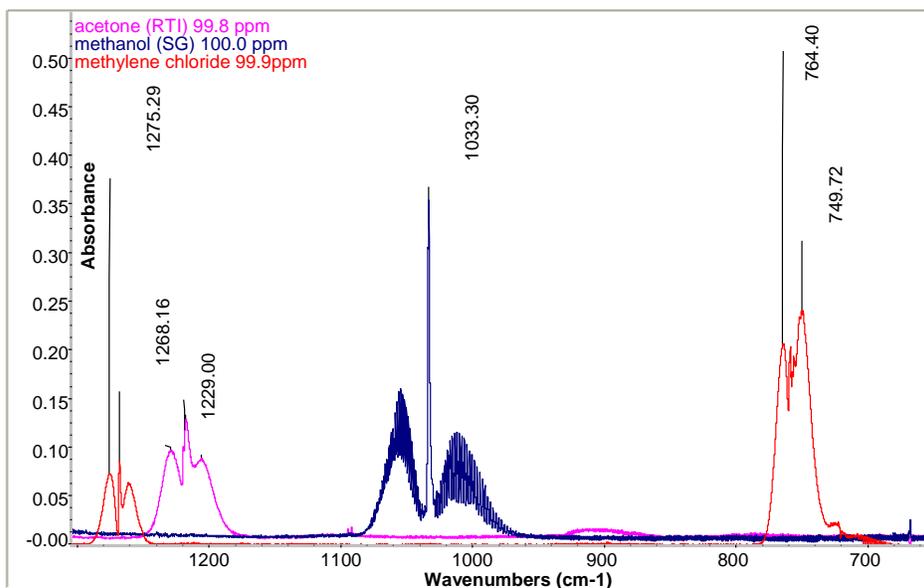


Figure 7. An overlay of acetone, methanol, and methylene chloride and the IR identifying peaks¹⁷

In the range of $600\text{-}1800\text{ cm}^{-1}$, Acetone has 3 peaks of interest, one is from the CO double bond at 1715 cm^{-1} that is typical of ketones, a peak at 1380 cm^{-1} for the CH_3 umbrella deformation, and a peak at 1230 cm^{-1} for the C-C stretching. (Figure 9). As For Methylene Chloride the vibrational modes reviewed occur at 1250 cm^{-1} is due to wagging

of the H-C-H bonds. The final peak is at 1850 cm^{-1} for the C-Cl asymmetric stretching and C-Cl symmetric stretch is 771 cm^{-1} . (Figure 9)

Good results were obtained with refinement of the instrument and the addition of organic and water filters. Five samples of varying concentrations (50,100,150,250,250 ml). The three samples can be seen in the fingerprint regions

Linearity of the Results

The first instrument made offered very little linearity of the sample data. Indeed the analyzed data showed very little reproducibility with respect sample sizes. As discussed earlier much of this problem was due to leakage through the system, recondensation of the sample into the Tedlar lines throughout the system, and the manner in which the sample was collected. Initially Tedlar bags were used to make samples for analysis. The bags have septa on valves that allow both a sample to be injected into the bag and the flow of gas into the bag started or stopped. This was a good starting platform, in particular because many environmental samples are collected into these bags and therefore the samples could be brought back to the lab and introduced into the instrument directly. Unfortunately, the samples were not always so easily analyzed. The bags had tendencies to get creases that would lead to leaks. In addition, placing a known amount of N_2 inside the bag for mixing purpose was difficult to monitor. Another problem was complete cleaning of these bags were difficult to accomplish and any remaining gas would be sampled with the next analysis. Ultimately, it was found that for samples acquired in the field could be analyzed in this manner, standards and samples were best

prepared and stored in the 6-L stainless steel canisters for subsequent GC/MS analysis.

The standardizations of methylene chloride and methanol can be seen below (Figures 8,9)

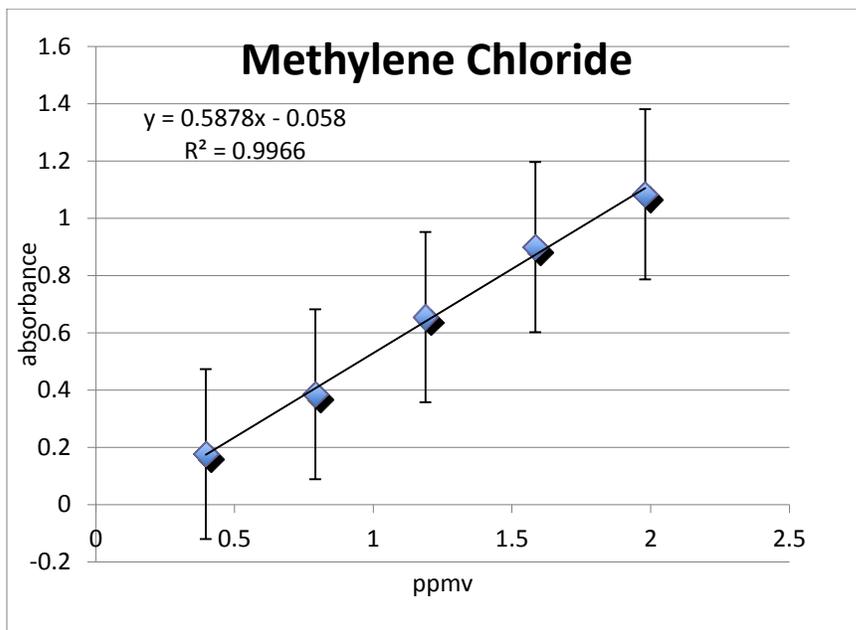


Figure 8. Linearity of methylene chloride in a multicomponent sample

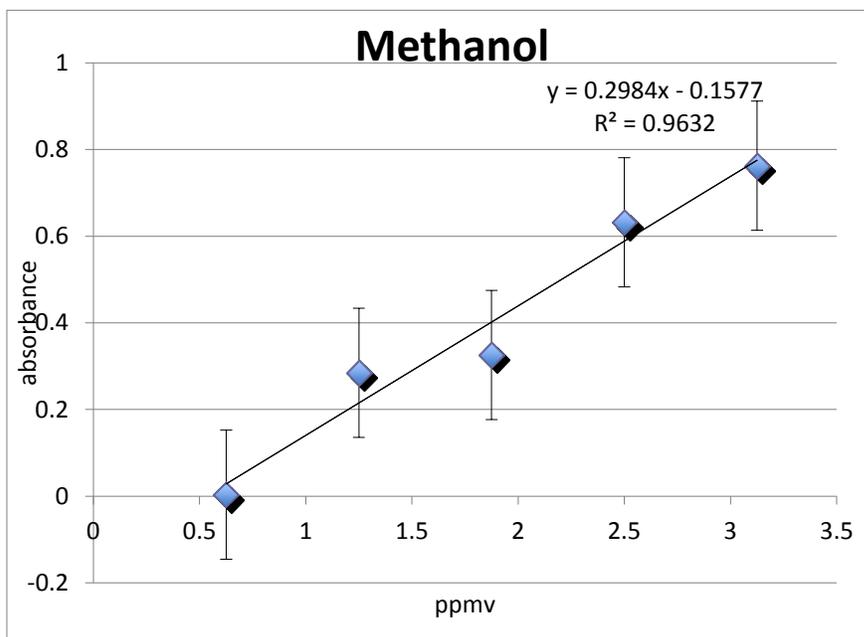


Figure 9. Linearity of methanol in a multicomponent sample

The following tables (Tables 5,6,7) show the current configurations ability to analyze the target compounds by comparing the target analytes by the TD-FTIR method or the direct analysis in the 10-meter gas cell. Target analytes were acetone, methanol, and methylene chloride. Exactly 1.0 μ l of each was placed in a 6-liter canister and pressurized to 25 psig with N_2 . For this research, all the target analytes are single carbon compounds. It has been shown in articles that molecular size is of concern because the sorbent inside the tube is specifically designed to collect small organics. Tables (5,6,7) show the percent recovery of the samples obtained during a sample run.

Table 5. Comparison of percent recovery of methanol directly into the cell and through the instrument

Sample size (ml)	Thermal Desorption	Directly into Cell	% Recovery
50	0.0346	0.0455	76
100	0.2324	0.1015	229
150	0.2186	0.1750	125
200	0.5339	0.2428	220
250	0.6208	0.3511	177

Table 6. Comparison of percent recovery of methylene chloride directly into the cell and through the instrument

Sample size (ml)	Thermal Desorption	Directly into Cell	% Recovery
50	0.1814	0.3650	50
100	0.3991	0.7156	56
150	0.6319	1.0709	59
200	0.8433	1.488	57
250	1.0224	1.7697	58

Table 7. Comparison of percent recovery of acetone directly into the cell and through the instrument

Sample size (ml)	Thermal Desorption	Directly into Cell	% Recovery
50	0.0808	0.1221	50
100	0.1362	0.2792	56
150	0.2709	0.4503	59
200	0.3672	0.6138	57
250	0.4272	0.7922	58

It is interesting to note here that the percentage of methanol is greater than 100%. It is believed that this is due to the breakdown of the sorbent material and the pyrolysis of the carbon in the sorbent material into methanol.

Variations and Limitations to Results

During analysis care must be taken to reduce the spectra overlap of the analytes. This technique offers the ability to look at 5-10 compounds simultaneously as there is no major overlap in the spectra. This indicates that the choice of analytes is limited to materials that don't interfere with other target compounds, if FTIR is used to characterize complex mixtures. This situation is further compromised due to contaminants in the system such as water and carbon dioxide as discussed above. There is a significant amount of papers written on the problem and the dealing with water vapor and CO₂. Our primary strategy was to use traps, which worked relatively well (Figure 17).

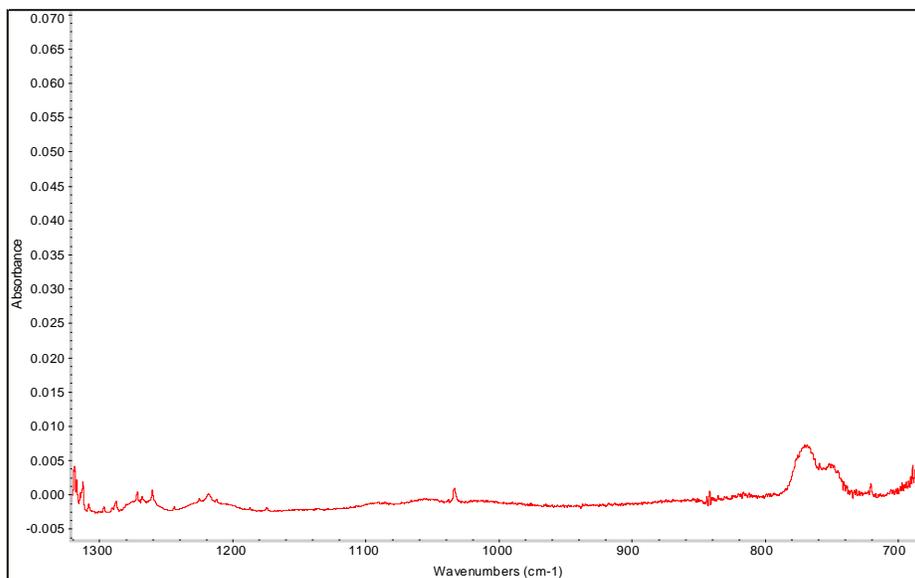


Figure 10. 50 ml sample through the instrument

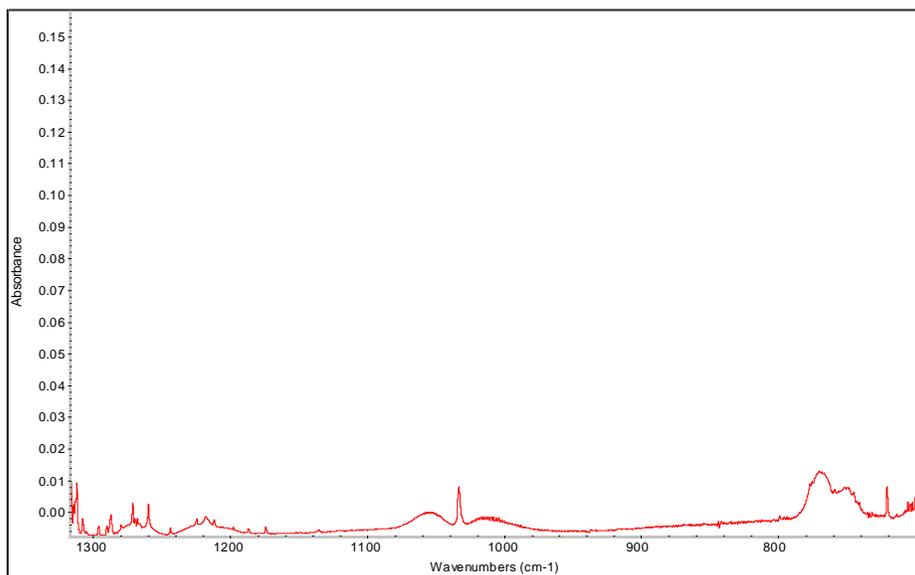


Figure 11. 100 ml sample through the instrument

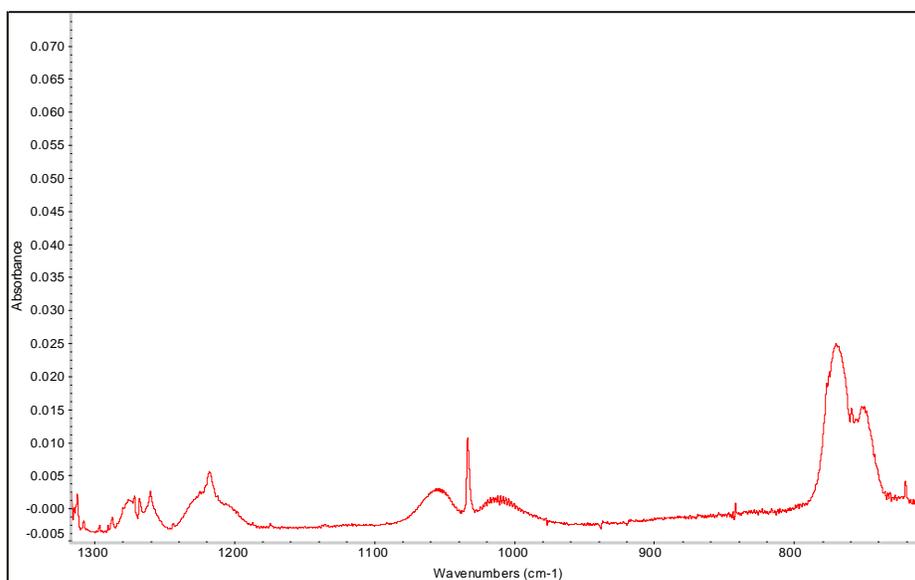


Figure 12. 150 ml sample directly into the cell and through the instrument

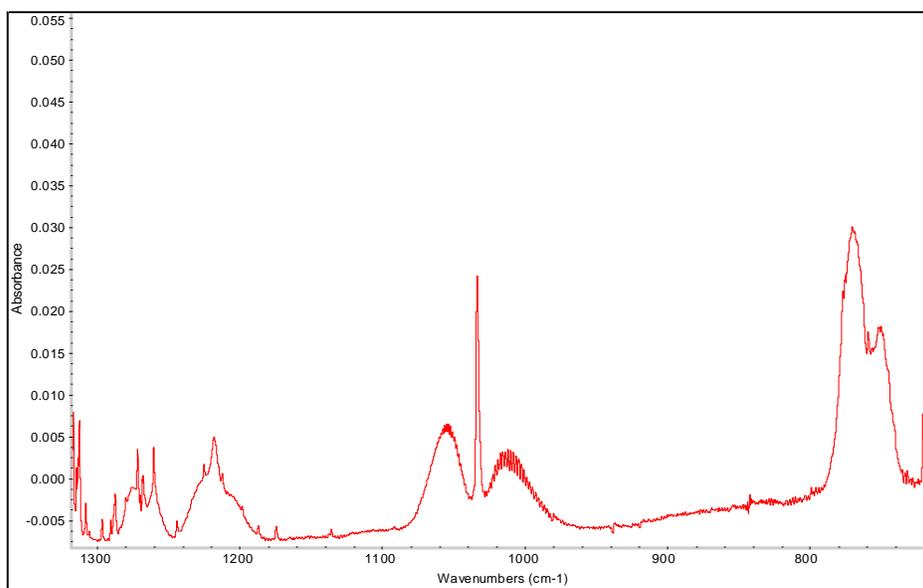


Figure 13. 200 ml sample directly into the cell and through the instrument

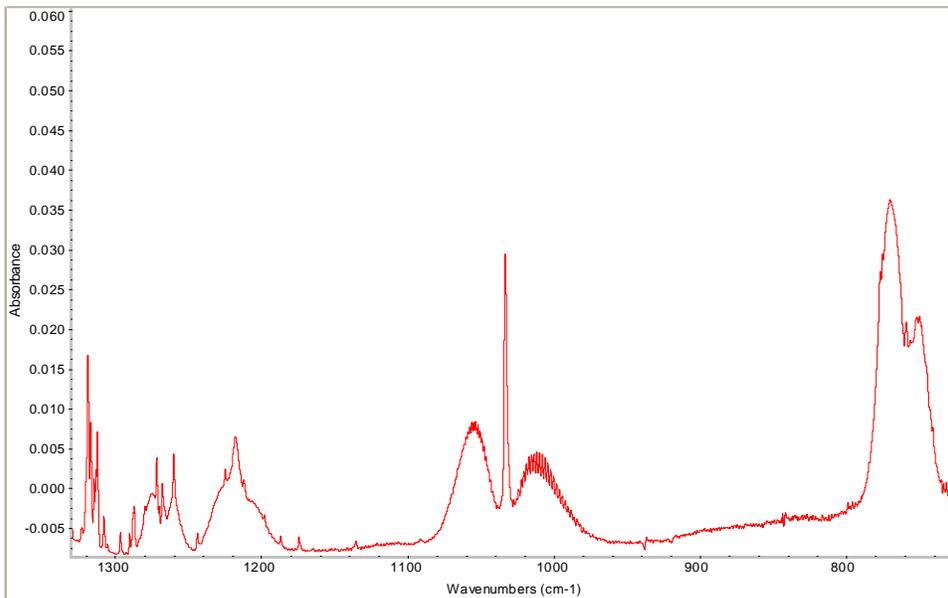


Figure 14. 250 ml sample directly into the cell and through the instrument

Many standard infrared spectra from public domain or commercial spectral libraries can be used by researchers for both qualitative and quantitative analysis. This gives a great deal of information to the analyst in knowing what to look for. A potential problem however is the overlap of the spectra of each individual component. Overlap of infrared spectral features from different compounds limits the ability to analyze a large number of components in one sample simultaneously. Typically, 5-10 compounds are the maximum number of components that can be reliably determined without spectral deconvolution. In infrared spectroscopy, there are two particular regions to look at. The quantitation of the total hydrocarbons is associated with the 2900-3080 cm^{-1} spectral region. All organic compounds have the characteristic carbon-hydrogen bond stretching mode at this wavenumber. To further identify a compound, one would rely on the fingerprint region from 1800 cm^{-1} to the 600 cm^{-1} . The National Institute of Standards

and Technology has compiled spectra of numerous compounds that have unique infrared spectral bands for both qualitative and quantitative gas phase analysis.

Reproducibility

As mentioned earlier with the first instrument reproducibility was a major problem. There were times when only a 30% yield was collected and other times much greater. After the system had been set up differently much more regular samples were collected. (Figure 15,16)

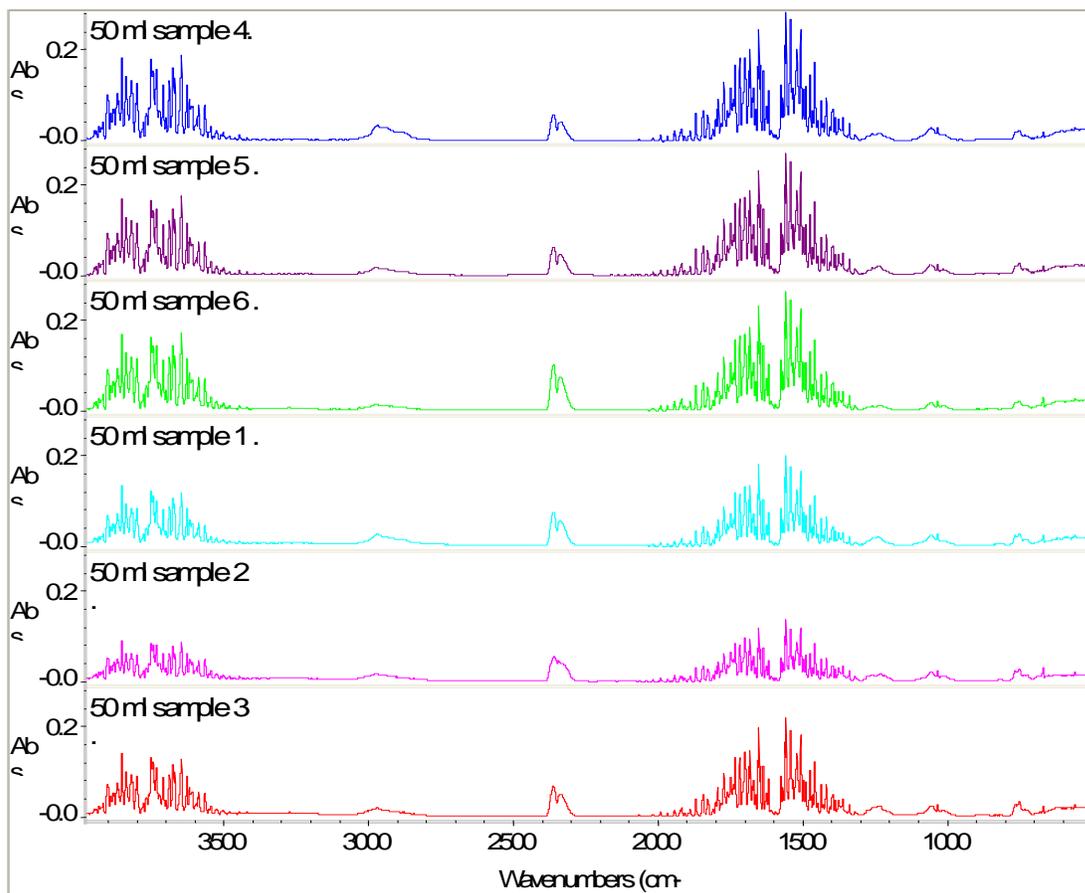


Figure 15. Six separate 50 ml samples taken on the same day

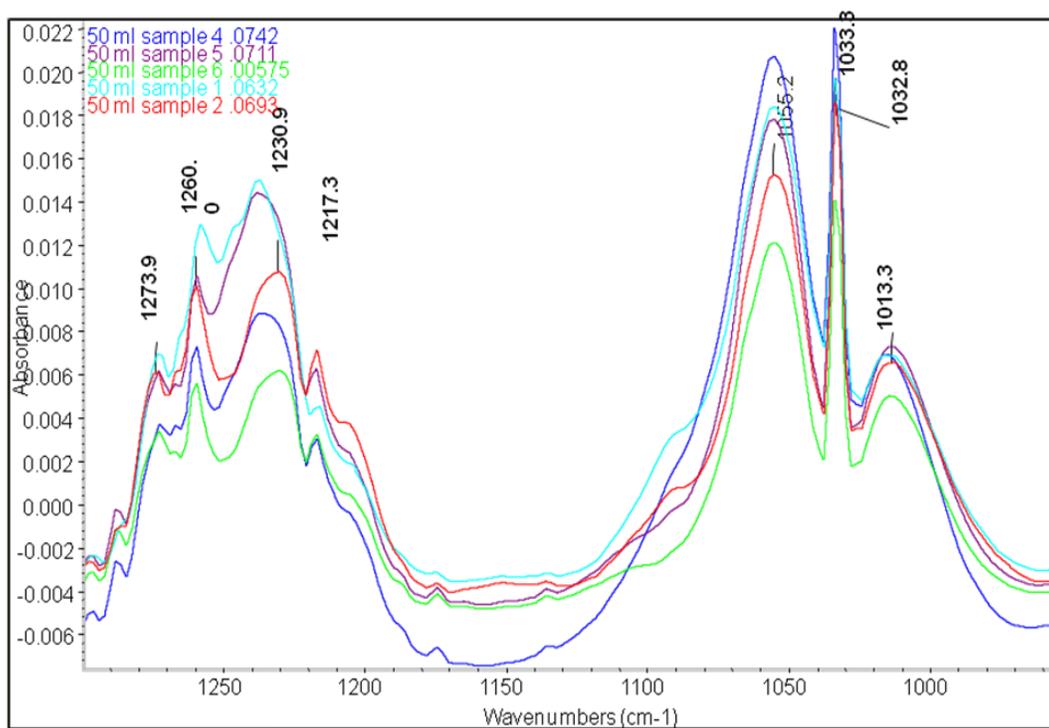


Figure 16. A close up of the comparison of 5 of the 6 methanol peaks associated with the Figure 15 along with the calculated peak area

Susceptibility to Interference by H₂O and CO₂

When the analysis was carried out, it is necessary to reduce the levels of H₂O and CO₂ in the cell prior to FTIR analysis. Much of the sampling was done in a room that had many other instruments in it and because of this there were inherent problems with the analysis. Of particular concern was the repetitive appearance of large amounts of H₂O and CO₂ in the analysis and many times the samples did not show the same amounts even when they were run right after another. Peaks generated from the analysis are much easier to see when little or no H₂O and CO₂ are not present. This is a particular concern when the analyte peak lies in the same region as the non-analyte gases.

Techniques for Reducing Water Vapor and CO₂ Interference

The reason of this problem is that the Varian 7000 has gaps inside the instrument. Humidity and any other atmospheric gases can seep into the instrument between the light source and the detector. In addition, other machinery is likely generating some of the gases. This is not only an issue with respect to this machine, but also to an environment that cannot control the climate. Reduction of these components can be accomplished with in line water and CO₂ traps. Supelco (and other companies) make both water and organic traps that can reduce the water vapor and organics coming from the sample itself, however as already mentioned there are areas in the instrument that cannot be reduced to zero for concentrations of those materials. The standards listed above were accomplished in low humidity environments. The sensitivity of the instrument is very good and therefore any moisture or organics will interfere with the target spectra.

CHAPTER FOUR

Discussion

Trace analysis of organic compounds with less than 5 carbon atoms were achieved with sorbent tube pre-concentration of analytes, which were subsequently thermally desorbed and analyzed with a FTIR. The sorbent tubes were effective for low concentration samples at the levels of a few ppm or lower and have been shown to be very effective for capturing a wide multitude of compounds. Methanol could be analyzed at levels as low as 1250 ppb, 792 ppb for methylene chloride and as small as 692 ppb were analyzed, for acetone. As mentioned above the sorbent tubes used were filled with Carbosieve S-III, and Carbopak B&C. These sorbents are very good at analyzing carbon compounds of C1 to C5 but many other compounds can be investigated. Sorbents are rapidly becoming more versatile in the analysis of the number of compounds that can be analyzed and the increasing numbers of techniques. Sorbent tubes are useful in air sampling scenarios for determining workplace air quality and in the ambient atmosphere.

Sorbent tubes are versatile, while still primarily for organics; there is a broad number of sorbent materials for different applications. While only carbon molecular sieves and graphitized carbon black sorbents were used in this research, many other types are available such as activated coconut charcoal, polymers coated adsorbents, glass beads. Tubes can also be made specific for specific analytes. Multiple bed sorbent tubes can investigate many compounds at one time. Methanol was found to have a recovery of greater than 100%. This is due to the breakdown of the sorbent tube. It was seen that the

thermal desorption setup has a recovery almost 60% for both methylene chloride and acetone.

In the tables below (Tables 8-12) the comparison of the analytes are shown from being directly injected into the cell and collected and sampled through the instrument.

Table 8. Comparison of the fingerprint region of a 50ml sample containing methanol, methylene chloride, and acetone

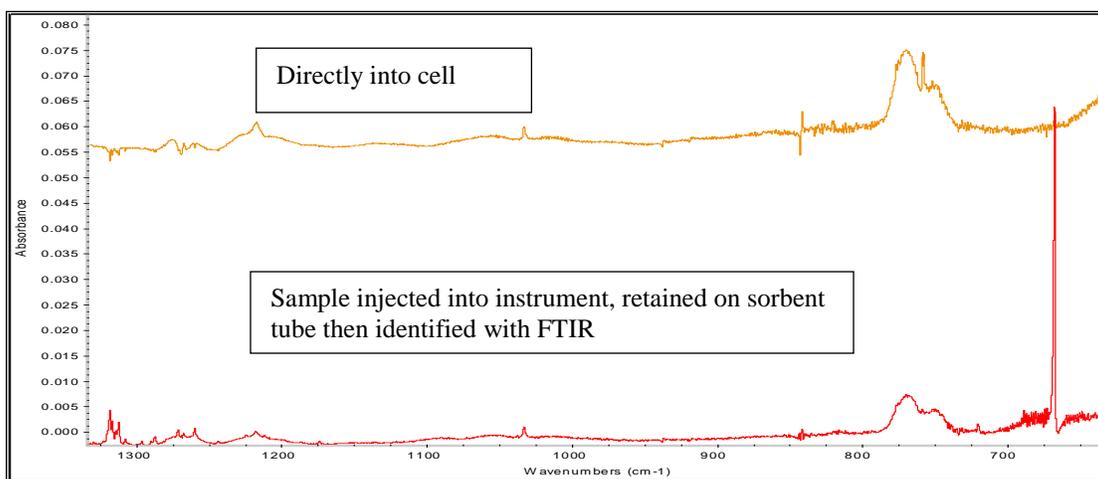


Table 9. Comparison of the fingerprint region of a 100ml sample containing methanol, methylene chloride, and acetone

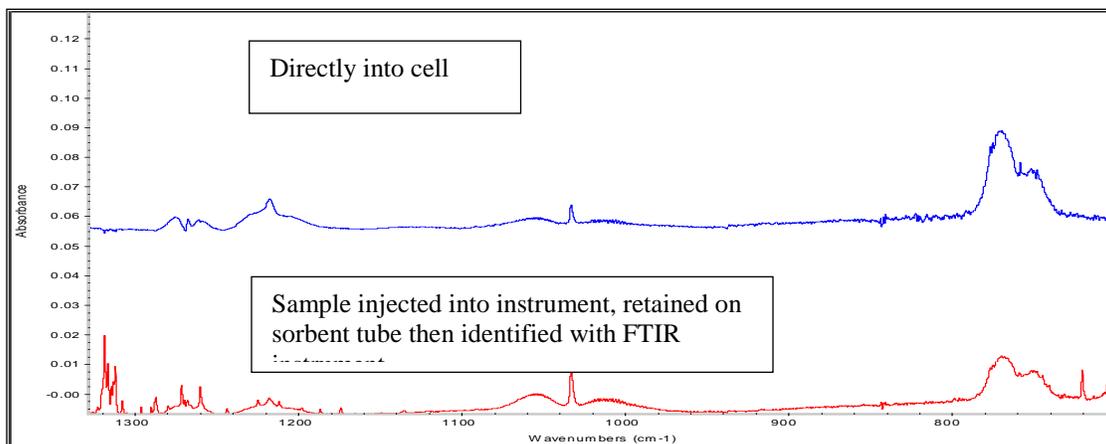


Table 10. Comparison of the fingerprint region of a 150ml sample containing methanol, methylene chloride, and acetone

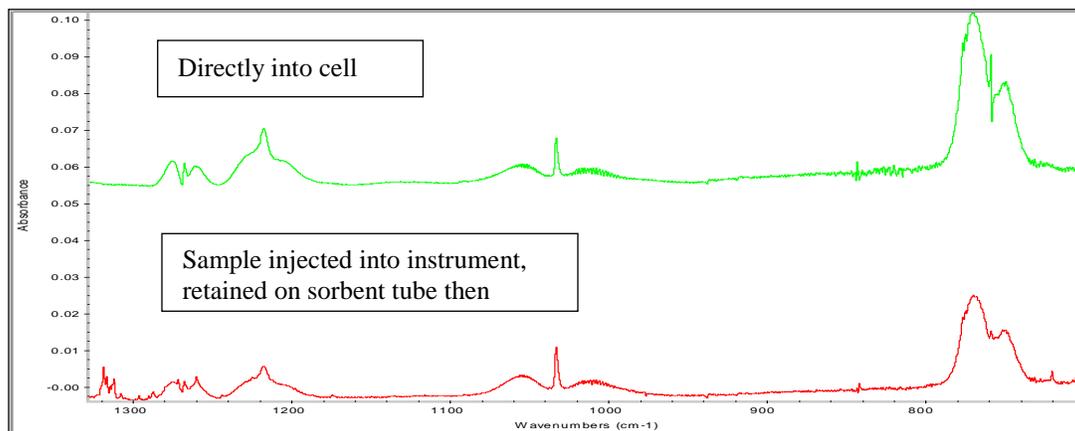


Table 11. Comparison of the fingerprint region of a 200 ml sample containing methanol, methylene chloride, and acetone

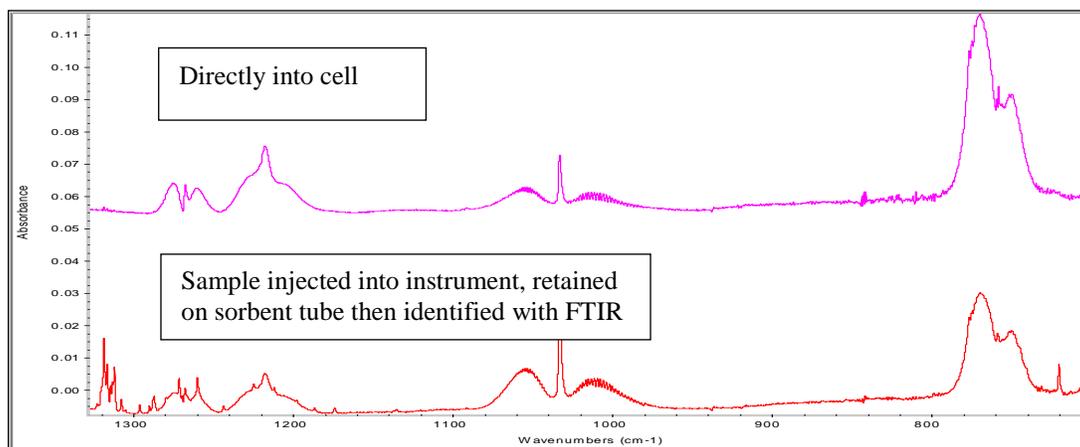
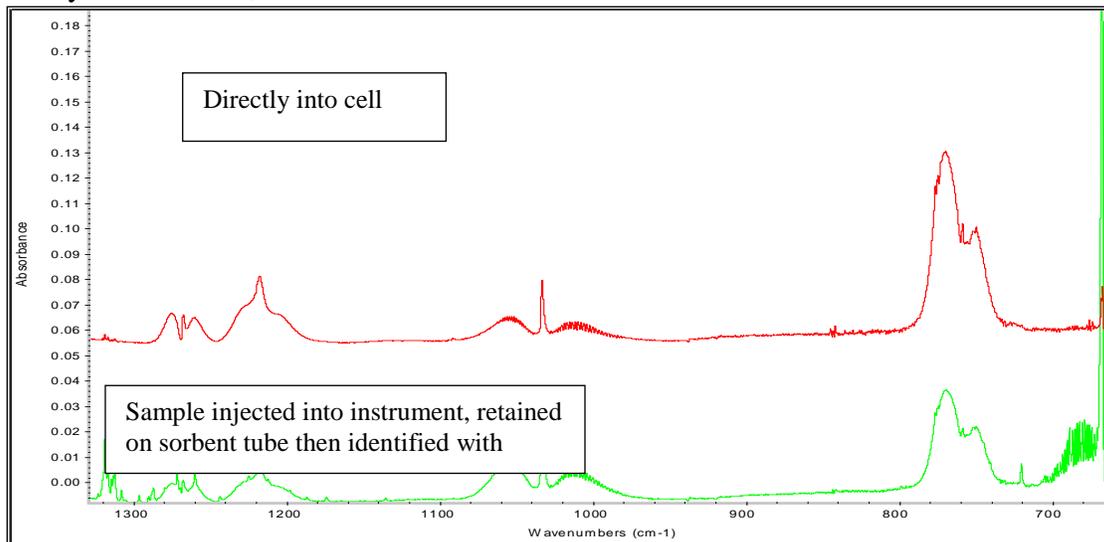


Table 12. Comparison of the fingerprint region of a 250 ml sample containing methanol, methylene chloride, and acetone



What is unique with respect to this research is implementing sorbent tubes along with FTIR as the analytical method. Sorbent tubes are used in many applications. SKC offers numerous methods with the sorbent tubes as the primary analyte collection device as well as Sigma Aldrich and Marks and other producers. The EPA test method TO 15 and TO 17 can be used for both Methanol and acetone to the low ppbv levels, depending on whether it's a workplace (TO 17) sample or in ambient air (TO 15). The EPA method uses a Summa canister. NIOSH list method 1300, and 2555 for collection of acetone. ASTM (American Society for Testing and Materials) D 5197 also has a method for analysis of acetone. All three methods use sorbent tubes to collect and retain the sample. FTIR is not the analytical technique of choice at this point, however TO 16 uses an open path monitoring but no sample is acquired for analysis. FTIR's offer the capacity for quick analysis time, high sensitivity, and low hazardous waste generation.

Possibilities for Remote Sampling

The use of this technique can be used in conjunction with other technologies to give a versatile tool to analyze small organics. A small remote sampler has also been built that collects a limited sample size (limited to the size of the tank attached). This setup is designed to be used in conjunction with a Tedlar balloon. (Figure 20 and 21) What is not known is just how many applications this technique can be implemented into. There are a significant amount of remote vehicles available and the true limiting factor is the weight of the system itself. It's already been mentioned that the system is very capable of being lightened significantly. In addition, the simplicity of the system is its biggest strength. In its current configuration it is capable of analyzing a myriad of sample, with minor modifications. It can be used in many different applications as well, because trace gas analysis is popular now with current research on CO₂ and other environmental issues. This research in addition to others will give more choices with respect to analytical techniques



Figure 17. Helium filled Neoprene balloon attached to a remote sampling device

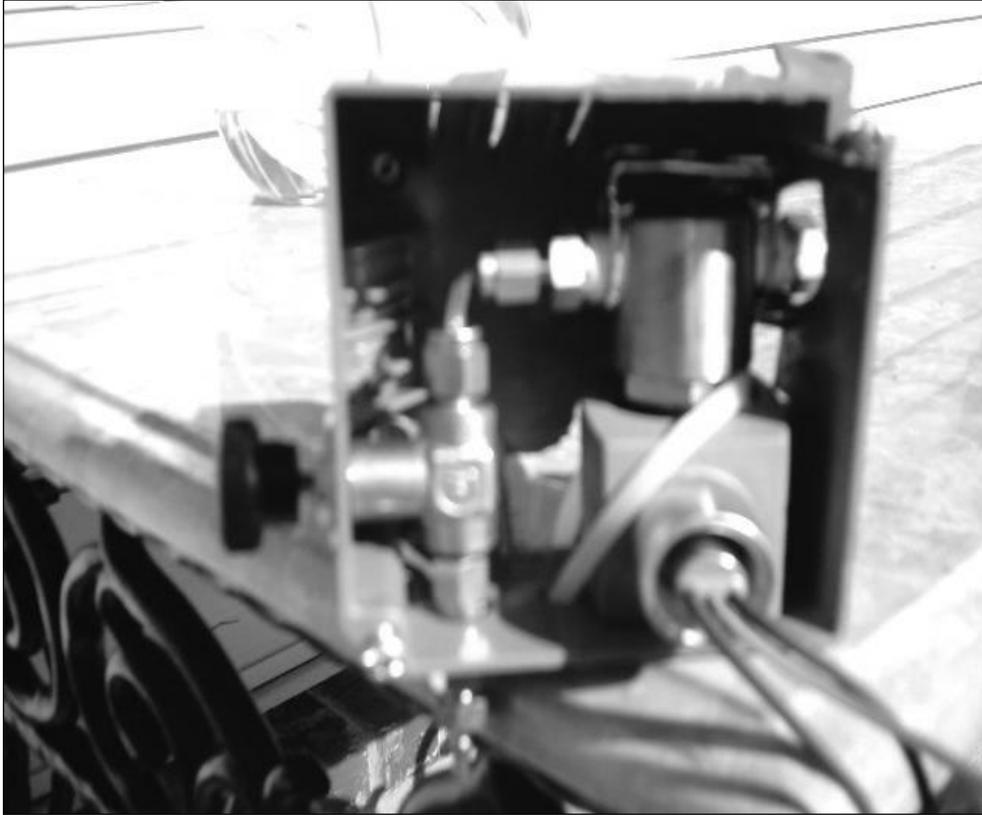


Figure 18. A close up of the internal components of the remote sample

A list of the components used in the manufacture of the remote sampling device is listed below with a measured weight of each component used in the current system.

584 gms

Solenoid



620 gms

1L Stainless tank



87 gms

Needle Valve



Neoprene Balloon

204 gms



Brass fittings

60 gms



Electrical wire

200 gms

Figure 19. Component list and weights of the component in the remote sampling device

These components can be made with smaller components with a wireless solenoid placed in the system to allow for sampling. A radio controller can be placed on other types of remote vehicles and used in many other applications, including stack emission analysis, mine gas analysis, sewer systems, or many other applications that the gases could be hazardous to people. The system shown is a device that uses power only to trigger the solenoid. The actual collection of sample is done through the tank having a negative pressure with respect to the surroundings. The sample area and the flow can be regulated with a flow controller. The collection is passive but a system could be made to collect the sample with a more regulated method including pumps. For this system, a balloon with Helium was used as the lifting force. In order to know the amount of Helium that was needed for lifting force was calculated by using this general calculation (below). The Lifting weight of helium is 28.2 gms/feet³. So to calculate lifting force all that is necessary is to calculate the volume of the balloon and multiply by the lifting force of helium. In addition the balloons shape is assumed to be a sphere and while this isn't completely accurate it is a reasonable assumption with respect to this research.

For a balloon with a diameter of 20 feet:

$$10\text{ft} * 10\text{ft} * 10\text{ft} * 3.14 * 4/3 = 4,186 \text{ feet}^3 \text{ of volume.}$$

$$4,186 \text{ cubic feet} * 28.2 \text{ grams/cubic feet} = 118,064 \text{ grams.}$$

$$118,064 \text{ grams} / 448 \text{ grams per pound} = 263 \text{ pounds of lifting force}$$

The balloon used here is 5 feet 4 inches across. So working backwards, the lifting force is

$$R=2 \text{ feet } 7 \text{ inches}$$

$$\text{So } (4/3) \pi r^3 = 19.2 \text{ feet}^3 * \text{lifting force of } 28.2 \text{ grams/feet}^3 = 5414.4 \text{ gms}$$

$$\text{And } 5414.4 \text{ gms} / 454 \text{ gms/lb} = 11.93 \text{ lbs}$$

The total weight for the remote sampling setup was around 3.9 lbs, so the balloon could lift it easily. For our use the balloon was tethered to the ground with high weight fishing line and the solenoid was attached directly to a battery, but a remote sensor could have been used just as easy and these types of balloon had the capability of a reported height of up to 30000-40000 feet

There are other types of remote sampling available. The U.S. military has many types of devices that could be used. A base platform is the most likely device that could be constructed to be placed on helicopters, blimps, cars, or boats that could be run remotely to limit the exposure to the air sampling personnel. Not only these devices could be made to access the sampling site, but the samples can be run from remote locations as well.

Sorbent tubes differ in capabilities and the target analytes. Tubes can be made with several materials so that numerous compounds can be analyzed at once. The more volatile the compound, the more break through is seen, thus the next layers should be placed so that the next material collects the compounds to suppress break through. In this research, only one directional sampling was used, however there are times in which the sorbent tube can be adsorbed in one direction and then desorbed in the other direction. This helps keep the higher molecular compounds from degrading during desorption. Since the materials are placed in the tube in a particular order to increase efficiency of the analysis, reversing the flow assists in removing the analytes with the least energy and without coming onto contact with the other sorbent material that may degrade or interact with the other analytes. The type of materials used in the sorbent tubes depends on the nature of analyte interacting with the sorbent material. As mentioned, there are two general types that can be used. One is a molecular sieve that is good for smaller compounds. Molecular sieves work on the basis of a filter but at the molecular level so they are

good for gases and liquids in the C₂ to C₆ range. The type of sorbent tube being used should also be based on the analyte levels, classes of analytes, sampling time, and sampling flow rate. The flow rate and sampling time are important factors to be considered in order to prevent analyte breakthrough, in which analyte molecules pass through the sorbent tube without being retained.

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